Nomenclature of the perovskite supergroup: A hierarchical system of classification based on crystal structure and composition

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ABSTRACT

On the basis of extensive studies of synthetic perovskite-structured compounds it is possible to derive a hierarchy of hettotype structures which are derivatives of the arisotypic cubic perovskite structure \(ABX_3\), exemplified by SrTiO_3 (tausonite) or KMgF_3 (parascandolaite) by: (1) tilting and distortion of the \(BX_6\) octahedra; (2) ordering of \(A\) - and \(B\) -site cations; (3) formation of \(A\) -, \(B\) - or \(X\) -site vacancies. This hierarchical scheme can be applied to some naturally-occurring oxides, fluorides, hydroxides, chlorides, arsenides, intermetallic compounds and silicates which adopt such derivative crystal structures. Application of this hierarchical scheme to naturally-occurring minerals results in the recognition of a perovskite supergroup which is divided into stoichiometric and non-stoichiometric perovskite groups, with both groups further divided into single \(ABX_3\) or double \(A_2BB'X_6\) perovskites. Subgroups, and potential subgroups, of stoichiometric perovskites include: (1) silicate single perovskites of the bridgmanite subgroup; (2) oxide single perovskites of the perovskite subgroup (tausonite, perovskite, loparite, lueshite, isolueshite, lakargiite, megawite); (3) oxide single perovskites of the macedonite subgroup which exhibit second order Jahn-Teller distortions (macedonite, barioperovskite); (4) fluoride single perovskites of the neighborite subgroup (neighborite, parascandolaite); (5) chloride single perovskites of the chlorocalcite subgroup; (6) \(B\) -site cation ordered double fluoride perovskites of the cryolite subgroup (cryolite, elpasolite, simmonsite); (7) \(B\) -site cation ordered oxide double perovskites of the vapnikite subgroup [vapnikite, (?) latrappite]. Non-stoichiometric perovskites include: (1) \(A\) -site vacant double hydroxides, or hydroxide perovskites, belonging to the söhngeite, schoenfliesite and stottite subgroups; (2) Anion-deficient perovskites of the brownmillerite subgroup (srebrodolskite, shulamitite); (3) \(A\) -site vacant quadruple perovskites (skutterudite subgroup); (4) \(B\) -site vacant single perovskites of the oskarssonite subgroup [oskarssonite, waimirite-(Y)]; (5) \(B\) -site vacant inverse single perovskites of the denmarkite and auricupride subgroups; (6) \(B\) -site vacant double perovskites of the diaboleite subgroup; (7) anion-deficient partly-inverse \(B\) -site quadruple perovskites of the hematophanite subgroup.

KEYWORDS: perovskite, group theory, ordered perovskites, hydroxide perovskites, crystal structure, hierarchical classification.

Introduction

SINCE the last revision to the nomenclature of the perovskite group of minerals by Nickel and McAdam (1963) several new members of this structural group have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA). These include the silicate perovskite, bridgmanite \([\text{Mg,Fe}]\text{SiO}_3\), which is now considered to be the dominant mineral of the silicate mantle of the Earth.
The recognition of Mg and Ca-based silicate perovskites, although these are stable only at high pressures, has stimulated an extraordinary interest in the stability and phase transformations of silicate perovskites (Liu, 1976; Hirose, 2014) and their fluoride analogues, such as the NaMgF$_3$-KMF$_3$ solid solution series (Zhao et al., 1994; Chakhmouradian et al., 2001). Contemporaneously, interest in perovskite as a petrogenetic indicator mineral resulted in numerous studies (see summary by Mitchell, 2002) of the paragenesis, composition and crystallography of minerals with the perovskite structure occurring in a wide variety of igneous and metamorphic rocks. Perovskite-group minerals have also gained importance in isotopic (Woodhead et al., 2009; Zurevinski et al., 2011) and geochronological (Smith et al., 1989; Wu et al., 2010) studies as it was recognized that their Sr and Nd isotopic compositions are sensitive indicators of the mantle sources of kimberlites, lamproites and melilitites. Perovskite-structured compounds of diverse composition are important constituents of slags produced by the aluminothermic reduction of pyrochlore (Mitchell and Mariano, 2016) and SYNROC-type nuclear waste forms (Ringwood, 1985; Lumpkin, 2014).

Simultaneously with renewed interest in naturally-occurring perovskites, studies of perovskites by the materials science and solid state chemistry communities have resulted in thousands of publications on the structure and properties of synthetic perovskites and related compounds. This work is driven by the actual, and potential, industrial uses of materials with the perovskite structure in applications ranging from ferroelectric ceramics through superconductivity and giant magnetoresistance devices to photovoltaic cells (Gallaso, 1990; Bruce et al., 2010; see also Table 1 of Chakhmouradian and Woodward, 2014). Much of this work was driven by the observation that the perovskite structure is extremely ‘flexible’ with regard to cationic and anionic replacements and tolerance to ionic defects. Unlike many other structural types, every element of the periodic table, including the noble gases (Shcheka and Kepller, 2012; Britvin et al., 2015; 2016), can be found in some variant of perovskite-structured compounds.

Of particular relevance to the mineralogical community were investigations of the P-T-X-driven distortions of the aristotypic cubic lattices of single (ABX$_3$) and ordered or double (A$_2$B$^{\prime}$X$_6$) perovskites. The application of group theory (Howard and Stokes, 1998, 2002, 2004, 2005; Stokes et al., 2002) resulted in the establishment of a hierarchy of space groups of perovskites with distorted crystal structures, termed hettotypes. Most perovskite supergroup minerals do not adopt the cubic space groups Pm3m or Fm3m and thus are considered as hettotypes of reduced symmetry. Synthetic perovskites can be classified according to a hierarchy of structural types (Fig. 1) ranging from simple ABX$_3$ compounds and ordered variants through cation- and anion-deficient varieties to layered complex derivatives (Mitchell, 2002). This classification is in principle applicable to naturally-occurring perovskite supergroup minerals and can be used to explain why particular space groups are adopted and to predict the structural and compositional variants of perovskites that might be expected to occur in nature. Note that many of the more complex non-stoichiometric or layered derivatives of the ABX$_3$ aristotype structure, such as high temperature superconducting compounds, depart too far in topology to be considered as members of the perovskite supergroup as defined in this work.

**Aristotype perovskite**

The ‘ideal’ perovskite structure (Goldschmidt, 1926) from which the structures of all other compounds having the perovskite structure are derived is illustrated in Fig. 2. Ideal, or single, perovskites, where ‘single’ refers to the number of symmetrically non-equivalent A and B sites, have the general formula ABX$_3$, where the A-site cations are larger than the B-site cations and similar in size to the X-site anions. To a first approximation the structure consists of a cubic close-packed array of X anions with one quarter of these replaced by A-site cations in an ordered manner. The A-site cations are surrounded by 12 anions in twelve-fold cubo-octahedral coordination, and the B-cations are surrounded by 6 anions in octahedral coordination. The X anions are coordinated by two B-site cations and four A-site cations (Goldschmidt, 1926). Perovskites having the ideal structure adopt the cubic space group Pm3m (P4/mn2/m; #221). The compound SrTiO$_3$ is commonly regarded as the archetypal cubic perovskite, although KMgF$_3$ is a better alternative as, unlike SrTiO$_3$, it remains cubic from 3.6 K to its melting point, and its structure is not affected by pressure up to 50 GPa (Mitchell et al., 2006; Aguado et al., 2008). Many naturally-occurring oxide and fluoride perovskites probably crystallized initially as cubic or tetragonal perovskites, and adopted their room temperature structure.
as a consequence of distortion of these structures during cooling. Other perovskite-group minerals, including CaTiO₃ perovskite, typically crystallize at temperatures below the temperature required for phase transitions to a higher symmetry (e.g. located at >1100°C for synthetic CaTiO₃; Redfern, 1996; Carpenter et al., 2006). It is essentially unknown what the effect of composition is on the phase transition temperatures of complex naturally-occurring perovskite-group minerals. For example, the cubic-to-tetragonal transition can be reduced by several hundred degrees with the substitution of 25% Ca for Sr in synthetic CaTiO₃ (Carpenter et al., 2006). Hu et al. (1992) used transmission electron microscopy to examine several perovskite-group minerals, including cumulus loparite from igneous rocks, and found no evidence for transformation twinning in any of the samples investigated as many twins appear to be growth twins. Note that hydroxide perovskites, such as dzhalindite or stottite, which form in supergene environments are unlikely to have undergone phase transitions in
nature, although these have been observed in some experimental studies (see below).

**Distorted ABX₃ perovskites**

The majority of simple synthetic and natural perovskites are distorted derivatives of the aristotypic perovskite structure resulting from: (1) tilting (i.e. rotation) of rigid BX₆ polyhedra; (2) first order Jahn-Teller distortion of BX₆ octahedra; (3) second order Jahn-Teller effects affecting the A- and B-cation polyhedra, and reflecting the mixing of molecular orbitals and/or lone-pair effects. Tilting of the BX₆ polyhedra is the commonest type of distortion found in naturally-occurring perovskites, although the other modes can be found in barioperovskite, macedonite and diaboleite.

**BX₆ octahedron tilting**

Octahedron tilting occurs when the size of the A cation is too small for the 12-fold site within the BX₆ polyhedral framework: e.g. Ca²⁺ in the synthetic (Sr,Ca)TiO₃ solid solution series (Yamanaka *et al.*, 2002). To accommodate such cations, the octahedra tilt about the three axes of the pseudocubic precursor cubic cell (x, y and z), so as to achieve the lowest energy mode for the crystal. In most tilting models it is assumed that the BX₆ octahedra are rigid, but not necessarily ideal, and the rotation does not disrupt their corner-sharing connectivity. Tilting results in changes in the A–X bond lengths so that they are no longer equal. This changes the A-site coordination, with concomitant reduction in symmetry from space group Pm3m to that of a hettotype. Coordination of the A-site cation as determined from bond valence analysis of the first coordination sphere can range from 12 to 8, depending upon the style and magnitude of the octahedron tilt. Many naturally-occurring ABX₃ perovskite-group minerals, including CaTiO₃ (perovskite sensu stricto), adopt the orthorhombic Pbnm GdFeO₃ structure type with the A-site cations in 8-fold coordination.

Distorted perovskites are commonly described using the nomenclature devised by Glazer (1972). In this scheme BX₆ octahedron rotations are described in terms of three orthogonal Cartesian axes coincident with the three axes of the aristotype cubic unit cell (Fig. 3). In the general case of unequal rotation angles about the x, y and z axes, the rotation scheme is denoted as α, β and γ degrees, with sense of the rotations (i.e. clockwise or anticlockwise) in successive layers of octahedra perpendicular to a specific rotation axis given as...
superscripts. A positive superscript indicates tilt of octahedra in successive layers in the same direction (i.e. an in-phase tilt), whereas a negative superscript indicates rotation of consecutive octahedra along a specific rotation axis in the opposite sense (i.e. an anti-phase tilt). Thus, the symbol $a^+b^-c^-$ indicates three unequal angles of rotation about $x$, $y$ and $z$ with consecutive octahedra along the same axis (i.e. $x$, $y$ or $z$) rotating in the same sense. For equal angles of rotation the notation would become $a^+a^-a^+$. A zero superscript is used for no rotations about a specific axis, e.g. the cubic aristotype lacking any octahedron tilting has the tilt symbol $a^0b^0c^0$ and space group $Pm3m$.

Glazer (1972) used crystallographic principles to evaluate all possible combinations of tilting for single $ABX_3$ perovskites and identified 23 tilt systems corresponding to particular space groups. Howard and Stokes (1998) using group theory, confirmed Glazer’s (1972) analysis, but reduced the number of tilt systems to 15, as some of Glazer’s tilt systems were combinations of one or more of the basic fifteen. Such combinations and their associated space groups are possible in principle but have not been observed in real crystals. Certain tilting patterns, e.g. those combining in-phase rotations about $x$ and/or $y$ with an antiphase rotation about $z$, cannot maintain the connectivity of rigid octahedra and hence require polyhedral distortions (Woodward, 1997). Figure 4 illustrates the space-group relationships associated with particular tilt systems for $ABX_3$ perovskites and identifies possible first and second order phase transitions from the cubic aristotype. These relationships are directly applicable to the $P-T-X$ space-group transitions possible for natural perovskite-group minerals.

Similar analyses of octahedron tilting have been subsequently provided for 1:1, 1:2, and 1:3 $B$-cation ordered perovskites by: Woodward (1997); Howard et al. (2003); Lufaso and Woodward (2004); Howard and Stokes (2004); and Lufaso et al. (2006). The tilt schemes and the hierarchy of phase transitions (Fig. 5) for 1:1 ordered (or double) perovskites are given by Howard et al. (2003) and are applicable.
directly to fluoride-based ordered perovskite-group minerals such as simmonsite and cryolite (see below).

**Perovskite nomenclature**

Perovskite-supergroup minerals as defined here are those minerals whose structures consist of three-dimensional networks of corner-sharing octahedra and which adopt the aristotypic ABX₃ perovskite structure or those of its derivatives. The octahedra can be tilted and/or distorted without destroying the connectivity. Cations at the B-site can be distributed randomly and termed single perovskites or ordered and termed double perovskites. The A-site can be filled or vacant, in the latter case forming A-site deficient single or double perovskites such as the hydroxide perovskites. The B-site can be partially, or entirely, vacant as in the minerals diaboleite or waimirite-(Y), respectively.

Naturally-occurring perovskite supergroup minerals occur as oxides, fluorides, chlorides, hydroxides, arsenides, antimonides, intermetallic compounds and silicates. Many of these have the ABX₃ perovskite structure and exhibit significant solid solution, coupled with the compositionally-driven space group changes which occur between potential ideal end-member compositions.

Perovskite supergroup minerals can be also described as ‘homeotypic’ in that they have the same essential topology but not necessarily the same space group.

Tables 1–3 together with Figs 6 and 7, present a hierarchical classification of the currently named members of the perovskite supergroup together with their room temperature space group as determined from diffraction studies of natural crystals or by analogy with synthetic analogues. This classification has been approved by the IMA-CNMNC (Hålenius et al., 2016). The etymology of members of the supergroup is given in the Appendix to this paper (deposited with the Principal Editor of Mineralogical Magazine and available from http://www.minersoc.org/pages/e_journals/dep_mat_mm.html).

Two major groups are recognized in the perovskite supergroup: stoichiometric and non-stoichiometric groups. The former have ABX₃ or A₂BB'X₆ stoichiometry, and the latter include hydroxide- and arsenide-based minerals, which are also known as defect perovskites, characterized by A- and/or B-site vacancies together with the anion-deficient minerals of the brownmillerite and hematophanite subgroups. Note that many ‘non-stoichiometric’ perovskites have well-defined fixed ratios of A- or B-site cations or X anions but are considered here as non-stoichiometric relative to

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**Fig. 5.** Group–subgroup relations associated with particular tilt systems for 1:1 B-site ordered, or double perovskites, perovskites as evaluated by Howard et al. (2003) using group theoretical methods. Space group Fm3m is the aristotype from which all hettotypes are derived. Red and black lines indicate possible first and second order phase transitions, respectively.
ABX₃ or A₂BB’X₆ perovskites. Within these groups following the dominant-constituent or dominant valency rules we recognize several compositional and structural subgroups depending on diverse combinations of the dominant A- or B-site cation or X anion. Together these constitute the perovskite supergroup.

We do not intend to use the modifying prefix ‘keno’ (from the Ancient Greek κενός = empty), as introduced by Atencio et al. (2010) for the A-site deficient minerals of the pyrochlore supergroup, as we consider this to be redundant for all A-site deficient perovskite structures. Moreover, the terms A-site deficiency, A-site vacancy, and defect perovskite are entrenched in the materials science and solid-state chemistry literature and thus have precedence; especially with regard to keyword search terms and potential interactions of mineralogists with those communities.

