

Accepted 8 March 2016

Stoichiometric partially-protonated states in hydroxide perovskites: the jeanbandyite enigma revisited.

Mark D. Welch ¹, Anthony R. Kampf ²

¹ Department of Earth Sciences, Natural History Museum, London SW7 5BD, U.K.

² Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA.

Abstract

The original description of the hydroxide perovskite jeanbandyite gives a formula $(\text{Fe}^{3+}_{1-x}, \square_x)(\text{Sn}_{1-y}, \square_y)(\text{OH})_6$ (\square = vacancy), which implies the possibility of stoichiometric vacancies at *B* and *B'* sites. The validity of this formula has been questioned subsequently. Furthermore, jeanbandyite has metrically cubic unit cell, but it is optically uniaxial. It is clear that a structure determination is needed to clarify the nature of this enigmatic mineral. Previous studies could not find crystals of sufficient quality for structure determination using X-ray diffractometers available at the time. Crystals of jeanbandyite from Hingston Downs, Cornwall, UK and the type locality Llallagua, Bolivia, have been found that are of a quality that allows structure refinement by single-crystal X-ray diffraction. Structural data for crystals from each locality are presented that clarify the nature of jeanbandyite and raise some interesting questions concerning the significance of partially deprotonated states in perovskite-type structures. The structures of both jeanbandyite crystals are cubic with space group *Pn*3 and unit-cell parameters $a = 7.658(2)$ Å (Llallagua) and $7.6427(2)$ Å (Hingston). The octahedral tilt system is $a^+a^+a^+$ and corresponds to that of the aristotype of $BB'(\text{OH})_6$

hydroxide double perovskites. Structure determination demonstrates that B is very Fe^{3+} -rich and B' is filled by Sn, thereby requiring revision of the general jeanbandyite formula to $\text{Fe}^{3+}_x\text{Fe}^{2+}_{(1-x)}\text{Sn}(\text{OH})_{(6-x)}\text{O}_x$ for $1 \geq x > 0.5$, with an ideal end-member formula $\text{Fe}^{3+}\text{Sn}(\text{OH})_5\text{O}$. As such, jeanbandyite corresponds to oxidised natanite with partially deprotonated oxygen sites. This stoichiometry cannot be represented in space group $Pn\bar{3}$ for the observed unit cell as it implies more than one non-equivalent oxygen atom. Consequently, it is inferred that there is no long-range ordering of deprotonated oxygen sites. It is, however, conceivable that the uniaxial optical character of jeanbandyite is linked to the local short-range order of deprotonated domains.

Key words: hydroxide perovskite, jeanbandyite, natanite, crystal structure

Introduction

Hydroxide perovskites are frameworks of corner-linked octahedra in which all oxygen atoms form OH groups. In contrast to perovskites *sensu stricto*, there is no A cation. There are two stoichiometries $BB'(\text{OH})_6$ or $B(\text{OH})_3$, corresponding to double hydroxide perovskites and single hydroxide perovskites, respectively. In the former group octahedra containing heterovalent cations alternate, whereas in the latter group octahedra are occupied by the same cation. Examples of double hydroxide perovskites include burtite $\text{CaSn}(\text{OH})_6$ (Basciano et al., 1998), natanite $\text{FeSn}(\text{OH})_6$ (Strunz and Contag, 1960), stottite $\text{FeGe}(\text{OH})_6$ (Ross II et al., 1988) mopungite $\text{NaSb}(\text{OH})_6$ (Bittarello et al., 2015) and schönfliesite $\text{MgSn}(\text{OH})_6$ (Basciano et al., 1998). Examples of single hydroxide perovskites are bernalite $\text{Fe}(\text{OH})_3$ (Birch et al., 1993), söhngeite $\text{Ga}(\text{OH})_3$ (Scott, 1971), and dzahlindite $\text{In}(\text{OH})_3$ (Mullica et al., 1979). Octahedra are fully occupied in all hydroxide perovskites. Each OH group is both a hydrogen-bond donor and acceptor, O-H...O-H...O-H.

The absence of an *A*-site cation and the presence of strong hydrogen-bonding between next-nearest-neighbour octahedra leads to collapse of the framework and highly tilted octahedra compared with conventional perovskites. Recent structural and spectroscopic studies have revealed a richness of crystal chemistry relating to partially occupied H sites (La Fuentes et al. 2015; Welch, in preparation) and transitional behaviour (Kleppe et al. 2012; Welch and Kleppe, in review).

In the original study by Kampf (1982) of jeanbandyite from the type locality of Llallagua, Bolivia, unit-cell parameters were refined from X-ray powder diffraction data as $a = c = 7.648(7) \text{ \AA}$, recognising that while the unit cell is metrically cubic the mineral is optically uniaxial and, therefore, likely to be tetragonal. Systematic absences were consistent with space groups $Pn\bar{3}$, $Pn\bar{3}m$ and $P4_2/n$, and so the latter was inferred to be the correct space group.

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. Poor crystal quality (extremely high mosaicity) prevented structure determination using X-ray diffractometers available at the time. Although identifying jeanbandyite as a hydroxide perovskite, the formula proposed by Kampf (1982) is problematic in that it implies that stoichiometric proportions of vacant octahedra can occur. The empirical formula given by Kampf (1982) is not consistent with full occupancy of octahedra that is characteristic of all hydroxide perovskites studied so far.

In the light of recent progress in understanding the crystal chemistry of hydroxide perovskites, and the vast improvement since 1982 of diffractometer performance in handling challenging materials, the present study of the hydroxide perovskite jeanbandyite was undertaken to resolve ambiguities relating to its stoichiometry and structural state.

The empirical formula of jeanbandyite from the type locality Llallagua, Bolivia, originally reported by Kampf (1982) is $(\text{Fe}^{3+}_{0.71} \text{Mn}^{2+}_{0.21} \text{Mg}_{0.04}) (\text{Sn}^{4+}_{0.84} \text{Si}_{0.03}) (\text{OH})_6$, which is not charge-balanced (an excess charge of +0.11), but was preferred over a charge-balanced formula requiring O^{2-} replacing some OH. The +0.11 excess charge was inferred to be due to some minor undetermined amount of Fe^{2+} . A general formula $(\text{Fe}^{3+}_{1-x} \square_x)(\text{Sn}_{1-y} \square_y)(\text{OH})_6$ (\square = vacancy) was proposed that implies the possibility of vacant octahedra.

Jeanbandyite was re-examined by Betterton et al. (1998) from Hingston Downs Quarry, Cornwall (UK), who noted that the empirical formula of Kampf et al. (1982) did not consider the presence of divalent cations and was not charge-balanced. They proposed a revised charge-balanced average empirical formula $(\text{Fe}^{3+}_{0.46} \text{Fe}^{2+}_{0.24} \text{Mn}^{2+}_{0.14} \text{Mg}_{0.03}) (\text{Sn}^{4+}_{0.90} \text{Si}_{0.05}) (\text{OH})_6$. However, this revised formula also implies 13 % vacancies at *B* sites.

In view of the inconsistencies described above and the improbability of stoichiometrically significant proportions of *B*-site vacancies in hydroxide perovskites (severe underbonding of oxygens), we have undertaken a structural study of jeanbandyite from Hingston and Llallagua using single-crystal X-ray diffraction, and report the results here.

Materials and methods

Samples

The two samples of jeanbandyite came from Hingston Downs, Cornwall, UK (Natural History Museum catalogue number BM1985,772) and the type locality Llallagua, Bolivia (Kampf, 1982). The jeanbandyite crystal from Llallagua was obtained from a specimen in the collections of the Natural History Museum of Los Angeles County (catalogue number

19756). This specimen was donated to the museum in 1978 by Jean Bandy as part of the Mark and Jean Bandy Collection. The specimen was presumably collected by Mark Chance Bandy in the late 1930s or early 1940s and is labelled as coming from the Contacto-Dolores vein. This was one of 36 specimens in the collection that contain jeanbandyite and it was examined for the description of the species by Kampf (1982); however, it is not designated as a cotype. The reader is referred to these two papers for details relating to the geological setting and petrogenesis of the jeanbandyite-bearing rocks. A more general description of the mineralogy and geology of Llallagua is provided by Hyršl and Petrov (2006).

Single-crystal X-ray diffraction

Structures were refined from SCXRD data collected for several jeanbandyite crystals from each locality. The structures of the best crystal from each locality are reported here. The dataset for the Hingston crystal ($0.09 \times 0.07 \times 0.06$ mm) was collected using an *XcaliburE* single-crystal X-ray diffractometer (Rigaku Oxford Diffraction) with graphite-monochromatised $\text{MoK}\alpha$ radiation operated at 45 kV, 40 mA and equipped an *EoS 1K* CCD area detector. The data collection strategy was based upon a 25-min pre-experiment. Reflection intensities were corrected for Lorentz-polarization effects and absorption (empirical multi-scan) and converted to structure factors using the program *CrysalisPro*[®] (Rigaku Oxford Diffraction).