Although many compounds termed hexagonal perovskites have been synthesized (Mitchell, 2002) only a few are found in nature (Krivovichev, 2008). The structures of the majority of these are hexagonal antiperovskite polytypes characterized by combinations of face- and corner-sharing of octahedra rather than corner-sharing alone (Krivovichev, 2008). For this reason we do not consider such minerals as: 2H-nacaphite.

Table 1. Classification of stoichiometric perovskites ABX₃ and A₂BB’X₆.

<table>
<thead>
<tr>
<th>Group/subgroup</th>
<th>Composition</th>
<th>Ideal</th>
<th>Sp. gp.</th>
<th>Tilt</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Single perovskites ABX₃</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bridgmanite subgroup</td>
<td>(Mg,Fe)SiO₃</td>
<td>MgSiO₃</td>
<td>Pbnm</td>
<td>a⁻a⁺c⁻</td>
</tr>
<tr>
<td>Unnamed</td>
<td>?</td>
<td>CaSiO₃</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td><strong>Perovskite subgroup</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baritoperoovskite</td>
<td>BaTiO₃</td>
<td>BaTiO₃</td>
<td>Amm2*</td>
<td>a⁺a⁺a⁻</td>
</tr>
<tr>
<td>Isolueshite</td>
<td>(Na,La,Ce)(Nb,Ti)O₃</td>
<td>(Na,La)NbO₃</td>
<td>Pm3m</td>
<td>a⁺a⁺a⁻</td>
</tr>
<tr>
<td>Lakargite</td>
<td>(Ca)(Zr,Sn,Ti)O₃</td>
<td>CaZrO₃</td>
<td>Pbnm</td>
<td>a⁺a⁺c⁻</td>
</tr>
<tr>
<td>Loparite</td>
<td>(Na,REE,Ca,Sr,Th) (Ti,Nb)O₃</td>
<td>(Na,REE)Ti₂O₆</td>
<td>Pbnm</td>
<td>a⁺a⁺c⁻</td>
</tr>
<tr>
<td>Lueshite</td>
<td>(Na,REE,Ca)(Nb,Ti)O₃</td>
<td>NaNbO₃</td>
<td>Pmmm</td>
<td>a⁺a⁺a⁻</td>
</tr>
<tr>
<td>Macedonite</td>
<td>(Pb,Bi)TiO₃</td>
<td>PbTiO₃</td>
<td>P4mm*(?)</td>
<td>a⁺a⁺a⁻</td>
</tr>
<tr>
<td>Megawite</td>
<td>(Ca)(Sn,Zr,Ti)O₃</td>
<td>CaSnO₃</td>
<td>Pbnm</td>
<td>a⁺a⁺c⁻</td>
</tr>
<tr>
<td>Perovskite</td>
<td>(Ca,REE,Na)(Ti,Nb)O₃</td>
<td>CaTiO₃</td>
<td>Pbnm</td>
<td>a⁺a⁺c⁻</td>
</tr>
<tr>
<td>Tausonite</td>
<td>(Sr,Ca,REE,Na,Ti,Nb)O₃</td>
<td>SrTiO₃</td>
<td>Pm3m</td>
<td>a⁺a⁺a⁻</td>
</tr>
<tr>
<td><strong>Neighborite subgroup</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neighborite</td>
<td>(Na,K)MgF₃</td>
<td>NaMgF₃</td>
<td>Pbnm</td>
<td>a⁺a⁺c⁻</td>
</tr>
<tr>
<td>Parascandolite</td>
<td>KMgF₃</td>
<td>KMgF₃</td>
<td>Pm3m</td>
<td>a⁺a⁺a⁻</td>
</tr>
<tr>
<td><strong>Chlorocalcite subgroup</strong></td>
<td></td>
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</tr>
<tr>
<td>Chlorocalcite</td>
<td>KCaCl₃</td>
<td>KCaCl₃</td>
<td>Pbnm</td>
<td>a⁺a⁺c⁺</td>
</tr>
<tr>
<td><strong>Double perovskites A₂BB’X₆</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elpasolite</td>
<td>K₂NaAlF₆</td>
<td>K₂NaAlF₆</td>
<td>Fm3m</td>
<td>a⁺a⁺a⁺a⁻</td>
</tr>
<tr>
<td>Cryolite</td>
<td>Na₂NaAlF₆</td>
<td>Na₂NaAlF₆</td>
<td>P2₁/n</td>
<td>a⁺a⁺c⁺</td>
</tr>
<tr>
<td>Simmonsite</td>
<td>Na₂LiAlF₆</td>
<td>Na₂LiAlF₆</td>
<td>P2₁/n</td>
<td>a⁺a⁺c⁺</td>
</tr>
<tr>
<td>Vapnikite subgroup</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapnikite</td>
<td>Ca₂CaUO₆</td>
<td>Ca₂CaUO₆</td>
<td>P2₁/n</td>
<td>a⁺a⁺c⁺</td>
</tr>
<tr>
<td>Latrappite (?)</td>
<td>(Ca,Na)(Nb,Fe⁵⁺,Ti)O₃</td>
<td>Ca₂NbFe⁵⁺O₆</td>
<td>P2₁/n</td>
<td>a⁺a⁺c⁺</td>
</tr>
<tr>
<td><strong>Double antiperovskites B₂XX’A₆</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphohalite subgroup</td>
<td>Na₆FCl(SO₄)₂</td>
<td>Na₆FCl(SO₄)₂</td>
<td>Fm3m</td>
<td>a⁺a⁺a⁺a⁻</td>
</tr>
</tbody>
</table>

* Octahedra in space groups Amm2 and P4mm are not tilted and the reduction in symmetry from Pm3m results from second order Jahn-Teller distortion.
**5H-galeite; 7H-schairerite; 9R-kogarkoite; and 9R-hatrurite, as members of the perovskite supergroup.** Only *sulphohalite*, Na₆FCl(SO₄)₂, an ordered double antiperovskite which adopts a cubic (Fm3m) anti-elpasolite 3C polytype structure, is considered here as a member of the perovskite supergroup, as corner-sharing of the FNa₆ and ClNa₆ octahedra is maintained. The minerals *palmierite*, a derivative of the 9R hexagonal perovskite structure type (Mitchell, 2002), and *orthorhombic Pnma javoreite* (KFeCl₃; Kodera, et al., 2016) contain only face-sharing octahedra and thus are not a members of the perovskite supergroup.

Recently, McDonald et al. (2013) have noted that *peatite-(Y)* and *ramikite-(Y)*, both complex Na-Li ± Zr phosphate carbonate minerals, can be described as cluster compounds based on simpler unit cells, and which are cation-deficient perovskite-related structures. Similar cluster compounds, such as Cs₂Zr₆Br₁₅C, are known as synthetic phases (Qi and Corbett, 1995) suggesting that there could exist a large number of perovskite-related cluster phases and minerals. In this work *peatite-(Y)* and *ramikite-(Y)* are not considered as members of the perovskite supergroup as their structures are far-removed from those of other members.

**Stoichiometric perovskite group – single ABX₃ perovskites**

The presence of silicates having the perovskite structure in the Earth’s mantle has long been postulated on the basis of experimental petrological studies of pyrolite and lherzolite at high pressures and temperatures (Ringwood, 1991; Jackson and Rigden, 1998; Hirose, 2014) together with circumstantial evidence based on the character of decompressed silicate inclusions in diamonds (Stachel et al., 2000). Recently, sub-micrometre crystals with the composition of (Mg,Fe)SiO₃ occurring in a four-phase mixture in shock-induced veins in the Tenham (L6) chondritic meteorite, were found by full profile refinement of X-ray diffraction (XRD) data to adopt space group *Pbnm*. This material with the perovskite structure was named bridgmanite by Tschauner et al. (2014). By analogy it is now

### Table 2 Classification of non-stoichiometric perovskites.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ideal</th>
<th>Sp. gp.</th>
<th>Tilt</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>A</em>-site vacant hydroxide perovskites</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Söhngeite subgroup</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dzhalindite</td>
<td>(In,Fe)(OH)₆</td>
<td>In(OH)₃</td>
<td>Im3</td>
</tr>
<tr>
<td>Söhngeite</td>
<td>(Ga,Al,Fe)(OH)₃·xH₂O</td>
<td>Ga(OH)₃</td>
<td>P4₂/nmc or P4₂/n</td>
</tr>
<tr>
<td>Bernalite</td>
<td>(Fe⁺⁺⁺⁺S₀.06Z₀.01)[(OH)₂.95O₀.04]</td>
<td>Fe(OH)₃</td>
<td>Pmnm</td>
</tr>
<tr>
<td>Double hydroxyperovskites</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schoenfliesite subgroup</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schoenfliesite#</td>
<td>(Mg₀.94,Mn₀.13)₁.₀7Sn₀.₀7(OH)₆</td>
<td>MgSn(OH)₆</td>
<td>Pn3</td>
</tr>
<tr>
<td>Burtite</td>
<td>(Ca₀.99,Mg₀.02)Sn(OH)₆·0.39H₂O</td>
<td>CaSn(OH)₆</td>
<td>Pn3</td>
</tr>
<tr>
<td>Jeanbandyite</td>
<td>Fe³⁺Fe²⁺(1-x)Sn(OH)₆·xO₁(1≥x≥0.5)</td>
<td>Fe³⁺Sn(OH)₆·O</td>
<td>Pn3</td>
</tr>
<tr>
<td>Mushistonite</td>
<td>(Cu₀.48Zn₀.39Fe₀.17)₁.₀₄Sn(OH)₅.₉₅</td>
<td>CuSn(OH)₆</td>
<td>Pn3</td>
</tr>
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STOICHIOMETRIC PEROVSKITES

SINGLE $A_B X_3$ GROUP
- Silicate Bridgmanite
- Oxide Perovskite
- Fluoride Neighborite
- Chloride Chlorocalcite

DOUBLE $A_2B_B'X_6$ GROUP
- Fluoride Cryolite
- Oxide Vapnikite
- Double $B_2X'X_A 6$ Antiperovskite
- Sulphate-Chloride Sulphohalite

Fig. 6. Hierarchical classification of the stoichiometric perovskite supergroup minerals.

NON-STOICHIOMETRIC PEROVSKITES

A-SITE VACANT
- Hydroxides
  - Single
    - Sohngite
  - Double
    - Schoenfliesite
    - Stottite
- Skutterudites

B-SITE VACANT
- Single
  - Oskarssonite
- Single Antiperovskite
  - Cohenite
  - Auricupride
- Double
  - Diaboleite
- Quadruple
  - Hematophanite
  - Brownmillerites

Anion Deficient

Fig. 7. Hierarchical classification of the non-stoichiometric perovskite supergroup minerals.
assumed that Pbnm bridgmanite is the most abundant mineral in the Earth and the dominant mineral in the lower mantle, i.e. from below ~700 km depth to near the core-mantle boundary where it probably transforms to a Cmcm CaIrO$_3$-type structure, commonly referred to as ‘post-perovskite’ by the geophysical community. This phase is stable above 120 GPa at 2500 K (Murakami et al., 2004; Oganov and Ono, 2004; Tsuchiya et al., 2004). These conditions correspond to a depth of ~2600 km and the location of the D” seismic discontinuity at the base of the lower mantle. The ‘post-perovskite’ CaIrO$_3$-type phase has a pseudo-two-dimensional layer structure (Sugahara et al., 2008) and is not a member of the perovskite supergroup. Experimental studies of the phase relationships of CaSiO$_3$ at high pressures (Gasparik et al., 1994) coupled with observations on decompressed calcium silicate inclusions in diamonds (Stachel et al., 2000; Kaminsky et al., 2001), clearly indicate that bridgmanite must be accompanied by CaSiO$_3$ with the perovskite structure in the lower mantle. The symmetry of this phase, initially identified as cubic (Liu and Ringwood, 1975), has been debated by Akber-Knutson et al. (2002), Caracas and Wentzcovitch, (2005); and Fang and Ahuja (2006). In situ experimental diffraction data relevant to resolution of this question are limited. As yet, quenched examples of this phase have not been found and the mineral remains unnamed.

Oxide single perovskites – perovskite subgroup

Members of this group (Table 1; Fig. 6) are characterized by oxygen as the dominant anion. Many of these ABO$_3$ perovskites are titanates which typically exhibit extensive solid solution between potential end-member compositions, as diverse cations can occupy the A and B sites. These minerals are the commonest members of the perovskite supergroup in the Earth’s crustal environment (Mitchell, 2002), and as calcium-aluminum-rich (CAI) inclusions in chondrite meteorites. The latter are considered to represent remnants of the earliest accretionary material in the Solar System (McPherson et al., 2005).

**Tausonite (SrTiO$_3$)**

Tausonite was described initially from the Little Murun potassic alkaline complex, Sakha (Russia) by Vorob’yev et al. (1984). Most tausonite from Little Murun is complexly zoned (Fig. 8) and contains significant amounts of Na and rare-earth elements (REE), representing a solid solution towards loparite (Vorob’yev et al., 1984; Mitchell and Vladykin, 1993). The material studied by Vorob’yev et al. (1984) represents an average composition in the tausonite–loparite series (~85 mol.% SrTiO$_3$), and thus is not that of pure SrTiO$_3$. In addition, silicate inclusions, represented by 2.2–5.0 wt.% SiO$_2$, were present in the material analysed by Vorob’yev et al. (1984). Calcium-bearing tausonite (2.1–2.5 wt.% CaO; 92–93 mol.% SrTiO$_3$) has been described from the P2-West lamproite, Wajrakurur (India) by Gurmeet Kaur and Mitchell (2013), where it occurs with baryte, pectolite and hydrogarnet as pseudomorphs after an unidentified primary phase. Tausonite with a composition close to that of pure SrTiO$_3$ (98 mol.%)

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**FIG. 8. Tausonite-strontian loparite from the Little Murun complex, Yakutia, Russia. Tausonite occurs in the core of this strongly-zoned crystal. (a) Plane polarized light optical image; (b) false coloured back-scattered electron image. See Mitchell and Vladykin (1993) for compositional data.**
has also been found in Sr-rich metamorphic rocks of the Itoigawa-Ohmi District (Japan) by Miyajima et al. (2002). Tausonite with elevated levels of CaO (5–9 wt.%) and Na2O (1.9–2.6 wt.%) has been described from several types of feldspathic hornfels xenoliths entrained in foyaite in the Khibiny alkaline complex (Kola Peninsula, Russia) by Yakovenchuk et al. (2005)

The crystal structures of tausonites from all of the above occurrences have not been determined. However, Vorob’yev et al. (1984) noted that as the powder XRD pattern (a = 3.9048 Å) of the holotype tausonite from Little Murun was similar to that of synthetic SrTiO3 (a = 3.9050 Å; Hutton and Nelmes, 1981), it was assumed, by analogy, that the mineral must adopt space group Pm\text{3}m. Synthetic compounds forming solid solutions in the binary system SrTiO3–NaNdTi2O6 with >90 wt.% SrTiO3 have cubic Pm\text{3}m structures (Ranjan et al. 2006; Mitchell and Tavener, unpublished data). Thus, although single-crystal determination of the structure of naturally-occurring pure tausonite has not been undertaken, it can be assumed reasonably that the end-member adopts space group Pm\text{3}m. Strontium-bearing perovskites exhibiting significant solid solution towards loparite most probably have tetragonal structures (Ranjan et al., 2006; Mitchell et al., 2000a) thus the strontian loparite described by Haggerty and Mariano (1983) as ‘cubic Sr-tausonite’ (sic), probably has an I4/mcm structure (see below).

We recommend that tausonite be retained as the name for perovskite-supergroup minerals with the...
general formula (Sr,Ca,REE,Na)(Ti,Nb)O₃ and no A- or B-site cation ordering, whose compositions (following the IMA dominant constituent/valency rules) are such that: (1) divalent cations predominate in the A-site with Sr as the dominant constituent; tetravalent cations predominate in the B-site with Ti as the dominant constituent. Compositions fall within the tausonite field in the ternary compositional (mol.%) system SrTiO₃–CaTiO₃ (Fig. 9).

Following IMA nomenclature protocols (Nickel and Grice, 1998; Hatert et al., 2013) ‘impurity-stabilized’ derivatives of tausonite, whose structures are topologically similar to, but depart from that of the cubic end-member, cannot be defined as distinct mineral species. We recommend that their relationship to tausonite be reflected in the root name, rather than an entirely new name to reduce the proliferation of mineral names that has plagued other mineral groups. Thus, the name of the tetragonal Na-REE-rich members of the tausonite–loparite series should indicate the true symmetry by means of a hyphenated suffix i.e. tausonite-I₄/mcm. Although these minerals, following the recommendations of Nickel and Grice (1998), could be referred to as ‘tausonite-Q’, we consider this symbolism not to be informative, or useful, especially if the true symmetry has been determined.

**Perovskite (CaTiO₃)**

Perovskite (sensu stricto), was initially described by Rose (1839) in calc-silicate contact metamorphic rocks in the Ural Mountains, Russia (Fig. 10). Perovskite is a characteristic minor-to-accessory mineral in a wide variety of undersaturated alkaline rocks ranging from kimberlite through melilitolites to carbonatites (Fig. 11). Investigations of the crystal structure have been hampered by the ubiquitous twinning, and initially the mineral was considered to be: orthorhombic (Bowman, 1908);
cubic (Barth, 1925); monoclinic $P2_1/m$ (Náray-Szabó, 1943); orthorhombic or monoclinic (Megaw, 1946). Kay and Bailey (1957) recognized that the powder XRD patterns of synthetic and natural CaTiO$_3$ were identical and suggested by analogy that the mineral adopts the orthorhombic space group $Pcmn$; a non-standard setting of space group $Pnma$ ($\#62$).

The determination of the room-temperature crystal structure of natural near end-member CaTiO$_3$ perovskite by single-crystal methods was not undertaken until that of Beran et al. (1996) on twin-poor crystals from the Benitoite Gem mine (San Benito, California), followed by that of Arakcheeva et al., (1997) using material from near the type locality (Akmatovskaya Kop) in the Kusinskii Massif, Urals (Russia). These studies demonstrated conclusively that CaTiO$_3$ perovskite adopts the space group $\#62$, with the structural data reported in the $Pnma$ setting. However, the structure is now commonly described in terms of the $Pbnm$ setting (Fig. 12; Glazer tilt system $a^* a^- c^+$), and considered to represent the GdFeO$_3$ structure type following the work of Geller (1956) and Sasaki et al. (1987).

We recommend that perovskite be retained as the name for a mineral in the perovskite supergroup with the general formula $(\text{Ca,REE,Na})(\text{Ti,Nb})\text{O}_3$ and no A- or B-site cation ordering, whose compositions are such that: (1) divalent cations predominate in the $A$ site with Ca as the dominant constituent; (2) tetravalent cations predominate in the $B$ site with Ti as the dominant constituent. Perovskite compositions fall within the perovskite field in the ternary compositional (mol.%) systems NaNbO$_3$–NaREE$\text{Ti}_2\text{O}_6$–CaTiO$_3$ (Fig. 13) and SrTiO$_3$–NaREE$\text{Ti}_2\text{O}_6$–CaTiO$_3$ (Fig. 9).

**Loparite** $(\text{Na,REE,Sr,Ca})(\text{Ti,Nb})_2\text{O}_6$

Loparite was the second oxide perovskite-structured mineral to be recognized and was described briefly from nepheline syenite of the Lovozero Penikaline complex (Kola Peninsula, Russia) as ‘Mineral no.1’ by Ramsay and Hackman (1894). Subsequently, the mineral was misinterpreted as being perovskite by Ramsay (1897). The first complete description of loparite as a member of the perovskite group was by Kuznetsov (1925) using material from a nepheline syenite pegmatite in the adjacent Khibiny alkaline complex (Fig. 14). The mineral is typically complexly-twinned both macroscopically and at the resolution of the transmission electron microscope (Hu et al., 1992). Loparite is, incorrectly, described in most glossaries of mineralogy as possessing cubic or pseudocubic symmetry. Loparite occurs principally
Importantly, none of the loparite samples analysed show the predominance of REE among the large cations present (Mitchell and Chakhmouradian, 1996, 1998; Chakhmouradian and Mitchell, 1997, 2002). As a consequence of the presence of Nb (±Ta) in this mineral, which requires the incorporation of monovalent cations for charge compensation, Na is invariably the predominant A-site cation in loparite, including material from the type locality (Chakhmouradian and Mitchell, 1997), and in samples investigated by X-ray diffraction from three different localities by Mitchell et al. (2000b). Given the disordered distribution of cations in the structure of this mineral (see below), the use of Levinson modifiers [e.g. loparite-(Ce)] to indicate the dominant REE species is clearly unwarranted. The ubiquitous presence of Nb, which can be assigned to the NaNbO₃ end-member, in natural loparite explains the predominance of Na over REE in its composition. The only exception is metamict loparite which has been affected to variable degrees by cation leaching. This primarily affects Na and produces a Na-deficient phase (or phases) of uncertain status, referred to in the literature as ‘metaloparite’ (Chakhmouradian et al., 1999).

Loparite (sensu lato) exhibits a very wide range in composition and is typically a quaternary solid solution. The space group adopted by any particular example is determined by whether the solid

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**FIG. 13.** Compositional variation (mol.%) of perovskite-group minerals from: (1) kimberlites; (2) alkaline ultramafic rocks and carbonatites; (3) Khibina nepheline syenites and ijolites; (4) Lovozero nepheline syenites and urtites; (5) Burpala albites and aegirinites; (6) Lueshe carbonatite, depicted in the ternary system NaNbO₃–NaCeTi₂O₆–CaTiO₃ (lueshite–loparite–perovskite) (after Mitchell, 2002). Note subdivisions of the compositional fields are used for the complete description of diverse compositions of these perovskite-supergroup minerals (Mitchell and Valdykin, 1993; Mitchell, 2002).
solution present is towards lueshite (NaNbO₃), tausonite (SrTiO₃) or perovskite (CaTiO₃). Very few single-crystal determinations of the structure of loparite have been undertaken, although the structures of synthetic analogues have been well-characterized by Rietveld methods. Mitchell et al. (2000b) determined the structures of three compositionally-distinct crystals by single-crystal methods and showed that depending on composition, loparite can adopt space groups Pbnm (#62) or I4/mcm (#140).

Strontium-poor niobian calcian loparite (mol. %: 3.4–3.5 SrTiO₃; 9.0–9.3 CaTiO₃; 24.0–25.4 NaNbO₃; 57.0–61.4 Na₀.₅REE₀.₅TiO₃; Mitchell et al., 2000b) similar in composition to the holotype material from Khibiny has a similar structure to Pbnm CaTiO₃, but with a smaller octahedron tilt angle resulting from the presence of the significant amounts of the large, relative to Ca, A-site disordered cations. This loparite is close to being metrically tetragonal as a > b, suggesting that a slight increase in Na or Sr content would result in adoption of the I4/mcm space group. Studies of synthetic NaREE₂O₆ compounds containing individual REE (Shan et al., 1998; Sun et al., 1997; Chakhmouradian et al., 1999) have shown that, with the exception of NaLaTi₂O₆, all adopt the Pbnm GdFeO₃ structure. Depending upon the synthesis method NaLaTi₂O₆ can be rhombohedral R₃c (Mitchell et al., 2000a), tetragonal I4/mcm (Feng et al., 2016) or orthorhombic Pbnm (Sun et al., 1997). Mitchell and Lifervich (2005) determined that light-REE-rich synthetic perovskites in the system Na₀.₇₅REE₀.₂₅Ti₀.₅Nb₀.₅O₃, apart from the La compound, adopt space group Pbnm. Chakhmouradian et al. (1999) considered that loparite from the Burpala complex (c. 81 mol.% NaREE₂Ti₂O₆) probably adopts the same structure, as determined by Rietveld methods, as the synthetic Pbnm compound NaCeTi₂O₆. Thus, given that the REE content of the majority of analysed loparite is dominated by Ce it is considered that the structures of synthetic Pbnm NaCeTi₂O₆ and Khibiny loparite as determined by single-crystal methods (Mitchell et al., 2000b) best reflects that of the natural material approaching the end-member composition.

Mitchell et al. (2000b) have determined by single-crystal methods that both calcian niobian loparite (mol. %: 4.3–4.8 SrTiO₃; 12.6–13.9 CaTiO₃; 10.7–15.7 NaNbO₃; 60.6–69.4 Na₀.₅REE₀.₅TiO₃ and strontian calcian loparite (mol. %: 7.2–8.2 CaTiO₃; 5.2–5.8 NaNbO₃; 27.1–32.0 SrTiO₃; 48.7–52.1 Na₀.₅REE₀.₅TiO₃) adopt the space group I4/mcm as a consequence of compositionally-driven space group changes in the quaternary solid solution series loparite–lueshite–tausonite–perovskite (Mitchell et al., 2000b). Thus, in common with tausonite (see above), without both structural and compositional data it is not possible to describe completely any particular loparite. Accordingly, we consider it is possible to recognize both Pbnm and I4/mcm varieties of loparite sensu lato.

We recommend that loparite be retained as the name for the mineral in the perovskite subgroup with the general formula (Na,REE,Ca,Sr,Th) (Ti,Nb)O₃ and no A- or B-site cation ordering, whose compositions are such that: (1) monovalent cations predominate in the A-site with Na as the dominant constituent; (2) tetravalent cations predominate in the B-site with Ti as the dominant constituent. Compositions fall within the loparite field in the ternary systems (mol.% ) SrTiO₃–Na REETi₂O₆–CaTiO₃ (Fig. 9) or NaNbO₃–NaREE₂Ti₂O₆–CaTiO₃ (Fig 13). Specific structural varieties can be named as loparite-Pbnm or loparite-I4/mcm, etc. if their crystal structures have been determined by either Rietveld or single-crystal methods.

For the reasons discussed above, the Levinson modifier, loparite-(Ce), as previously used in descriptions of loparite should be discontinued. The hypothetical end-member loparite (sensu stricto) can be defined as Pbnm NaREE₂Ti₂O₆ for the purposes of calculation of end-member molecules from the compositions of natural loparite (sensu lato), where REE is the sum of the rare-earth elements present (atoms per formula unit, apfu) combined with an equivalent amount of Na (apfu). Any remaining Na is assigned with Nb to lueshite as NaNbO₃.
Lueshite (Na,REE)(Nb,Ti)O₃

Lueshite (Fig. 15) was originally described by Safianikoff (1959) from the Lueshe carbonatite complex (North Kivu, Democratic Republic of the Congo). Simultaneously, Danø and Sørenson (1959) described a mineral of similar composition in agpaitic nepheline syenite from the Ilímaussaq complex (Greenland). This mineral was provisionally termed ‘igdloite’. Because this mineral was inadequately characterized with respect to its composition and properties, the name was abandoned in favour of lueshite in the revision of perovskite-group nomenclature by Nickel and McAdam (1963).

Safianikoff (1959) noted that the powder XRD pattern of lueshite was ‘similar’ to that of synthetic NaNbO₃ studied by Vousden (1953), who claimed that the room temperature space group was orthorhombic P22₁₂ (#17). Safianikoff (1959) did not determine the actual crystal structure of lueshite and merely assumed this was identical to that determined by Vousden and reported the structure in the conventional setting P222₁. This space group has been assigned to lueshite in some glossaries of mineral names (Blackburn and Dennen, 1997). Other glossaries (Anthony et al., 1993) following the determination of the crystal structure of synthetic NaNbO₃ by Sakowski-Cowley et al. (1969) and Hewat (1974) consider by analogy that lueshite adopts space group Pbma (#57; a non-standard setting of Pbcm). Note that the many crystal structures of synthetic NaNbO₃ remain under active discussion (Johnson et al., 2010; Peel et al., 2012; Cheon et al., 2015).

No determinations of the actual structure of lueshite were undertaken until those of Mitchell et al. (2002; 2014) who showed that the XRD powder patterns of lueshite were not compatible with synthetic NaNbO₃ and that the mineral probably adopts the space group Pbnm (#62). Single-crystal X-ray determinations of the structure of lueshite from several localities by Mitchell et al. (2014) indicated that the mineral might adopt the space group Pbnm. However, conventional and time-of-flight powder neutron diffraction methods of structure determination were inconclusive, but indicated that lueshite at room temperature might consist of intergrown pinned metastable domains with orthorhombic (Pbnn + Cmcm) and/or monoclinic (P2₁/n) structures. Such structural changes are analogous to those observed for NaTaO₃ during cooling which shows phase coexistence of Pbnn + Cmcm structures at room temperature (Knight and Kennedy, 2015). Arulesan et al. (2016a,b) have demonstrated, using K- and CaTiO₃-doped NaNbO₃, that the phase coexistence is not a function of hysteresis on cooling but is related to compositional heterogeneities or defects stabilizing the Cmcm phase. These data could explain why lueshite does not exhibit the same crystal structure as pure NaNbO₃. However, recently, we have re-assessed the room-temperature structure of lueshite using time-of-flight high-resolution neutron diffraction data and concluded that a phase coexistence model is not appropriate (Mitchell, Kennedy and Knight, unpublished data). Instead we have determined that lueshite at room temperature adopts the space group Pmmn [a = 7.8032(4) Å; b = 7.8193(4) Å; c = 15.6156(9) Å], analogous to that of phase S of synthetic NaNbO₃ at 480–510°C (Peel et al., 2012) with a 2ap × 2ap × 4ap superlattice. This structure cannot be described using the original Glazer tilt scheme as there are compound octahedron tilts along the c axis. Peel et al. (2012) describe the structure as resulting from combinations of zero (0), in-phase (C) and anti-phase tilts (A) along the c axis, with the compound tilt scheme being a* b* c* where c*, represents a compound tilt system composed of three distinct contributions; ACAC, CCCC; A0C0.

We recommend that lueshite be retained as the name for perovskite-group minerals with the general formula (Na,REE,Ca)(Nb,Ti)O₃ and no A- or B-site cation ordering, whose compositions are such that: (1) monovalent cations predominate in the A-site with Na as the dominant constituent; (2) pentavalent cations predominate in the B-site with Nb as the dominant constituent. Compositions fall within the lueshite field in the ternary compositional system (mol.%) NaNbO₃–NaREETi₂O₆–CaTiO₃ (Fig. 13).
Recently, Menesez Filho et al. (2015) have described a polymorph of NaNbO$_3$ with a trigonal structure from the Jacupiranga carbonatite complex (Brazil). The mineral, named pauloabibite, adopts an ilmenite-type structure and is thus not a member of the perovskite supergroup.

Isolueshite (Na,La,Ce,Ca,Sr)(Nb,Ti,Ta)O$_3$

Isolueshite is found only in a hydrothermally-altered pegmatite vein in urtite-ijolite at the Khibiny alkaline complex (Chakhmouradian et al., 1997). Isolueshite exhibits discontinuous compositional zoning with the La/Ce ratio, Nb, Th, Sr and Ca contents decreasing from the cores of cubo-dodecahedral crystals to their margin. The mineral in terms of its composition, but not structure, can be regarded as REE-rich (La-dominant) lueshite, and is approximately an intermediate member of the solid solution series between NaNbO$_3$ and NaREETi$_2$O$_6$. Isolueshite is not an end-member NaNbO$_3$ composition and is considered by Chakhmouradian et al. (1997) not to be a dimorph of lueshite, although the mineral is listed simply as NaNbO$_3$ in the current IMA list of mineral names. Krivovichev et al. (2000) have shown by single-crystal diffraction methods that the mineral is cubic $Pm\bar{3}m$ and, unlike other cubic perovskites, is characterized by a disordered arrangement of the oxygen atoms in the 12 $h$ site. The $A$-site is cation deficient (0.05–0.07 apfu) and the presence of hydroxyl groups (0.1 apfu) replacing oxygen was confirmed by infrared spectrometry.