The dataset for the Llallagua crystal ($0.04 \times 0.04 \times 0.03$ mm) was obtained using a R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatic $\text{MoK}\alpha$ radiation operated at 50 kV, 40 mA. The Rigaku CrystalClear software package was used for processing of structure data, including the application of an empirical multi-scan absorption correction using ABSCOR (Higashi, 2001).

Information relating to the data collections for the two crystals is given in **Table 1**.

Results

Crystal structure refinement

The unit cells of both crystals are, within the small standard uncertainties, metrically cubic. Systematic absences for both crystals indicate space group $Pn\bar{3}$. Structure refinements were carried out in cubic space group $Pn\bar{3}$ and, given the uniaxial optics reported by Kampf (1982), also in tetragonal space group $P4_2/n$ in order to see how the latter structure compares with the cubic structure. Space group $Pn\bar{3}m$ was discounted on the grounds that its mirror planes bisect all octahedra and lead to gross geometrical distortions, as exemplified by the published structure of natanite by Strunz and Contag (1960). Atom coordinates of wickmanite and tetrawickmanite (Lafuente et al. 2015) were used for refinement of cubic and tetragonal structures, respectively, substituting Fe for Mn. Neutral atomic scattering factors for Fe, Sn and O were taken from *International Tables for Crystallography, Volume A* (Wilson, 1992). The structures of both crystals were refined using SHELX (Sheldrick, 2008) within the WinGX program suite (Farrugia, 1999).

Isotropic refinement of the cubic structure of Hingston jeanbandyite converged to $R_1 = 0.064$, $wR_2 = 0.155$, $GoF = 1.236$, with a maximum residual of $2.1 \text{ e}/\text{\AA}^3$ at 0.98 \AA from the oxygen atom. Anisotropic refinement at this stage did not allow meaningful reflection weighting to be refined (SHELX weighting coefficients were $a = 0$, $b = 32.2$). The residual electron-density maxima and the list of “most disagreeable reflections” indicated the possibility of merohedral twinning, as has been observed in several other cubic and tetragonal hydroxide perovskites (Welch in prep.). Consequently, a twinning operation $(0 \ 1 \ 0/1 \ 0 \ 0/0 \ 0 \ 0$

–1) was tested and isotropic refinement improved significantly with stable reflection weighting to $R_1 = 0.032$, $wR_2 = 0.082$, $\text{GoF} = 1.246$ and maximum residual of $0.9 \text{ e}/\text{\AA}^3$. Finally, full anisotropic refinement with reflection weighting gave $R_1 = 0.027$, $wR_2 = 0.079$, $\text{GoF} = 1.238$ and maximum residual of $0.7 \text{ e}/\text{\AA}^3$. No plausible positions for H atoms were evident in the final difference-Fourier map. Refinement of Llallagua jeanbandyite in $Pn\bar{3}$ had very similar characteristics to those just described for the Hingston crystal. Again, no plausible H positions were evident.

In contrast to the good results obtained for both cubic structures, refinements of both crystals in $P4_2/n$ were problematic. Data reduction for reflections and unit-cell parameters for both crystals was done for a tetragonal structure with $P4_2/n$ symmetry, for which Hingston has $a = 7.6469(2) \text{ \AA}$, $c = 7.6329(4) \text{ \AA}$, $V = 446.34(3) \text{ \AA}^3$, and Llallagua has $a = 7.671(1) \text{ \AA}$, $c = 7.6616(6) \text{ \AA}$, $V = 450.9(1) \text{ \AA}^3$. Initial isotropic refinement of the Hingston crystal resulted in several very similar electron-density residua ($4\text{--}5 \text{ e}/\text{\AA}^3$) that were associated with oxygens O(1) and O(2) three non-equivalent oxygen atoms; at this stage $R_1 = 0.114$, $wR_2 = 0.477$ and $\text{GoF} = 3.125$, with no reflection weighting possible. The positions of residual maxima suggested the possibility of merohedral twinning by $(0\ 1\ 0/1\ 0\ 0/0\ 0\ -1)$, as used for the cubic refinements. Isotropic refinement with merohedral twinning resulted in only minor improvement to $R_1 = 0.098$, $wR_2 = 0.442$ and $\text{GoF} = 2.867$, but it did allow refinement of reflection weights. Isotropic refinement with twinning and reflection weighting converged to $R_1 = 0.097$, $wR_2 = 0.337$ and $\text{GoF} = 1.197$, with a persistent residual maximum of $\sim 4 \text{ e}/\text{\AA}^3$ and large U_{iso} values for O(1) and O(2) atoms (0.059 \AA^2 and 0.068 \AA^2 , respectively), contrasting with the relatively small U_{iso} value of 0.011 \AA^2 for O(3). Finally full anisotropic weighted refinement of the Hingston crystal gave $R_1 = 0.077$, $wR_2 = 0.287$, $\text{GoF} = 1.169$ and the $4 \text{ e}/\text{\AA}^3$ remained. The persistence of the significant residual electron density near O(1) and