The status of isolueshite as a distinct mineral species rather than a higher-symmetry variety of lueshite is perhaps ambiguous. However, isolueshite is topologically distinct from lueshite in that the oxygen atoms are disordered (Krivovichev et al., 2000), thus justifying a different root name (Nickel and Grice, 1998). Applying the dominant constituent rule, Na and Nb are the dominant cations in the $A$- and $B$-sites with REE occurring as subordinate $A$-site constituents. As isolueshite is an IMA approved mineral name we recommend retention of this name.

Lakargiite (CaZrO$_3$)

Lakargiite occurs in high-temperature skarns in calc-silicate rocks found as xenoliths in ignimbrites of the Upper-Chegem volcanic structure, North

These data were compatible with structural data from electron back-scattered diffraction patterns. Diffraction methods and the structure was determined for CaTiO3, CaSnO3, and in some examples, minor CaZrO3 (Fig. 16), with the remainder consisting of Ca2(Fe3+Nb)O6. Galuskin et al. (2008) were unable to obtain structural data using single-crystal methods because of the complex twinning of all crystals examined. However, powder X-ray diffraction patterns could be refined by Rietveld methods in space group Pbnm in accord with the space group of synthetic CaZrO3 (Koopmans et al., 1983). Note that all end-members of the ternary system CaZrO3–CaTiO3–CaSnO3 (Fig. 15) are Pbnm-GdFeO3-structured compounds, thus it is reasonable to assume that all samples of lagarkiite are orthorhombic Pbnm minerals. Lagarkiite has also been found as sub-micrometre crystals in a carbonaceous chondritic meteorite (Ma, 2011).

We recommend that lagarkiite be retained as the name for perovskite-group minerals with the general formula (Ca)(Zr,Sn,Ti)O3 and no A- or B-site cation ordering, whose compositions are such that: (1) divalent cations predominate in the A-site with Ca as the dominant constituent; (2) tetravalent cations predominate in the B-site with Sn as the dominant constituent. Compositions fall within the lagarkiite field in the ternary compositional (mol.%) system CaZrO3–CaTiO3–CaSnO3 (Fig. 16).

**Oxide single perovskites with second order Jahn-Teller distortions**

Second order Jahn-Teller distortions result from weak covalent bonding and/or lone-pair effects. Compounds having the perovskite structure exhibiting this style of distortion are characterized by displacements of the A- and B-site cations from the centres of coordination polyhedra with (e.g. PbHfO3) or without (e.g. PbTiO3) octahedron tilting. Megaw (1968, 1973) noted that three styles of Jahn-Teller distortion are possible for perovskite BX6 polyhedra: (I) along the tetrad axis resulting in a tetragonal unit cell; (II) along a diad giving an orthorhombic unit cell; (III) along a triad giving a rhombohedral unit cell. Macedonite and barioperovskite are examples of types I and II distortion, respectively (see below).

**Macedonite (PbTiO3)**

Macedonite was initially described from Crni Kamen (or Kara Kamen), near Prilep, south-central Republic of Macedonia (Radusinovic and Markov, 1971). The holotype mineral consisted of small (<0.2 mm) crystals in amazonite quartz syenite veins emplaced in pyroxene amphibole schist. Subsequently, macedonite was found as small inclusions (<50 μm) within hematite and ganomalite from Mn-rich skarns at Långban and Jakobsberg, Värmland (Sweden) by Burke and Kieft (1971) and Dunn et al. (1985). Macedonite from Crni Kamen is the only natural perovskite mineral known to contain significant amounts of Bi2O3 (2.2 wt.%). The crystal structure has not been determined by single crystal or Rietveld methods, but is considered on the basis of the powder X-ray diffraction pattern to be isomorphous with synthetic tetragonal P4mm PbTiO3 (Nelmes and Kuhs, 1985) and BaTiO3 (Buttner and Maslen, 1992).

Macedonite, if analogous in structure to PbTiO3, is the only known example of a perovskite-group mineral whose structure is determined by...
type I second order Jahn-Teller effects from the aristotype. For synthetic $P4_{2}2_{1}2$ PbTiO$_3$, the Ti atoms are displaced 0.32 Å along the $c$ axis of the TiO$_6$ polyhedra with the Pb cations displaced in the same sense, but with a different magnitude (0.48 Å), resulting in the adoption of tetragonal symmetry.

We recommend that macedonite be retained as the name for naturally-occurring PbTiO$_3$ whose compositions are such that: (1) divalent cations predominate in the $A$-site with Pb as the dominant constituent; (2) tetravalent cations predominate in the $B$-site with Ti as the dominant constituent.

Barioperovskite ($BaTiO_3$)

Barioperovskite occurs as micro-to-nanocrystals in a host of amorphous material within hollow tubular inclusions in benitoite at the Benitoite Gem mine, California (Ma and Rossman, 2008). Although Ma and Rossman (2008) report the presence of 0.89 wt.% SiO$_2$, this is considered to result from excitation of the host matrix. The crystals found were too small for single-crystal X-ray diffraction studies and the structure was determined from electron back-scattered diffraction patterns as compared to those of synthetic BaTiO$_3$. These patterns gave a best fit with the orthorhombic $Amn2$ structure, which is stable between 183 and 278 K. This orthorhombic polymorph of BaTiO$_3$ is an example of a type II second order Jahn-Teller distortion. Note that synthetic BaTiO$_3$ also adopts a $P4_{2}2_{1}2$ structure between 278 and 393 K (Kwei et al., 1993) and that the material examined by Ma and Rossman (2008) could have inverted from this tetragonal precursor. Note also that structural studies of BaTiO$_3$ are hampered by the development of metastable monoclinic and rhombohedral domains in tetragonal and orthorhombic crystals (Cao et al., 2009; Tsuda et al., 2013). The only other report of a natural occurrence of BaTiO$_3$, in the matrix of the Allende meteorite (Tanaka and Okumura, 1977), was not confirmed by Ma and Rossman (2008).

We recommend that barioperovskite be retained as the name for naturally-occurring BaTiO$_3$ where the compositions are such that: (1) divalent cations predominate in the $A$-site with Ba as the dominant constituent; (2) tetravalent cations predominate in the $B$-site with Ti as the dominant constituent.

Fluoride single perovskites – neighborite subgroup

The fluoride single perovskites $ABF_3$ (Table 1; Fig. 6) are the fluoride analogues of the oxide single perovskites. The structures of minerals in this group can be described by the octahedron tilting schemes used for $ABO_3$ perovskites.

Neighborite ($Na,K)(Mg,Ba)F_3$

Neighborite, NaMgF$_3$, was initially described by Chao et al. (1961) from a dolomitic shale of the Eocene Green River Formation, South Ouray, Uintah County, Utah, USA. Subsequently, neighborite has been found in a variety of parageneses ranging from biotite albite through alkaline granites to calcite carbonatites (see Mitchell, 2002). In all of these examples the mineral is essentially pure NaMgF$_3$. Only, the neighborite occurring in the natrocarbonatite lavas erupted by the volcano Oldoinyo Lengai (Tanzania) differs in containing 15.5–16.8 wt.% K and 8.0–15.2 wt.% Ba, thus exhibiting solid solution towards KMgF$_3$ and KBaF$_3$ (Mitchell, 1997).

Chao et al. (1961) were unable to determine the crystal structure of neighborite, and on the basis of the similarity of the powder XRD pattern with that of CaTiO$_3$, following Kay and Bailey (1957), assigned it to space group $Pcmn$. As the mineral is effectively pure NaMgF$_3$, and in keeping with the space group settings used for other members of the supergroup, neighborite is best described in the orthorhombic $Pbnm$ setting (Zhao, 1998; Chakhmouradian et al., 2001).

We recommend that neighborite be retained as the name for naturally-occurring (Na,K)(Mg,Ba)F$_3$, whose compositions are such that: (1) monovalent cations predominate in the $A$-site with Na as the dominant constituent; (2) divalent cations predominate in the $B$-site with Mg as the dominant constituent.

Parascandolaite ($KMgF_3$)

Parascandolaite, KMgF$_3$, occurs as a volcanic sublimate in a fumarole developed on scoria produced by the 1944 eruption of Vesuvius (Demartin et al., 2014). Previously, a mineral with the probable composition of KMgF$_3$ had been reported in sublirates from Nyiragongo volcano (Democratic Republic of Congo) by Herman et al. (1960), although this was not recognised as a novel mineral species. Parascandolaite, has also been found as nano-inclusions in diamonds from Juina by Kaminsky et al. (2016).

Parascandolaite is pure KMgF$_3$, and single-crystal X-ray diffraction studies show conclusively that it adopts the cubic space group $Pm\bar{3}m$, in
common with the synthetic analogue (Zhao, 1998; Chakhmouradian et al., 2001).

The material from Oldoinyo Lengai shows that neoborite and parascanodolaite undoubtedly form a continuous solid solution series in agreement with studies of the synthetic system NaMgF3–KMF3 (Zhao, 1998; Chakhmouradian et al., 2001). Note that intermediate members (35–55 mol.% KMgF3) of this solid solution adopt the tetragonal space group P4/mnm (#127; Glazer tilt a‘a’c’). Thus, potassium neoborite and sodian parascanodolaite are probably tetragonal minerals. These fluoroperovskites provide a good illustration of how the room temperature structure of single \( ABX_3 \) perovskites change as a consequence of compositional changes not involving any variations in intensive parameters.

We recommend that parascanodolaite be retained as the name for naturally-occurring (K,Na)(Mg,Ba)F3, whose compositions are such that: (1) monovalent cations predominate in the \( A \)-site with K as the dominant constituent; (2) divalent cations predominate in the \( B \)-site with Mg as the dominant constituent.

**Chloride single perovskite – chlorocalcite subgroup**

Chlorocalcite, KCaCl3, was recognized in 1872 as a sublimate in fumaroles from Vesuvius volcano (Palache et al., 1951). No single-crystal X-ray diffraction studies of the mineral have apparently been undertaken although synthetic KCaCl3 adopts the space group Phnm (Midorikawa et al., 1979).

**Stoichiometric double perovskites \( A_2BB'X_6 \)**

Ordered members of the perovskite supergroup (Table 1; Fig. 6) are derivatives of the aristotype \( Pm\bar{3}m \) structure formed when either or both of the \( A \)- and \( B \)-site cations are replaced by a combination of other cations located at a specific crystallographic site. If these cations are ordered at only one site the compounds are termed double perovskites, whereas if ordering occurs at both sites they are referred to as complex or quadruple perovskites.

The commonest of the \( B \)-site ordered perovskites have the general formula \( A_2BB'X_6 \), where \( B \) and \( B' \) are different cations in octahedral coordination situated in crystallographically-distinct sites. The \( A \)-site ordered double perovskites \( AA'BX_6 \) and quadruple perovskites \( AA'BB'X_6 \) have not yet been found as minerals but are well-known as synthetic phases. Skutterudites can be considered as non-stoichiometric \( A \)-site vacant quadruple perovskites \( \square\square BB'X_6 \). The quadruple perovskite KCa(NaXe)O6 with Na8+ and Xe8+ ordered on \( B \) and \( B' \) sites synthesized by Britvin et al. (2015) is possibly important with respect to terrestrial noble gas geochemistry. Britvin et al. (2015) have suggested that the observed depletion in Xe in the Earth’s atmosphere could result from trapping of Xe in lower mantle perovskites.

Compounds with equal proportions of \( B \) and \( B' \) cations are termed 1:1 \( B \)-site ordered perovskites. In these, the \( B \) cations are ordered along (111), planes (Fig. 17). Ideally, they exhibit long range order with no mixing of the cations over the two available crystallographic sites. However, site mixing is well-known in synthetic double perovskites and can be quantified by X-ray diffraction by calculation of a long range order parameter (Sléght, 1963; Mitchell, 2002). Such \( B \)-site mixing is present in vapnikite (see below). If the \( BO_6 \) and \( B'O_6 \) octahedra are not tilted, the compounds adopt the space group \( Fm\bar{3}m \) (#225) with a 2\( a_\rho \) (~8 Å) unit cell. With octahedron tilting, eleven space groups (Fig. 5) of reduced symmetry are possible (Howard et al., 2003). The majority of natural minerals are fluorides of monovalent and trivalent cations with 1:1 \( B \)-site ordering (i.e. \( A_2^+ \alpha'B'^+B^{3+}F_6 \)), although a hydroxy-chloride (diaboleite) and an oxide (vapnikite) have also been recognized.

**Double fluoride perovskites – cryolite subgroup**

**Cryolite (Na2NaAlF6)**

Cryolite is the commonest mineral of the double fluoride perovskite subgroup. Cryolite was discovered during the latter part of the eighteenth century in pegmatites associated with F-rich albitized riebeckite granites at Ivgitut, West Greenland. The first description by Abilgaard (1799) predates that of CaTiO3-perovskite by Rose (1839), making cryolite the earliest perovskite-supergroup mineral to be recognized. Cryolite occurs in a very wide range of parageneses (see Mitchell, 2002 for a summary).

Initial optical studies (Krenner, 1883; Böggild, 1912) indicating that cryolite adopts monoclinic symmetry were confirmed by Náray-Szabó and Sasvári (1938), who determined the space group to be monoclinic \( P2_1/n \) (#14: an unconventional setting of \( P2_1/c \)). Subsequently, the crystal structure has been confirmed and refined using single-crystal (Hawthorne and Ferguson, 1975) and Rietveld (Ross et al., 2003) methods. Thus, cryolite is a 1:1 \( B \)-site ordered fluoride perovskite characterized by
tilting of the NaF₆ and AlF₆ octahedra about three axes (a⁺b⁻b⁻). The mineral is typically complexly twinned, possibly as a consequence of inversion from the high temperature Fm3m structure, via a first-order phase transition to a monoclinic C2/m (12; a₀b⁻b⁻) intermediate structure, with the transition from the latter to the room temperature monoclinic P2₁/n structure being a second-order phase transition (Howard et al., 2003). Solid solution between cryolite and elpasolite has not been reported.

**Elpasolite (K₂NaAlF₆)**

Elpasolite, was described initially from quartz riebeckite microcline pegmatites of the Mount Rosa area of the St. Peter’s Dome district, El Paso County, Colorado (Cross and Hillebrand, 1885). Subsequently, the mineral has been found in a wide variety of parageneses [see Mitchell (2002) for a summary].

Frondel (1948) on the basis of a powder XRD pattern of the holotype material concluded that elpasolite adopts the space group Fm3m. Subsequently, Sabelli (1987), using single-crystal diffraction confirmed this hypothesis and determined that the mineral is a 1:1 B-site ordered perovskite. The NaF₆ and AlF₆ octahedra are neither tilted nor distorted. The presence of the large K⁺ cations in the 12-fold coordinated A-site prevents tilting of the BF₆ octahedra.

**Simmonsite (Na₂LiF₆)**

Simmonsite was described initially from the Zapot pegmatite amazonite-topaz-zinnwaldite pegmatite, Hawthorne, New Mexico (Foord et al., 1999). Here the mineral occurs in a late-stage breccia pipe with cryolite, cryolithionite and elpasolite. Simmonsite has been reported, but not described, from the cryolite-bearing Katuginskoye peralkaline granite (Seltman et al., 2010), Transbaikalia, Eastern Siberia.

Foord et al. (2009) were unable to determine the crystal structure because of the ubiquitous twinning, although suggesting the mineral was monoclinic. Ross et al. (2003) have shown that synthetic Na₂LiF₆, in common with cryolite, adopts space group P2₁/n and concluded that the natural material must adopt this space group.

In summary, we recommend retention of the mineral names elpasolite, cryolite and simmonsite and classify them as members of the cryolite
subgroup of 1:1 ordered double fluoride perovskites.

Oxide double perovskites – vapnikite subgroup

Vapnikite (Ca$_2$CaUO$_6$)

Although 1:1 B-site ordered double perovskites are one of the commonest structural types of synthetic perovskite (Mitchell, 2002), the only bona fide naturally-occurring example is vapnikite (Galuskin et al., 2014). Other minerals with this structure recognised in the future would be members of a potential vapnikite (or latrappite see below) subgroup. Vapnikite occurs as small (<10 μm) crystals in larnite-bearing pyrometasomatic rocks of the Hatrurim Formation at Jabel Harmun, Israel. Single-crystal structure determination showed that the mineral adopts the monoclinic space group $P2_1/n$ (#14), as a consequence of ordering and tilting of the CaO$_6$ and UO$_6$ octahedra. The mineral is the natural analogue of $\beta$-Ca$_2$CaUO$_6$, a member of a large group of synthetic U-bearing double perovskites (Knyazev et al., 2011).

Numerous compounds with Te$^{6+}$ instead of U$^{6+}$, including the Te-analogue of vapnikite have also been synthesized (Christy et al., 2016). Vapnikite differs from the synthetic compound in having a larger degree of Ca and U disorder at the octahedral sites and minor incorporation of U$^{6+}$ at the A site coupled with splitting of the O3 site. The structural formula for vapnikite proposed by Galuskin et al. (2014) is [(Ca$_{1.96}$U$_{0.04}$)(Ca$_{0.92}$U$_{0.08}$)(U$_{0.83}$Ca$_{0.17}$)(O$_2$O$_2$O$_3$,85O$_3$A$_{0.15}$)]$\cdot$3H$_2$O. Vapnikite does not exhibit any solid solution with any other elements but is hydrated (1.3–3.4 wt.% H$_2$O) at the margins of the crystals. We recommend retention of the name vapnikite and recognise a vapnikite subgroup, into which other oxide double perovskites could be placed upon their recognition.

Nb- and Fe-rich perovskites – The status of latrappite

The nomenclature of niobium- and iron-rich perovskites has not yet been satisfactorily resolved. In the older literature niobium-rich perovskite was termed ‘knopite’, ‘nioboloparite’ or ‘dysanalyte’. Nickel and McAdam (1963) recommended that both knopite and dysanalyte be abandoned as these minerals are merely Nb-bearing perovskites and members of the loparite–perovskite solid solution series. However, ‘dysanalyte’ from the Kaiserstuhll and Oka carbonatite complexes contains significant amounts of Fe$^{3+}$ and in this respect is not similar to other Nb-bearing perovskites (Mitchell et al., 1998). Following Bonshtedt-Kupletskaya (1946), Tikhnenkov and Kazakova (1957) recognized that Ca$_2$Fe$^{3+}$NbO$_6$ could be a significant, though not dominant component of ‘dysanalyte’. This component was not given a specific name. Regardless of Nickel and McAdam’s (1963) recommendations the term ‘dysanalyte’ remains in use as a varietal name for Nb-Fe-rich perovskites. The name nioboloparite was discredited by Mitchell et al. (1996) as this mineral was shown to be niobian calcian loparite and/or niobian loparite.

The name ‘latrappite’ was introduced by Nickel (1964) on the grounds that unlike CaTiO$_3$ perovskite, the Nb content was greater than the Ti content, although the significant Fe$^{3+}$ content was not considered. It is important to note that the material investigated by Nickel (1964) and Nickel and McAdam (1963) is not a potential end-member composition, and is actually a complex quaternary solid solution involving the components Ca$_2$Nb$_2$O$_7$, Ca$_2$Fe$_3$NbO$_6$, CaTiO$_3$ and NaNbO$_3$ (Fig. 18). The dominant components of this solid solution are Ca$_2$Nb$_2$O$_7$ and Ca$_4$Fe$_3$NbO$_6$. The latter component was termed ‘latrappite’ by Mitchell et al. (1998) and Mitchell (2002), following Tikhnenkov and Kazakova (1957).

In this work, Na-poor, very Ca-Nb-Fe-rich perovskites are considered as unlikely to be a simple solid solution given that one of the three synthetic polymorphs of Ca$_2$Nb$_2$O$_7$ (Scheunemann and Müller-Buschbaum, 1974: Ishizawa et al., 1980; Lewandowski, et al., 1992; Levin and Bendersky, 1999) is an orthorhombic $Pbn$$_2$ layered perovskite (Scheunemann and Müller-Buschbaum, 1974; Levin and Bendersky, 1999) belonging to the $A$_{$m$}$_n$$_{p}X$_{$m$+2} structural group. The orthorhombic, and monoclinic Ca$_4$Nb$_2$O$_7$ compounds, are different in topology from ‘true’ perovskites in that the B-X-B links are broken and slabs of perovskite-like units are mutually displaced (see below). Note that if the Ca$_2$Nb$_2$O$_7$ component of Nb-rich perovskite is considered to have the same structural topology as $ABX_3$ perovskite it would be required to have A- and B-site vacancies i.e. (Ca$_{1.714}$□$_{0.286}$)(Nb$_{1.714}$□$_{0.286}$)O$_3$.

Synthetic Ca$_2$Fe$^{3+}$NbO$_6$ is a 1:1 B-site ordered double perovskite which adopts the monoclinic space group $P2_1/n$ (tilt scheme $a\ a\ c^*$; Chakhmouradian and Mitchell, 1998; Barnes et al., 2009). In addition, synthetic Ca$_2$Fe$^{3+}$NbO$_6$ has also been shown by Chakhmouradian and
Mitchell (1998) to exhibit B-site mixing. Simple continuous solid solutions between these potential end-member compounds is extremely unlikely, except for examples in which \((\text{Nb} + \text{Fe}^{3+}) < \text{Ti}\) (apfu). Note that most natural \(\text{Pbnm CaTiO}_3\) perovskites exhibit very limited substitution of Ti by Fe\(^{3+}\) (1–2 wt.% \(\text{Fe}_2\text{O}_3\)) even in Fe-rich parageneses (Mitchell, 2002). Kimura and Muan (1971a,b) have shown that under strongly reducing conditions in the system \(\text{CaO–FeO–TiO}_2\) there is no appreciable solid solution of Fe in \(\text{CaTiO}_3\), whereas in air, perovskite can contain up to 83 wt.% Fe substituting for Ti. Chakhmouradian and Mitchell (2001) have found some groundmass perovskite in kimberlites to contain up to 8.3 wt.% \(\text{Fe}_2\text{O}_3\) which is present as an orthoferrite component (6–13 mol.% \(\text{REEFeO}_3\)).

Mitchell et al. (1998), on the basis of Rietveld refinement of the laboratory powder X-ray diffraction pattern, claimed that latrappite from Oka is an orthorhombic \(\text{Pbnm}\)-structured mineral. However, Barnes et al. (2009) and Lufaso and Woodward (2004) note that neutron and/or synchrotron diffraction methods are required for determination of the correct crystal structure of many single and double perovskites. Thus, it is highly probable that standard powder laboratory X-ray diffraction methods do not have the required resolution to distinguish between the \(\text{Pbnm}, \text{P2}_1/n\) and \(\text{Pbn}2_1\) space groups.

In their structural study of synthetic binary perovskites with compositions \(\text{CaTi}_{3-x}\text{Fe}_x\text{Nb}_x\text{O}_3\) (\(0 \leq x \leq 0.5\)), Chakhmouradian and Mitchell (1998) found that all had the \(\text{Pbnm}\) structure with complete disorder of Fe\(^{3+}\), Ti\(^{3+}\) and Nb\(^{5+}\) at the B-site. Stachowicz, Welch and Mitchell (unpublished data) have determined the crystal structures of eleven natural Nb-rich \((\text{Na}, \text{Ca})_2(\text{Fe}^{3+},\text{Ti}^{3+},\text{Nb}^{5+})_2\text{O}_6\) perovskites having \(\text{Ca}_2\text{Fe}^{3+}\text{Nb}_x\text{O}_6\) (latrappite) contents of 25–62 mol.% \(\text{Na}_2\text{Nb}_2\text{O}_6\) contents of 25–48 mol.% \(\text{Ca}_2\text{Fe}^{3+}\text{Nb}_2\text{O}_7\) contents of 8–24 mol.%.

There is a clear negative correlation between \(\text{Ca}_2\text{Nb}_2\text{O}_7\) and \(\text{Ca}_2\text{Fe}^{3+}\text{Nb}_2\text{O}_6\) contents. All of these perovskites have the \(\text{Pbnm}\) structure, with Nb\(^{5+}\), Fe\(^{3+}\) and Ti\(^{4+}\) disordered at the B-site. Refinements in space group \(\text{P2}_1/n\), which allows for ordering at two non-equivalent B-sites, indicated almost identical compositions (refined site-scattering values) for these two sites, demonstrating that the disordered \(\text{Pbnm}\) model is correct. No evidence for a ‘defect’ \(\text{Ca}_2\text{Nb}_2\text{O}_7\)-type structural component was found, e.g. anomalous displacement parameters of oxygen atoms; superlattice reflections violating the \(\text{Pbnm}\) cell. Thus, any \(\text{Ca}_2\text{Nb}_2\text{O}_7\) component in these perovskites would appear to be incorporated as a part of the general disorder at the B-sites and does not have a distinctive structural signature.

It remains to be shown if latrappites with higher \(\text{Ca}_2\text{Nb}_2\text{O}_7\) and \(\text{Ca}_2\text{FeNbO}_6\) contents can have a structural signature associated with
vacancies, ordering, or Ca$_2$Nb$_2$O$_7$ polysomatic intergrowths (see below). The compositions of the latrappites chosen for structural studies undertaken so far confirm the dominance of the characteristic Ca$_2$FeNbO$_6$ component in solid solutions.

The orthorhombic compound Ca$_2$Nb$_2$O$_7$ (actually Ca$_4$Nb$_4$O$_{14}$) is the $n=4$ member of the homologous $A_nB_nX_{3n+2}$ series (Levin and Bendersky, 1999). These compounds consist of perovskite-like slabs containing $n$ layers of BO$_6$ octahedra (Fig. 19). The perovskite slabs are off-set from each other by crystallographic shear with a translation vector of about $(\sqrt{3}/2)a_p$. In effect extra oxygen is added to the vacancies in the BO$_6$ lattice created by the crystallographic shear. Of relevance to latrappite is that high resolution transmission electron microscopy (HRTEM) studies have revealed that many synthetic $A_nB_nX_{3n+2}$ compounds are actually composed of ordered intergrowths of different members of a homologous series, i.e. a polysomatic series. Portier et al. (1974) initially recognized that the (NaCa)$_n$Nb$_{n}O_{3n+2}$ or, the Ca$_2$Nb$_2$O$_7$–NaNbO$_3$ solid solution series, with $n=4.5$ were composed of slabs with 4 and 5 layers of octahedra which formed ordered intergrowths in the sequence 5-4-4-5-4-4-5 (NaCa$_{12}$Nb$_{13}$O$_{45}$) and 4-5-4-5 (NaCa$_{8}$Nb$_{9}$O$_{31}$). Other studies (Nanot et al., 1975; Williams et al., 1993; Levin et al., 2000) have reported blocks of 'normal' perovskite interspersed with slabs of layered perovskites. From these studies it is apparent that the homologous series of compounds between Ca$_2$Nb$_2$O$_7$ and NaNbO$_3$ (Portier et al., 1974) or Ca$_2$Nb$_2$O$_7$ and CaTiO$_3$ (Nanot et al., 1975) form a polysomatic series rather than atomic solid solutions. As applied to latrappite it is possible that increasing Nb contents are accommodated by the formation of slabs of layered perovskite between blocks of normal perovskite. Mitchell et al. (1998) attempted to obtain evidence for this hypothesis from HRTEM lattice images. However, high-resolution images did not reveal any intergrowths for any of the grains examined. Either these samples did not contain sufficient amounts of the Ca$_2$Nb$_2$O$_7$.
component to permit formation of discrete poly-synthetic intergrowths, or such layers occurred in an orientation that was not visible in this preliminary study. In summary, the mechanism by which Fe$^{3+}$ and Nb$^{5+}$ are accommodated as either Ca$_2$Fe$_3^+$NbO$_6$, Ca$_3$Nb$_2$O$_7$ or Ca(Fe$_{3+}$,Nb)$O_3$ with or without lattice vacancies remains elusive. Further study of the crystal structure of Ca$_2$Fe$_3^+$NbO$_6$–Ca$_2$Nb$_2$O$_7$-rich latrappite by HRTEM and synchrotron X-ray diffraction is desirable to determine whether cation ordering, cation vacancies, polysomatic intergrowths, or other compositional domains are present or not. The formation of discrete short-range ordered domains with cation vacancies is one possibility.

How is latrappite to be defined if the name is to be retained? The mineral is not merely a Nb-rich Pbnm CaTiO$_3$ perovskite and the original definition by Nickel (1964) ignores the Fe$_{3+}$ content. Given the observation that the dominant molecules in very Nb-and Fe$_{3+}$-rich perovskites appear to be Ca$_2$Nb$_2$O$_7$ and Ca$_2$Fe$_3^+$NbO$_6$, we suggest that the potential end-member latrappite be considered as analogous to synthetic 1:1 ordered Ca$_2$Fe$_{3+}$NbO$_6$. However, without further crystallographic data, and in order to retain the name latrappite, we recommend that Ca-rich, Nb- and Fe-rich perovskites [(Ca$_2$Na)$_2$(Nb,Fe$_{3+}$,Ti)$_2$O$_6$] whose compositions are such that: (1) divalent cations prevail in the A-site with Ca dominant; and (2) pentavalent cations prevail in the B-site(s) with Nb dominant be termed latrappite. Compositions (mol.%) plotting within the Ca$_2$Fe$_{3+}$NbO$_6$ and Ca$_2$Nb$_2$O$_7$ fields in the quaternary compositional system Ca$_2$Nb$_2$O$_7$–CaTiO$_3$–Ca$_2$Fe$_{3+}$NbO$_6$–NaNbO$_3$ (Fig. 18) can be termed latrappite. Note: Ca$_2$Nb$_2$O$_7$ is another potential naturally-occurring perovskite supergroup end-member composition for which a name would be desirable.

Double antiperovskite group $B_2XX'A_6$

Sulphohalite subgroup

Sulphohalite, Na$_6$FCl(SO$_4$)$_2$, was originally described from the Searles Lake (California) inter-montane evaporate deposits by Hidden and MacKintosh (1888), and its cubic structure determined by Pabst (1934). Sulphohalite has recently been identified by Kaldos et al. (2015) in carbonate-rich melt inclusions in jacupirangite from Kerimasi volcano (Tanzania). Krivovichev
Perovskite Supergroup

(2008) has recognized that sulphohalite is an ordered double antiperovskite with the anti-elpasolite structure and the space group \( Fm\bar{3}m \). Double antiperovskites have the general formula \( B_2X X' A_6 \) (Mitchell, 2002, Krivovichev, 2008). In sulphohalite the structure consists of a framework of alternating anion-centred \([FNa_6]\) and \([ClNa_6]\) octahedra with tetrahedral \((SO)_4\) units occupying the cavities in this framework (Fig. 20). We consider that sulphohalite is a member of the perovskite supergroup and recommend retention of the name.

Non-stoichiometric perovskites

Here we define ‘non-stoichiometric’ specifically in relation to the stoichiometry of \( ABX_3 \) perovskites in which all sites (cation and anion) are fully occupied, i.e. a non-stoichiometric perovskite has partial occupancy of cation \((A, B)\) and/or anion \((X)\) sites. Such perovskites (Tables 2 and 3; Fig. 7) include: (1) \( A \)-site vacant double hydroxides, or hydroxide perovskites, belonging to the söhngeite, schoenfliesite and stottite subgroups; (2) Anion-deficient perovskites of the brownmillerite subgroup (brownmillerite; srebrodolskite, shulamitite); (3) \( A \)-site vacant quadruple perovskites (skutterudite subgroup); (4) \( B \)-site vacant single perovskites (oskarssonite subgroup); (5) \( B \)-site vacant inverse single perovskites (cohenite and auricupride subgroups); (6) \( B \)-site vacant double perovskites (diaboleite subgroup); (7) Anion-deficient partly-inverse quadruple perovskites (hematophanite subgroup).