O(2) atoms can be rationalised as being due to the wrong of space group, rather than merohedral twinning.

A very similar result was obtained for tetragonal refinement of the Llallagua crystal, except that it was not possible to refine atoms anisotropically, as non-positive-definite U_{ij} values for oxygen atoms were obtained and refinement was slow to converge, with persistent weighting problems. Isotropic refinement with reflection weighting and merohedral twinning gave final values of $R_1 = 0.068$, $wR_2 = 0.237$, $GoF = 1.061$, and a residual electron-density maximum of $3 \text{ e}/\text{\AA}^3$. Consequently, it is clear that the correct space group of jeanbandyite is $Pn\bar{3}$.

Information relating to the structure refinements is summarised in **Table 1**. Atom coordinates and displacement parameters are given in **Table 2**. CIF files and tables of structure factors for both jeanbandyite crystals are deposited with the journal. Bond distances, bond valences and site-scattering values for jeanbandyite are also given in **Table 1**. **Figure 1** shows the structure of Hingston jeanbandyite for cubic and tetragonal refinements. $\text{Fe}(\text{OH})_6$ and $\text{Sn}(\text{OH})_6$ octahedra of the tetragonal structure (**Fig. 1c,d**) have highly variable bond-lengths that reflect the incorrect space group.

The structures of the Hingston and Llallagua crystals are very similar. With the exception of the B site of Llallagua jeanbandyite, the observed site-scattering values for B and B' sites of the two jeanbandyite crystals are in good agreement with those calculated from their average empirical formulas reported by Betterton et al. (1998) and Kampf (1982), when these formulas are correctly formulated as described above.

Bond valence sums of the B sites of the two jeanbandyite crystals (**Table 1**) clearly demonstrate that Fe is predominantly ferric. The volume of the $\text{Fe}(\text{OH})_6$ octahedron of Hingston jeanbandyite is 11.15 \AA^3 . This value compares with 10.80 \AA^3 for $\text{Fe}^{3+}(\text{OH})_6$ in

bernalite $\text{Fe}(\text{OH})_3$ (Birch et al. 1993), and 13.13 \AA^3 for $\text{Fe}^{2+}(\text{OH})_6$ in stottite $\text{FeGe}(\text{OH})_6$ (Kleppe et al. 2012). Assuming a linear variation in octahedral volume with composition, then the value observed for Hingston jeanbandyite implies 85% Fe^{3+} , 15% Fe^{2+} at this site. A similar calculation for Llallagua jeanbandyite, which has an $\text{Fe}(\text{OH})_6$ octahedral volume of 11.31 \AA^3 , implies a composition 78% Fe^{3+} , 22% Fe^{2+} . Thus, the high Fe^{3+} content of jeanbandyite is confirmed. The higher volume of the $\text{Fe}(\text{OH})_6$ octahedron of Llallagua jeanbandyite is consistent with the higher Mn content of this sample.

The volumes of the $\text{Sn}(\text{OH})_6$ octahedron of both jeanbandyite crystals are similar (11.79 \AA^3 , 11.86 \AA^3), but they are significantly larger than those of burtite (11.54 \AA^3), schönfliesite (11.44 \AA^3) and wickmannite (11.48 \AA^3) (Basciano et al. 1998). This difference can be rationalised in terms of the higher Fe^{3+} content of the *B* site which shortens Fe-O bonds and expands the Sn-O bond-length. The tilt angle Fe-O-Sn of jeanbandyite is 137.6° (Hingston) and 137.5° (Llallagua). These values compare closely with 136.8° for schönfliesite and 135.4° for wickmanite. Thus, the larger volume of the $\text{Sn}(\text{OH})_6$ octahedron in jeanbandyite is likely a consequence of the contraction of the Fe site due to Fe^{3+} , rather than being due to tilting of octahedra.