A-site vacant hydroxide perovskites

Natural and synthetic examples of both single and double perovskites are known for hydroxides lacking \( A \)-cations and having the general stoichiometry \( \square_{2}(BB')(OH)_6 \). The octahedral framework sites can accommodate homovalent and heterovalent cations. The primary distinction made in this classification of hydroxide perovskites is between those with one or two different cations in their end-member formula. Following our hierarchical classification (Table 2; Fig. 7) we refer to these fundamentally different types as ‘single’ and ‘double’ hydroxide perovskites.

Paragenesis and current nomenclature

Detailed descriptions of the compositional variation and parageneses of hydroxide perovskite minerals can be found in Mitchell (2002). The currently IMA-approved nomenclature together with our hierarchical classification of these minerals is given in Table 2. Note that some of the components reported in published analyses may reflect the presence of impurities.

Hydroxide perovskite aristotypes

The aristotype of single hydroxide perovskites (Fig. 21), as represented by synthetic \( \text{In(OH)}_3 \) (Mullica et al., 1979) and \( \text{Sc(OH)}_3 \) (Schubert and Seitz, 1948) has space group \( \text{Im}\bar{3} \) (\#204) and tilt system \( \langle a'a' a' \rangle \). The structure of natural \( \text{In(OH)}_3 \), the mineral dzhalindite, is unknown, but assumed to be \( \text{Im}\bar{3} \) as powder XRD data indicate a cubic unit cell.

In double hydroxide perovskites (Fig. 22), the ordering of the \( B \) and \( B' \) cations leads to the loss of \( I \)-centring and the aristotype has space group \( Pn\bar{3} \) (\#201), but with the same tilt system \( \langle a'a'a' \rangle \). Numerous natural stannate hydroxide perovskites have this space group, including: schoenfliesite \( \text{MgSn(OH)}_6 \); wickmanite \( \text{MnSn(OH)}_6 \); and nata- nite \( \text{FeSn(OH)}_6 \).

Topological constraints on space groups

The presence of an \( O-H \) bond forces the \( B-O-B' \) linkages to be non-linear, resulting in highly-tilted octahedra and rendering impossible the aristotypic tilt system \( a'^0a'^0a'^0 \) (space group \( Pm\bar{3}m \)) of hydroxide perovskites. Hence, no hydroxide perovskite has a zero tilt. Furthermore, mirror symmetry is only possible for single hydroxide perovskites, such as söhngeite \( \text{Ga(OH)}_3 \) (\( P4_2/nmc \), \#137; or \( P4_2/n \), \#86) and \( \text{In(OH)}_3 \) (\( \text{Im}\bar{3}, \#204 \)), as the mirror planes pass through the oxygen atoms between octahedra. In contrast, while it is theoretically possible for double perovskites to have mirror planes, these must bisect octahedra and the resulting structures have gross distortions due to size mismatch between cations, as seen in the previously reported structures of natanite \( \text{FeSn(OH)}_6 \) (\( Pn\bar{3}m \); Strunz and Contag, 1960) and
Three natural homovalent, or single, hydroxide perovskites have been found: bernalite [Fe(OH)$_3$] (Birch et al., 1993; Welch et al., 2005); dzhalindite [In(OH)$_3$] (Mullica et al., 1979; Genkin and Mura’eva, 1964); and söhngeite [Ga(OH)$_3$] (Scott, 1971). In addition, a synthetic single hydroxide perovskite, δ-Al(OD)$_3$ (Matsui et al., 2011), has been synthesized which is orthorhombic with space group $P2_1_2_1_2_1$ (tilt system $a' a' c'$). Dzhalindite is the only single hydroxide perovskite having a cubic structure (space group $I m$
overline{3}) at ambient conditions.

A definitive structure for bernalite has yet to be reported. Originally, the structure of bernalite was determined in space group $I m mm$ (#71; tilt scheme $a' b' c'$) by Birch et al. (1993). Subsequently, space
group $Pmmn$ ($\#71$; tilt scheme $a' b' c'$) was proposed by McCammon et al. (1995) and Welch et al. (2005), as numerous strong reflections violating $I$-centring were observed.

The original reported structure of söhngeite, Ga(OH)$_3$, from Tsumeb (Scott, 1971) was orthorhombic with the non-centrosymmetric space group $Pmn2_1$ ($\#31$; tilt scheme $a$–$b$–$c$). A recent structure determination of söhngeite using single-crystal XRD (Welch and Kleppe, 2016) found that it adopts either space group $P4_2/nmc$ ($\#137$) or $P4_2/n$ ($\#86$) with a very different tilt system ($a' a' a'$), and on heating to 423 K transforms to an $Im\overline{3}$ structure ($a' a' a'$).

Double hydroxide perovskites

All heterovalent double hydroxide perovskites $\Box_2BB'(OH)_6$ have ordered frameworks in which different cations alternate on crystallographically non-equivalent $B$-sites e.g. schoenfliesite $[\text{MgSn} (\text{OH})_6]$; burtite $[\text{CaSn(OH)}_6]$; stottite $[\text{FeGe(OH)}_6]$; and mopungite $\text{NaSb(OH)}_6$. Complete ordering of heterovalent cations in double hydroxide perovskites is required to satisfy bond-valence constraints of bridging O atoms, each of which is bonded to an H atom as OH. Disorder in heterovalent structures is prohibited by under- or over-bonding of these O atoms, e.g. $\text{Mg}–\text{O}–\text{Mg} + \text{O}–\text{H} = 1.67$ valence units (vu), $\text{Sn}–\text{O(H)}–\text{Sn} + \text{O}–\text{H} = 2.33$ vu, compared with $\text{Mg}–\text{O}–\text{Sn} + \text{O}–\text{H} = 0.33 + 0.67 + 1 = 2$ vu. The motifs of burtite and stottite are shown in Fig. 21.

Most double hydroxide perovskites reported to date are stannates and, with the exception of tetrawickmanite $\text{MnSn(OH)}_6$, and synthetic $\text{CuSn(OH)}_6$, are cubic (reported space groups $Pn\overline{3}$ or $Pn\overline{3}m$). Of the non-stannates, stottite $\text{FeGe(OH)}_6$ (Strunz et al., 1958; Strunz and Giglio, 1961; Ross II et al., 1988) and mopungite $\text{NaSb(OH)}_6$ (Williams, 1985) are reported as tetragonal with space group $P4_2/n$ ($\#86$). $\text{CuSn(OH)}_6$ was reported as having space group $P4_2/nmn$ (Morgenstern-Badarau, 1976), but this is almost certainly incorrect as the mirror planes of this structure bisect octahedra (see above).

Jeanbandyite Fe$^{3+}$Sn(OH)$_5$O

Kampf (1982) refined unit-cell parameters of type jeanbandyite from Llallagua, Bolivia, from powder X-ray diffraction data as $a = c = 7.648(7)$ Å, recognizing that while this cell is metrically cubic, the mineral is optically uniaxial and, therefore, probably tetragonal. The identification of jeanbandyite as a hydroxide perovskite was based upon the similarity of its unit-cell parameters, powder diffraction pattern and general stoichiometry to stottite-group minerals. The empirical formula of jeanbandyite from the type locality Llallagua, Bolivia, originally reported by Kampf (1982) is $(\text{Fe}^{3+}_{0.71},\text{Mn}^{2+}_{0.21},\text{Mg}_{0.04}) (\text{Sn}_{0.78}\Box_{0.02})$ (OH)$_6$, which is not charge-balanced (an excess charge of $+0.11$), but was preferred over a charge-balanced formula requiring $\text{O}^{2-}$ replacing some OH. The $+0.11$ excess charge was inferred to be due to some minor undetermined amount of $\text{Fe}^{2+}$. Kampf (1982) gave a general formula $(\text{Fe}^{3+}_{1-x}\Box_x)(\text{Sn}_{1-x}\Box_x)$.
Jeanbandyite was re-examined by Betterton et al. (1998) from Hingston Down Quarry, Cornwall (UK), who noted that the empirical formula of Kampf (1982) did not consider the presence of divalent cations and was not charge-balanced. They proposed a revised empirical formula \( \text{Fe}_{1.28}^{3+}\text{Sn}_{0.28}^{4+}\text{Mn}_{0.03}^{2+}\text{Mg}_{0.03}^{2+}(\text{OH})_{9}^{6-} \), which is charge-balanced. However, this revised formula also implies 13% vacancies at B-sites (and 5% vacancies at B’-sites).

In view of the uncertainties in the formula of jeanbandyite and the absence of a structure determination, Welch and Kampf (2017) re-examined samples from Llallagua (Kampf, 1982) and Hingston Down (Betterton et al., 1998), and determined the structures of crystals from both localities. All crystals are cubic with space group \( \text{Pn}\overline{3} \) and have fully-occupied B- and B’-sites (Fe and Sn, respectively). Welch and Kampf (2017) emphasize that \( \text{Pn}\overline{3} \) and \( \text{P4}_2/\text{n} \) structures have significantly different octahedral tilt systems \( (a’+a’+a)c’ \), respectively) that lead to different oxygen arrays which can be distinguished by single-crystal XRD. Bond-valence sums and octahedral volumes of the B-sites show clearly that Fe is predominantly in the ferric state. For example, the volume of the \( \text{Fe(OH)}_{6} \) octahedron of Hingston jeanbandyite is 11.15 Å\(^3\). This value compares with 10.80 Å\(^3\) for \( \text{Fe}^{3+}(\text{OH})_{6} \) in bernalite \( \text{Fe(OH)}_{3} \) (Birch et al., 1993), and 13.13 Å\(^3\) for \( \text{Fe}^{2+}(\text{OH})_{6} \) in stottite \( \text{Fe}^{2+}\text{Ge(OH)}_{6} \) (Klepppe et al., 2012). Assuming a linear variation in octahedral volume with composition, the volume observed for Hingston jeanbandyite implies 85% \( \text{Fe}^{3+} \) and 15% \( \text{Fe}^{2+} \) at this site. This calculation for Llallagua jeanbandyite gives 78% \( \text{Fe}^{3+} \) and 22% \( \text{Fe}^{2+} \). Bond-valence sums for the B-sites of these two crystals are 2.93 vu and 2.82 vu, respectively. Welch and Kampf (2017) confirm that jeanbandyite is a \textit{bona fide} mineral species and revise its end-member formula to \( \text{Fe}^{3+}\text{Sn}^{4+}(\text{OH})_{2} \). As such, jeanbandyite corresponds compositionally to oxidized natanite; it is an example of a stoichiometric partially-protonated hydroxide perovskite. What appears to be an analogous synthetic phase was reported by Nakayama et al. (1977) using powder XRD. The reader is referred to Welch and Kampf (2017) for a full discussion of the crystal chemistry of jeanbandyite.

Wunder et al. (2011) reported that the synthetic high-pressure \( 3.65\text{Å-phase} \), \( \text{MgSi(OH)}_{6} \), is also a hydroxide perovskite. Originally, the space group was determined as orthorhombic \( \text{Pnam} \) (765), but has been shown subsequently to be monoclinic with a space group that is either \( \text{P2}_1 \) (46) by density-functional theory (Wunder et al., 2012) or \( \text{P2}_1/\text{n} \) (14) by single-crystal XRD (Welch and Wunder, 2013).

### Synthetic hydroxide perovskites

The synthesis of stannate hydroxide perovskites has been investigated extensively by the materials science community in the search for non-spherical hollow nanostructures. Synthesis methods typically involve fast stoichiometric precipitation from alkaline solution (Kramer et al., 2010; Wang et al., 2013) or sonochemical (Cheng et al., 2013) methods at ambient conditions. Numerous synthetic analogues of stannate hydroxide perovskites have been produced by diverse hydrolysis reaction involving metal chlorides and either stannous chloride (\( \text{SnCl}_2 \)) with sodium citrate (Wang et al., 2013), or alkali hexa-hydroxide stannates under alkaline conditions (\( \text{NH}_3\text{OH} \) or \( \text{NaOH} \), e.g.

\[
\text{CaCl}_2 + \text{K}_2\text{Sn(OH)}_6 . 3\text{H}_2\text{O} \\
\rightarrow \text{CaSn(OH)}_6 + 2\text{KCl} + 6\text{H}_2\text{O}
\]

The hydroxide perovskites formed in these reactions are very insoluble in water and precipitate immediately on mixing of the reagents. Rinsed products are usually pure and well-crystallized with no amorphous residue. Studies of synthetic hydroxide perovskites should be particularly useful for understanding the structures and potential solid solutions of natural examples e.g. the schoenfliesite–wickmanite–natanite solid solution series (see below). For example, Neilson et al. (2011), in contrast to natural hydroxide perovskites, have shown that precipitation can yield ordered compounds only when the \( B \) cation is \( \text{Mn}^{2+} \) or \( \text{Co}^{2+} \) and not when it is any other transition metal or \( \text{Zn}^{2+} \).

### Solid solutions

Most natural hydroxide perovskites exhibit very limited solid solution and occur as near end-member compositions. It appears that the framework does not tolerate large differences in atomic radii of divalent cations at the B-sites, suggesting that next-nearest-neighbour interactions between homovalent cations are important.

The only examples of significant solid solution found so far are: mushistonite (\( \text{Cu, Mn}^{2+}, \text{Fe}^{2+} \)) \( \text{Sn(OH)}_6 \) (Marshukova et al., 1978, 1984); natural and
synthetic CuSn(OH)$_6$–ZnSn(OH)$_6$ hydroxide perovskites (Marshukova et al., 1984; (Mn$^{2+}$, Fe$^{2+}$, Mg)Sn(OH)$_6$ in schoenfliesite–wickmanite (Nefedov et al., 1977) and (In, Fe)(OH)$_3$ in dzhalindite (Kiseleva et al., 2008).

The type-locality mushistonite, from the Mushiston tin deposit (Tadzhkistan) is reported by (Marshukova et al., 1978) to exhibit a wide range of composition, i.e. $(Cu^{0.68}–0.41Zn^{0.14}–0.41Fe^{0.23}–0.40)Sn^{0.82}–1.25(OH)_{5.69}–6.0$. Natural mushistonite, defined generally as $(Cu,Zn,Fe^{2+})Sn(OH)_6$, has been reported as cubic $Pn$3$m$. However, the synthetic end-member CuSn(OH)$_6$ has a metrically tetragonal unit cell and its structure has been refined in space group $P4_2/nnm$ (Morganstern-Badarau, 1976), corresponding to tilts of $a_0b_1$ $b_2$. However, as noted above, the reported structure is improbable as it requires extremely distorted Cu(OH)$_6$ and Sn(OH)$_6$ octahedra. In addition, a zero tilt is very unlikely on account of the strong hydrogen-bonded bridges and an empty $A$-site. The structure of mushistonite and synthetic CuSn(OH)$_6$ requires re-evaluation and investigation of potential Jahn-Teller effects.

Synthetic vismirnovite ZnSn(OH)$_6$ adopts space group $Pn$3 (Morganstern-Badarau, 1968). For solid solutions between ZnSn(OH)$_6$ and CuSn(OH)$_6$, the cubic ($Pn$3) structure extends from vismirnovite ZnSn(OH)$_6$ to (Cu$_{0.4}$Zn$_{0.6}$)Sn(OH)$_6$. Bulk compositions from Cu$_{50}$Zn$_{50}$ to Cu$_{80}$Zn$_{20}$ produce mixtures of tetragonal ($P4_2/n$?) and cubic phases. There is very limited solid solution in the tetragonal phase (Cu$_{90}$Zn$_{10}$–Cu$_{100}$). The Raman spectrum of synthetic CuSn(OH)$_6$ contains six peaks and is consistent with space group $P4_2/n$. Vismirnovite from the type locality, the Trudovoe tin deposit (Kyrgyzstan) has the composition $(Zn_{0.89}Cu_{0.1}Fe_{0.08})Sn_{1.0}(OH)_{6.04}$ (Marshukova et al., 1981) and presumably adopts space group $Pn$3.

In a study of hydrothermally-mineralized skarns at Pitkäranta, Nefedov et al. (1977) showed that minerals of the schoenfliesite–wickmanite series exhibited a wide range in composition ranging from Mn-rich schoenfliesite (up to 55 atomic % wickmanite) to Fe-rich wickmanite (up to 50 atomic % natanite). The minerals were found to be compositionally heterogeneous on a scale of micrometres and did not represent any regular core–rim zoning. Nefedov et al. (1977) concluded that there is undoubtedly a continuous solid solution series between schoenfliesite, wickmanite and natanite. Further study is required to verify this hypothesis.

Kiseleva et al. (2008) have described optically- and compositionally-zoned dzhalindite from the Bugdaya Au-Mo-(W)-porphyry deposit (E. Transbaikalia, Russia). The 30–94 μm oscillatory-zoned cubic crystals (Fig. 23) consist of colourless zones with 0.6–1.1 wt.% Fe and light brown zones with up to 3.6 wt.% Fe. Kiseleva et al. (2008) have suggested that the Fe is present as microinclusions of Fe$^{3+}$ compounds and that Fe does not replace In at the lattice site. Further study is required to verify this hypothesis.

Hydrogen-bonding topologies of hydroxide perovskites

The octahedra of hydroxide perovskites are corner-linked and there is no $A$-site cation. Thus, hydrogen-bonded linkages can assume a potentially significant role in controlling the degrees of rotation of octahedra, and prevent zero tilts; they may also drive phase transitions.

Hydrogen positions have been determined using powder neutron diffraction for schoenfliesite, burtite (Basciano et al., 1998) and synthetic In(OH)$_3$ (Mullica et al., 1979). The hydrogen-bonding connectivity of the framework of octahedra as defined by O–H···O donor-acceptor bridges, can be inferred. These bridges form across the shorter O···O distance (2.5–2.7 Å) in each quartet of octahedra; the other O···O distance is far too long (>4 Å) for such bridges to form. Different tilt systems lead to different hydrogen-bonding topologies. Knowing the tilt system permits inference of the hydrogen-bonding connectivity and thereby evaluation of plausible H positions in difference-Fourier maps.
FIG. 24. The three different components of hydrogen-bonding topologies of hydroxide perovskites: isolated ring; crankshaft; and zigzag chain. The inferred local occupancy of hydrogen sites is shown. Hydrogen positions have been located in the cubic phases dzhalindite, schoenfliesite, wickmanite and burtite, all of which have only isolated rings. In these three phases there are two \( \frac{1}{2} \)-occupied H sites.

FIG. 25. Hydrogen bonding topologies of hydroxide perovskites determined by single-crystal XRD. Isolated 4-membered rings in (a) söhngeite Ga(OH)\(_3\) (\(P4_2/mmc\)) and (b) burtite (\(Pn\bar{3}\)). Crankshafts in (c) söhngeite Ga(OH)\(_3\) and (d) stottite FeGe(OH)\(_6\) (\(P4_2/\text{I}n\)). All H sites are half-occupied in the averaged structure determined by diffraction methods. The number of non-equivalent OH groups in söhngeite (five) and stottite (six) have been confirmed by Raman spectroscopy. In the ring of söhngeite the pairs of H sites are mirror-related, whereas they are non-equivalent in stottite which being a double-perovskite lacks mirror symmetry.
PEROVSKITE SUPERGROUP

Very recent single-crystal XRD studies of hydroxide perovskites with space groups $Pn\bar{3}$ and $P4_2/n$ have found that [110] merohedral twinning is common (Lafuente et al., 2015; Welch and Kleppe, 2016). Merohedral twinning has been recognized in all $Pn\bar{3}$ and $P4_2/n$ hydroxide perovskites including Mn-schoenfliessite, wickmannite, tetrawickmanite and stottite. Once merohedral twinning has been refined a key aspect of the crystal structure emerges in difference-Fourier maps: the presence of half-occupied H sites, as discussed in detail below. It is, perhaps, surprising that it is possible to assign $\frac{1}{2}$ electron to a plausible half-occupied H site, but the close correspondence between approximate H positions found by single-crystal XRD in wickmannite–schoenfliessite and those determined by neutron diffraction for schoenfliessite, burtite and In(OH)$_3$ leaves little room for doubt.

Once H sites have been located, it is possible to make sense of vibrational (infrared and Raman) spectra in the OH-stretching region which, for non-cubic species, seem to be at variance prima facie with the determined space group. The presence of such half-occupied H sites increases the number of OH peaks in spectra beyond that expected for full occupancy. For example, the O–H spectrum of tetrawickmanite (Lafuente et al., 2015) has five resolved peaks, which is incompatible with $P4_2/n$ symmetry if all H sites are full (three non-equivalent OH). The tetrawickmanite structure determined by Lafuente et al. (2015) has four half-occupied H sites and a fifth fully-occupied H site in a very different type of location from those of the other four H sites. Analogous features have now been recognized in stottite and synthetic MgSi(OH)$_6$.

Three different components of the hydrogen-bonding connectivities of hydroxide perovskites have been identified: (1) isolated four-membered rings; (2) crankshafts; (3) zigzag chains. Figure 24 shows the local configurations of OH groups associated with each component. Figure 25 shows the hydrogen bonding topologies of söhngeite and stottite determined by single-crystal XRD. In stottite and tetrawickmanite (both $P4_2/n$) pairs of half-occupied H sites lie along the O–(H)–O crankshaft and there is only a single fully-occupied H site in the 4-membered ring, giving five non-equivalent H sites in all. In söhngeite ($P4_2/nnm$) there are again four non-equivalent half-occupied H sites in the crankshaft, but the $\{100\}$ mirror planes produce four pairs of half-occupied equivalent sites in the four-membered ring.

**Tilt systems of hydroxide perovskites**

The tilt systems of hydroxide perovskites are shown in Table 2. As with other perovskites, the tilt notation is based upon the orientation of the rotation axes of the cubic aristotype (Glazer, 1972). Natural hydroxide perovskites studied so far have tilt systems $a^* a^* a^+$ ($Pn\bar{3}$ and $Im\bar{3}$), $a^* a^+ c^-$ ($P4_2/nnm$, $P4_2/n$, $P2/n$), $a^+ b^+ c^-$ ($Pmmm$), $a a b^+$ ($P2_1/n$), $a b b^+$ ($P2_1$) and $a b b^+$ ($Pnma$ and $P2_1$) have been reported for synthetic hydroxide perovskites. Each tilt system is associated with a distinctive hydrogen-bonding connectivity, as described below.

The two cubic space groups of hydroxide perovskites, $Im\bar{3}$ and $Pn\bar{3}$, with the tilt system $a^* a^* a^+$ are the aristotypes of the single and double perovskites, respectively. Both have a unique large vacant cage site located at a centre of symmetry and defined by twelve oxygen atoms at the apices of an icosahedron (Fig. 26). Each pentagonal face of this icosahedron consists of three oxygen and two cation sites. Six O···O distances bounding this cage are O–H···O bridges associated with one of the two non-equivalent H atoms. The hydrogen-bonding connectivity consists only of isolated 4-membered rings.
It has been suggested that the icosahedral cage site might host H₂O (Birch et al., 1993), but there is no clear evidence so far to support this suggestion. For example, no significant residual electron density within the cage site cavity has been found by diffraction methods. However, it is conceivable that H₂O could be disordered over several partially-occupied sites within this large cavity.

The second type of non-framework ‘cavity’ in these cubic structures is much more restricted in volume and is defined by eight cation and eight oxygen sites, with pentagonal bounding faces. A 4-membered ring lies at the centre of this volume.

Hydroxide perovskites with space groups Pnma \((a^+b^-c^-)\), \(P4_{2}/nmc\), \(P4_2/n\ \((a^+a^-c^-)\) and \(P2/n\ \((a^+b^-c^-)\) are characterized by one antiphase tilt and two in-phase tilts. The hydrogen bonding connectivity consists of alternating layers of crankshafts and isolated 4-membered rings. The example of stottite is shown in Fig. 27.
\( P_{21} (a' a'^{-} c'^{-}) \), are characterized by having two anti-phase and one in-phase tilt. Their hydrogen-bonding connectivity consists of interleaved crankshafts and zigzag chains. The example of synthetic \( \delta\)-Al(OH)\(_3\) (Matsui et al., 2011), space group \( Pnma \), is shown in Fig. 27.

**Phase transformations of hydroxide perovskites**

Compared to oxide and fluoroperovskites, very few investigations of phase transitions of hydroxide perovskites have been undertaken. Possible continuous transitions can, in principle, be postulated using a group theoretical approach. However, account must be taken of the potential effects of strong hydrogen bonding, which might inhibit tilting-related transitions. As such hydroxide perovskites are very suitable structures for evaluating the role of hydrogen bonding in phase transitions. Examination of group-subgroup relations for known hydroxide perovskite space groups suggests that continuous transitions might be rare, due to the avoidance of structures with zero tilts i.e. due to strong hydrogen bonds.

A further constraint on phase transitions relates to the absence of mirror symmetry in double hydroxide perovskites. Only single hydroxide perovskites can have mirror symmetry, as these planes must pass through shared oxygen atoms. As discussed above this is not possible for double hydroxide perovskites as adjacent octahedra are occupied by different cations, and mirror planes bisecting octahedra result in implausible distortions.

In the absence of continuous phase transitions in double hydroxide perovskites involving the creation of mirror symmetry and/or zero tilts, the options seem to be limited. The most obvious possibilities are \( P2/n \leftrightarrow P4_{2}/n \leftrightarrow P4_{2}/nmc \) in single hydroxide perovskites and \( P2/n \leftrightarrow P4_{2}/n \) in double hydroxide perovskites. Transitions involving loss or gain of centrosymmetry might also be possible i.e., \( P2_{1}/n \rightarrow P2_{1} \) or \( P2_{1}/n \rightarrow Pn \). Evidence, from Raman spectra, for a pressure induced transition \( P2/n \leftrightarrow P4_{2}/n \) at \( \sim 11 \) GPa in stottite, was reported by Kleppe et al. (2012). This transition is reversible but shows clear hysteresis on decompression.

Polymorphism involving structures with different tilt systems can occur in hydroxide perovskites. However, as far as we are aware, the only example of polymorphism in hydroxide perovskites is that of MnSn(OH)\(_6\) for which the polymorphs are wickmanite (cubic \( Pn3 \)) and tetrawickmanite (tetragonal \( P4_{2}/n \)). Following our comments above on space group nomenclature for polymorphs note that tetrawickmanite could also be termed wickmanite-\( P4_{2}/n \). The cubic polymorph has a cell volume (489 Å\(^3\)) that is 2% larger than that of tetrawickmanite.
(480 Å³); evidently, the change in tilt system permits a marked contraction of the framework. Welch and Kleppe (2016) report a temperature-induced structural transformation in söhngeite Ga(OH)₃ from the ambient P4₃/nmc (or P4₁/n) structure to cubic Im3 at ~150°C. This transition has considerable hysteresis and the cubic polymorph is preserved metastably on cooling to room temperature.

**Classification of hydroxide perovskites**

The hierarchical classification of hydroxide perovskites is given in Table 2 and is based upon composition and symmetry. It highlights the major distinctions and similarities between these phases. In developing this classification we intend to provide a basis for predicting further possible structures, and to allow for the incorporation of future discoveries of new stoichiometries.

The classification of hydroxide perovskites follows that proposed above for ABX₃ and A₂BB’X₆ perovskites. Thus, the fundamental distinction is between ‘single hydroxide perovskites’ and ‘double hydroxide perovskites’. This classification of hydroxide perovskites leads to the recognition of three subgroups: the single hydroxides of the söhngeite subgroup; and the double hydroxide perovskites of the cubic schoenfliesite and the tetragonal stottite subgroups. Table 2; Fig. 7).

Finally, it is evident that there are several interesting avenues of research for future study of hydroxide perovskites namely: (1) What are the correct space groups of hydroxide perovskites? (2) What phase transitions occur in hydroxide perovskites? (3) What is the interplay between composition and tilt system? (4) What is the physical significance of the different hydrogen-bonding topologies, e.g. upon compressional behaviour?

**A-site vacant quadruple perovskites**

**Skutterudite subgroup**

The skutterudite group (Table 3; Fig. 7) are derivatives of ordered quadruple perovskites [AA′B₄X₁₂] characterized by vacant A-sites i.e. □B₄X₁₂ (B = Fe, Co, Ni, Ru, Rh, Ir, Os; X = As, Sb, P). Many synthetic skutterudite-group compounds have been synthesized but only four minerals have been recognized, namely: skutterudite (CoAs₃; Haidinger, 1845); ferroskutterudite [(Fe,Co)As₃; Spiridonov et al., 2007]; nickelskutterudite (NiAs₃; Spiridonov and Gritsenko, 2007); and kieftite [CoSb₃; Dobbe et al., 1994]. Other synthetic skutterudites are known with the large A-site filled partially e.g. □₃B₄X₁₂ (A = La–Yb, U, Th), such as La□₃Fe₄P₁₂ (Jaitscho and Braun, 1977), but are as yet unknown as minerals.

All skutterudites adopt the space group Im3 with the tilt system a⁺a⁻a⁺. The structure consists of a framework of corner-sharing CoAs₆ or CoSb₆ octahedra (Fig. 28). The As and Sb anions in the skutterudite subgroup are bonded to form square planar tetramers [X₄]⁺, making them also good examples of Zintl compounds (Luo et al., 2014). To date B-site ordered derivatives have not been recognized. The structure of the skutterudites is nearly identical to that of the single hydroxide perovskite dzhalindite [In(OH)₆], except that in the latter the anion bonds are asymmetrical O···H···O rather than the symmetrical X···X bonds of the skutterudites. Dzhalindite could be also considered as an A-site vacant quadruple perovskite.

**B-site vacant perovskites**

**B-site vacant single perovskites A□X₃**

**Oskarssonite subgroup**

Two B-site vacant single fluoride perovskites (Table 3; Fig. 7), oskarssonite (ideally AlF₃) and waimirite-(Y) [ideally YF₃], have been approved as valid members of the perovskite supergroup (Table 3; Fig. 7). Both are derivative structures of the cubic ReO₃ aristotype formed by tilting of AlF₆ octahedra. In common with ReO₃ no cations occupy the B site of the octahedron framework.

Although Al-fluorides had been recognized in fumaroles from the Hekla (Oskarsson, 1981) and Mount Erebus (Rosenberg, 1988) volcanoes, a complete structural characterization was not available until material from fumaroles of the Eldfell volcano (Iceland) was undertaken by Jacobsen et al. (2014). A mineral with the composition of oskarssonite, together with parascandolaite, has also been found as nano-inclusions in diamonds from Juina by Kaminsky et al. (2016). Oskarssonite [Al(F₂.62(OH)0.49)] adopts the rhombohedral space group R3c (#167) in common with the synthetic analogue α-AlF₃ (Le Bail and Calvayrac, 2006). Oskarssonite is the only known natural perovskite-supergroup mineral with the a⁺a⁻a⁻ tilt scheme resulting in an anticlockwise rotation angle (ω) of 10.65° about [111]ₐ of the AlF₆ octahedra (Fig. 29). Oskarssonite transforms to the cubic ReO₃ structure above 450°C (Jacobsen et al., 2014).
The B-site vacant single perovskite, waimirite-(Y), [(Y,REE)(F,O)₃], has been recognized from A-type granitic rocks occurring at Pitinga (Brazil) and Jabal Tawlah (Saudi Arabia) by Atencio et al. (2015), and as a hydrothermal mineral in REE-enriched granites from Myanmar (Sanematsu et al., 2016). Single-crystal XRD studies of the material from Jabal Tawlah show that the mineral adopts space group Pbnm and is the natural analogue of synthetic β-YF₃ (ÖKeefe and Hyde, 1977; Galashina et al., 1980). The A site is dominated by Y coupled with substantial amounts of the heavy REE (Y₀.69–0.79REE₀.21–0.28), and the X site contains significant O and vacancies (F₂.54,□₀.25, O₀.21).