Discussion

Crystal structure determination shows unambiguously that jeanbandyite is cubic with space group $Pn\bar{3}$ and that Fe is predominantly in the ferric state. The implied ideal formula is $\text{Fe}^{3+}\text{Sn}(\text{OH})_5\text{O}$. If we recalculate the empirical formula of Betterton et al. (1998) assuming that all Fe^{3+} was *originally* Fe^{2+} , we obtain a much more reasonable stoichiometry, which is very near to that of a binary natanite-wickmanite solid solution: calculated to six negative charges (six OH) the revised formula is $(\text{Fe}^{2+}_{0.76} \text{Mn}^{2+}_{0.15} \text{Mg}_{0.04})_{\Sigma=0.95} (\text{Si}_{0.05} \text{Sn}_{0.98})_{\Sigma=1.03}$

(OH)₆. Jeanbandyite is then derived from natanite by oxidation involving Fe³⁺ and partial deprotonation: FeSn(OH)₆ → FeSn(OH)₅O + ½H₂. Recalculating the original formula of Betterton et al. (1998) (Fe³⁺_{0.46} Fe²⁺_{0.24} Mn²⁺_{0.14} Mg_{0.03}) (Sn⁴⁺_{0.90} Si_{0.05}) (OH)₆ to seven negative charges gives (Fe³⁺_{0.82} Mn²⁺_{0.16} Mg_{0.04})_{Σ=1.02} (Sn⁴⁺_{1.05} Si_{0.06})_{Σ=1.11} (OH)₅O. If the very minor Si content is ignored (Kampf 1982 comments that it is questionable as to whether or not it is meaningful) and the formula recalculated to one Sn *apfu*, then a charge-balanced formula (Fe³⁺_{0.78} Mn²⁺_{0.15} Mg_{0.04})_{Σ=0.97} Sn (OH)_{5.28}O_{0.72} is obtained that has, within the small analytical uncertainties, fully occupied cation sites.

We note that in their study of synthetic natanite FeSn(OH)₆, Nakayama et al. (1977) found evidence for a phase corresponding to oxidised natanite for which they proposed a formula FeSn(OH)₅O. Although no structural data was presented, the powder diffraction pattern could be indexed as a cubic unit cell with $a = 7.64 \text{ \AA}$ for synthetic “FeSn(OH)₅O” compared with $a = 7.83 \text{ \AA}$ for their synthetic natanite. The former value is close to those reported here for jeanbandyite.

Identification of $Pn\bar{3}$ as the correct space group of jeanbandyite, rather than $P4_2/n$ as originally proposed by Kampf (1982), is significant inasmuch as the oxygen positions and hydrogen-bonding topologies of the two structures are very different, reflecting their different tilt systems ($Pn\bar{3}$ is $a^+a^+a^+$, $P4_2/n$ is $a^+a^+c^-$). The reverse tilt of the tetragonal structure (**Fig. 1b**) leads to chains of hydrogen-bonded ...O-H...O-H...O-H... linkages that are absent from the cubic structure, which has only isolated rings of four hydrogen-bonded OH groups.

A consistent picture has emerged: jeanbandyite is compositionally equivalent to oxidised natanite and is a *bona fide* hydroxide perovskite and mineral species in its own right. Despite its uniaxial optical character, jeanbandyite is cubic, space group $Pn\bar{3}$. How partial deprotonation is achieved at the local level remains to be explored. If there are short-range-

ordered domains containing deprotonated sites, then these may lead to the anomalous uniaxial optical behaviour that appears to be characteristic of jeanbandyite. The recognition of such stoichiometric partially-deprotonated states raises interesting questions concerning their stability relative to fully-protonated hydroxide perovskites. It is conceivable that the $M^{3+}\text{Sn}(\text{OH})_5\text{O}$ stoichiometry could be accessed by other elements with variable oxidation states, such as Co and Mn. Furthermore, the extent of solid solution between divalent and trivalent cations could be increased, corresponding to a general stoichiometry $M^{3+}_xM^{2+}_{(1-x)}\text{Sn}(\text{OH})_{(6-x)}\text{O}_x$ ($1 \geq x > 0.5$).

Acknowledgments

MDW acknowledges support of his research on hydroxide perovskites by Roy Kristiansen through the provision of high-quality samples. We thank reviewers Peter Leverett, Adam Pieczka and Daniel Atencio for their helpful comments on the manuscript. Associate Editor Stuart Mills is thanked for his efficient handling of the review process.