**B-site vacant single antiperovskites X□A₃**

Stoichiometric antiperovskites (Table 3; Fig.7) have the composition A₃BX or XBA₃ e.g. K₃OBr; Ca₃NAs (Mitchell, 2002, Krivovichev, 2008). When the B-site is vacant, as in X□A₃, derivative synthetic compounds such as Au□Cu₃ (auricupride) and C□Fe₃ are formed (ÖKeefe and Hyde, 1977) Note synthetic auride antiperovkites containing Au⁻¹ anions e.g. AuOK₃, have been synthesized by Feldmann and Jansen (1995).

**Cohenite Subgroup**

Cohenite, C(Fe,Ni,Co)₃ is a B-site vacant carbide antiperovskite which adopts the space group Pbnm. The mineral was initially found in the Magura meteorite (Slovakia) and is a common constituent of other iron meteorites. Other occurrences are in highly reducing environments produced when high temperature basaltic lavas have invaded coal deposits e.g. Qeqertasuaq (Disko) Island, Greenland (Pauly, 1969). Kaminsky et al. (2015) have reported the presence of a N-bearing mineral similar to cohenite as nano-inclusions in Juina diamonds.

**Auricupride subgroup**

Auricupride is a B-site vacant intermetallic antiperovskite (Au□Cu₃) formed in serpentinites by the low-temperature unmixing of Au-Cu alloys. Palladium-bearing varieties were formerly described by the now discredited name rozhokovite. Auricupride and the synthetic analogue adopt the space group Pm/am (Megaw, 1973), although a tetragonal P4/mmm polymorph is also known (Bayliss, 1990). Although many intermetallic antiperovskites have been synthesized the only varieties which occur as minerals in a wide variety of serpentinites and platinum-group element ore deposits include: Pm/am awaruite (Fe□Ni₃); chengdeite (Fe□Ir₃); isoferriplatinum (Fe□Pt₃); yixunite (In□Pt₃); and zvyagintsevite (Pb□Pt₃); together with Pm/am rustenburgite (Sn□Pt₃); and atokite (Sn□Pd₃). Rustenburgite and atokite form a complete solid solution series. The reduction in symmetry from Pm/am in the synthetic analogues to...
Fm3m is considered to result from strain induced during mineral processing (Mihalik et al., 1975).

**B-site vacant ordered double perovskites**

**Diaboleite subgroup**

The chloro-hydroxy double perovskite diaboleite (Pb2Cu□Cl2(OH)4; P4mm) is unusual in that in addition to having vacancies at one octahedral site, its structure exhibits both first order Jahn-Teller and lone-pair effects arising from the presence of Cu and Pb, respectively. Diaboleite was described originally from the iron ore mine located at Higher Pitts Quarry, Mendip Hills, Somerset (UK) by Spencer and Mountain (1923), and has been found subsequently in a variety of parageneses, particularly as a secondary phase in oxidized Ag-Pb veins and chemically-weathered metallurgical slags.

The crystal structure was initially determined by Byström and Wilhelmi (1950) and refined by Rouse (1971) who recognized the mineral is a tetragonal P4mm (##99) defect perovskite. Subsequent work by Cooper and Hawthorne (1995) confirmed the structure as a B-site defect perovskite of the type Pb2(Cu□)X6 in which half of the octahedra are not occupied by cations. In diaboleite the Pb coordination is highly asymmetric as it is surrounded on one side by four OH– anions (Pb–OH = 2.46 Å), and on the other by four Cl– anions (3.22 Å and 3.40 Å) in square antiprismatic coordination (Fig. 30). The lone pair electrons project towards the Cl– anions. The Cu2+ site exhibits strong [4+2] first order Jahn-Teller distortion and is surrounded by four equatorial OH– anions (Pb–OH = 1.97 Å) and two apical Cl– anions (Pb–Cl 2.55 Å and 2.95 Å) with Cu2+ displaced 0.34 Å from the centre of the polyhedron (Fig. 30). The coordination can be considered as intermediate between octahedral and square pyramidal.

**Anion-deficient or defect oxide perovskite subgroups**

Anion-deficient, non-stoichiometric perovskites (Table 3; Fig. 7) typically range in composition from ABO3 to ABO2.5, and have the general formula ABO3−δ (0 < δ ≤ 0.5). The anion deficiency reflects the replacement of cations by other ions in a lower oxidation state (e.g. Ti4+ by Fe3+ in CaTiO3; Becerro et al., 1999). The vacancies created can be ordered or random. In the ordered structures the vacancies are arranged in parallel rows along [101]p of the original cubic cell forming layers on either side of a layer of tilted corner-sharing perovskite BO6 octahedra. Within the oxygen-deficient layers cations occur as pairs of corner-sharing tetrahedra (Fig. 31). The original perovskite stoichiometry is thus modified to A2B2TX3□, where T represents a tetrahedral coordinated cation. The compounds with the maximum oxygen vacancy are termed brownmillerites in the materials science literature, after the compound Ca2Fe3+AlO5, occurring as a
mineral and a major component of Portland cement (Colville and Geller, 1971).

**Brownmillerite-subgroup**

**Brownmillerite \([\text{Ca}_2(\text{Fe}^{3+}\text{Al})\text{O}_5]\)**

Brownmillerite was recognized, and named (without IMA approval), as a constituent of Portland cement (Hansen et al., 1928; Bogue, 1955) prior to its discovery as a mineral. Natural brownmillerite was recognized subsequently in spurrite- and larnite-bearing metamorphosed argillaceous limestones of the Hatrurim Formation (Israel) and thermally-metamorphosed limestone xenoliths in the lavas of the Ettringer Bellerberg volcano, Eifel District (Germany) by Bentor et al. (1963) and Hentschel (1964), respectively. Although, the proposal of Hentschel (1964) to name the material from Bellerberg ‘brownmillerite’ appeared after the publication of Bentor et al. (1963), the latter report did not actually contain any analytical information about the new mineral, and hence, Bellerberg should be considered as the type locality. Compositional data obtained by electron microprobe analysis indicates that the Hatrurim material ranges from Fe-dominant compositions with \(\sim 20\) mol.% Ca\(_2\)Al\(_2\)O\(_5\) (Sharygin et al., 2008) to varieties with Al > Fe (up to 54 mol.% Ca\(_2\)Al\(_2\)O\(_5\); Gross, 1977; Sokol et al., 2011). Minor constituents exceeding 0.12 apfu are Mg, Ti and Cr. The crystal structure of neither Hatrurim or Bellerberg samples was determined and, on the basis of the powder XRD patterns, was assumed to be identical to that of synthetic orthorhombic \(\text{Ibm2}\) (\#46) \(\text{Ca}_2(\text{Fe}^{3+}\text{Al})\text{O}_5\). Note, however that compositions with < 28 mol.% Ca\(_2\)Al\(_2\)O\(_5\) (e.g. samples M5–31 and H–201 in Table 2 of Sharygin et al. (2008) probably adopt space group \(\text{Pnma}\) (see below).

**Srebrodolskite \((\text{Ca}_2\text{Fe}^{3+}\text{O}_5)\)**

Srebrodolskite, Ca\(_2\)Fe\(_{5}^{3+}\)O\(_5\), was initially described from petrified wood ‘baked’ by burning coal in mines at Kopeisk in the Chelabynsk coal basin, Urals (Chesnokov and Bazhenova, 1985). Note that the mineral and name were approved prior to the IMA decision not to approve technogenic phases as new species. The type material contains 0.08 apfu Mg and 0.03 apfu Mn and is devoid of detectable Al. Subsequently, srebrodolskite has been found in the Clearwater impact crater (Rosa and Martin, 2010), the Bellerberg volcano, the Hatrurim Formation (Sharygin et al., 2008), Lakargi Mountain (Galuskin et al., 2008), and several other less well-characterized localities.

The crystal structure has not been determined by single-crystal methods for any of these examples but is assumed (Chesnokov and Bazhenova, 1985), on the basis of the powder XRD pattern, to be that of synthetic Ca\(_2\)Fe\(_{5}^{3+}\)O\(_5\) i.e. \(\text{Pnma}\) (\#62: Berggren, 1971). Note that the structural data for synthetic srebrodolskite are also reported in the \(\text{Pcmn}\) (\#62: cba) setting (Bertaut et al., 1959).

Brownmillerite and srebrodolskite adopt different space groups as the orientation of the \(\text{TO}_4\) tetrahedra in the two structure types differ. In brownmillerite, all tetrahedra point in the same
direction, to form the sequence $T_{\text{up}}O_{\text{up}}^O$ (Fig. 31), whereas in srebrodolskite the sequence is $T_{\text{up}}O_{\text{down}}^O$. Regardless of this structural difference, studies of synthetic compounds show there is continuous solid solution between brownmillerite and the ferric end-member with the transition from $Ibm_2$ to $Pcmn$ occurring at $Ca_2Fe^{3+}_{2.43}Al_{0.56}O_5$ (Collville and Geller, 1972; Redhammer et al., 2004). The $Ca_2Al_2O_5$ end-member exists only as a quenchable high-pressure phase ($P = 2.5$ GPa) isomorphous with brownmillerite (Kahlenberg et al., 2000). At ambient pressure, Al-dominant compositions with as much as 70 mol.% $Ca_2Al_2O_5$ can be prepared (Taylor, 1997).

Pure $Ca_2Fe^{3+}_2O_5$ and compositions in the solid solution series $Ca_2Fe^{3+}_{2-x}Al_xO_5$ with $x$ up to 0.56 adopt space group $Pnma$, whereas compounds with $x > 0.56$ have $Ibm_2$ symmetry (Redhammer et al., 2004). Thus, synthetic stoichiometric brownmillerite ($Ca_2Fe^{3+}AlO_3$), and Al-dominant phases adopt space group $Ibm_2$. If naturally-occurring phases conform to the same structural principles as their synthetic counterparts, the name brownmillerite should be applied to all intermediate members of the $Ca_2Al_2O_5$-$Ca_2Fe^{3+}_2O_5$ series which adopt space group $Ibm_2$ and those adopting space group $Pnma$ should be termed srebrodolskite. However because of preferential partitioning of Al into the $T$-site, regardless of the Fe/Al ratio. This is because Al is partitioned strongly into the $T$ site until about 2/3 of this site is occupied (Redhammer et al., 2004). However, any Al exceeding 2/3 $T$-site occupancy is distributed equally between the tetrahedrally and octahedrally coordinated sites (Redhammer et al., 2004). Clearly, in addition to brownmillerite sensu stricto, where Al is the dominant cation in the $T$-site and Fe$^{3+}$ in the $B$ site, compositions with Al as the dominant species in both sites could possibly exist in nature (including high-pressure phases approaching $Ca_2Al_2O_5$ in their composition). These hypothetical phases will represent a mineral species distinct from brownmillerite and hence require a different name. If naturally-occurring brownmillerite-type phases exhibit the same pattern of cation distribution as their synthetic counterparts, at least $\sim 25$ wt.% $Al_2O_3$ is required from Al to be the dominant cation in both the $T$- and $B$-sites. The greatest $Al_2O_3$ reported to date (23.2 wt.%; Sokol et al., 2011) falls short of that value. A possible high-pressure $Ca_2Al_2O_5$ brownmillerite-type phase was reported by Rappenglück et al. (2013) as inclusions in Fe-silicides from the Holocene Chiemgau impact strewnfield in southern Germany, but no structural data to support this interpretation were presented.

In summary, recognizing the complexities of Al distribution in this solid solution series we recommend that brownmillerite and srebrodolskite be retained as valid names and that: (1)
brownmillerites are minerals in the solid solution series Ca$_2$Fe$_{3-x}$Al$_x$O$_5$ with $x > 0.56$ which adopt space group $Ibm\bar{2}$; (2) srebrodolskites are minerals in the solid solution series Ca$_2$Fe$_{3-x}$Al$_x$O$_5$ with $x < 0.56$ which adopt space group $Pnma$.

Shulamitite ($Ca_3TiFe^{3+}AlO_8$)
Shulamitite, occurs as a major to accessory mineral in high-temperature metacarbonate larnite rock of the Hatrurim Basin, Israel (Sharygin et al., 2013). The mineral can be considered as an intermediate compound between CaTiO$_3$ perovskite and Ca$_2$(Fe$^{3+}$,Al)O$_5$ brownmillerite and is the natural analogue of synthetic orthorhombic $Pcm2_1$ Ca$_3$TiFe$_{3+}^+$O$_8$ (Rodrigues-Carvajal et al., 1989). The holotype mineral has the composition Ca$_3$TiFe$^{3+}$Al$_{0.7}$Fe$^{3+}_{0.3}$O$_8$, Sharygin et al. (2013) recognize other examples for which Fe$^{3+} >$ Al i.e. an unnamed Fe-analogue [Ca$_3$(TiFe$^{3+}$)Fe$^{3+}$O$_8$] of shulamitite assuming the existence of a solid solution between Ca$_3$TiFeAlO$_8$ and Ca$_3$TiFeFeO$_8$. Single-crystal structure determination shows that shulamitite adopts the orthorhombic space group $Pnma$, that there is no preferred octahedral site occupancy for Ti or Fe$^{3+}$, and that the majority of the Al (with some Fe) is in tetrahedral coordination. The crystal structure of shulamitite consists of double layers of tilted (Ti,Fe)O$_6$ octahedra separated by single layers of paired (Al,Fe)O$_4$.
tetrahedra. The latter have different orientations between each octahedral double layer (Fig. 32).

**Partially vacant B-site quadruple perovskites – hematophanite subgroup**

Hematophanite was initially recognized from Jakobsberg and Långban, Värmland, Sweden (Johansson, 1928). It is also occurs in slag from Reichelsdorf, Hesse, Germany and at the Kombat Cu-Pb-Ag mine, Namibia.

Rouse (1973) recognized that hematophanite, ideally $\text{Pb}_4(\text{Fe}^{3+}\square)(\text{Cl},\text{OH})(\text{O}_6\square_3)$ (or $\text{Pb}_4\text{Fe}^{3+}\text{O}_8\text{Cl}$), was a derivative of the perovskite structure produced by the stacking of four PbFeO$_3$ perovskite-like cells leading to the hypothetical quadruple perovskite Pb$_4$Fe$_4$O$_{12}$. In order to achieve charge balance every fourth Fe$^{3+}$ cation must be replaced by Cl$^-$ (and/or Br$^-$ and OH$^-$) leading to the introduction of B-site vacancies. The X-sites that are adjacent to the Cl anion are vacant resulting in partial occupation by oxygen anions.

Thus, the structure of $P4/mmm$ hematophanite consists of incomplete perovskite Pb$_2$Fe$_2$O$_5$ blocks separated by layers of (Cl,OH) anions. Each perovskite block consists of a corner-sharing FeO$_6$ octahedral layer that is sandwiched between two FeO$_2$ square pyramids. Lead atoms occur at sites within this framework (Fig. 33). Batuk et al. (2013) have shown hematophanite is actually the $n=3$ member of a homologous series of layered synthetic perovskites with the general formula $A_{3n+1}B_nO_{3n+1}\text{Cl}$.

No other minerals with this structure have been found. We recommend that the name be retained and hematophanite be recognised as a bona fide member of the perovskite supergroup.

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PEROVSKITE SUPERGROUP


ADDENDUM

Popova et al. (2017) have recently described a non-centrosymmetric variety of loparite from the Khibiny complex with space group Imma $2\ a = 5.5129(2); b = 5.5129(2); c = 7.7874(5) \ \text{Å}$. This loparite adopts this space group and the tilt scheme $a^0b^1b^2$ as result of being richer in the Na$_{0.5}$Ce$_{0.5}$TiO$_3$ component than the $Pbnm$ loparite described by Mitchell et al. (2000b) from the same locality.