References

- Basciano, L., Peterson, R.L. (1998) Description of schoenfliesite, $\text{MgSn}(\text{OH})_6$, and roxbyite, $\text{Cu}_{1.72}\text{S}$, from a 1375 BC shipwreck, and Rietveld neutron-diffraction refinement of synthetic schoenfliesite, wickmanite, $\text{MnSn}(\text{OH})_6$, and burtite $\text{CaSn}(\text{OH})_6$. *Canadian Mineralogist*, 36, 1203-1210.
- Betterton, J., Green, D.I., Jewson, C., Spratt, J., Tandy, P. (1998) The composition and structure of jeanbandyite and natanite. *Mineralogical Magazine*, 62, 707-712.

- Bittarello, E., Cámara, F., Ciriotti, M.E., Marengo, A. (2015) Ottensite, brizziite and mopungite from Pereta mine (Tuscany, Italy): New occurrences and crystal structure refinement of mopungite. *Mineralogy and Petrology*, 109, 431-442.
- Birch, W.D., Pring, A., Reller, A., Schmalte, H.W. (1993) Bernalite, $\text{Fe}(\text{OH})_3$, a new mineral from Broken Hill, New South Wales: Description and structure. *American Mineralogist*, 78, 827-834.
- Brown, I.D. and Altermatt, D.A. (1985) Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallographica*, B41, 244-247.
- Farrugia, L. J. (1999) WinGX: An integrated system of Windows Programs for the solution, refinement and analysis of single-crystal X-ray diffraction data. *Journal of Applied Crystallography*, 32, 837-838.
- Higashi, T. (2001). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Hyrsl, J. and Petrov, A. (2006): Famous mineral localities: Llallagua, Bolivia. *Mineralogical Record*, 37, 117-162.
- Kampf, A.R. (1982) Jeanbandyite, a new member of the stottite group from Llallagua, Bolivia. *Mineralogical Record*, 13, 235-239.
- Kleppe, A.K. Welch, M.D., Crichton, W.A., Jephcoat, A.P. (2012) Phase transitions in hydroxide perovskites: a Raman spectroscopic study of stottite $\text{FeGe}(\text{OH})_6$ to 21 GPa. *Mineralogical Magazine*, 76, 949-962.
- Lafuente, B., Yang, H., Downs, R.T. (2015) Crystal structure of tetrawickmanite $\text{Mn}^{2+}\text{Sn}^{4+}(\text{OH})_6$. *Acta Crystallographica*, E71, 234-237.

- Mullica, D.F., Beall, G.W. and Milligan, W.O. (1979) The crystal structure of cubic $\text{In}(\text{OH})_3$ by X-ray and neutron diffraction methods. *Journal of Inorganic and Nuclear Chemistry*, 41, 277-282.
- Nakayama, N., Kosuge, K., Kachi, S. (1977) Magnetic properties of $\text{FeSn}(\text{OH})_6$ and its oxidation product $\text{FeSnO}(\text{OH})_5$. *Materials Research Bulletin*, 13, 17-22.
- Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science*, 172, 567–570.
- Scott, J.D. (1971) Crystal structure of a new mineral, söhngeite. *American Mineralogist*, 56, 355.
- Ross II, C.R., Bernstein, L.R. and Waychunas, G.A. (1988) Crystal-structure refinement of stottite, $\text{FeGe}(\text{OH})_6$. *American Mineralogist*, 73, 657-661.
- Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, A64, 112–122.
- Strunz, H von., Contag, B. (1960) Hexahydroxostannate Fe, Mn, Co, Mg, Ca[$\text{Sn}(\text{OH})_6$] und deren kristallstruktur. *Acta Crystallographica*. 13, 601.
- Wilson, A.J.C. (ed.) (1992) *International Tables for Crystallography, Volume C*. Kluwer Academic Publishers, Dordrecht.

Figure Caption.

Figure 1. Comparison of cubic and tetragonal crystal structures of Hingston jeanbandyite projected onto (001). **(a)** Polyhedral representation of the cubic structure showing in-phase tilts and with hydrogen-bonded OH...OH... linkages shown as dashed blue lines. **(b)** Polyhedral representation of the tetragonal structure showing the reverse tilt along [001]. **(c)** A pair of Fe(OH)₆ and Sn(OH)₆ octahedra of the cubic structure showing anisotropic displacement ellipsoids for all atoms drawn at the 68% level. **(d)** A pair of Fe(OH)₆ and Sn(OH)₆ octahedra of the tetragonal structure showing anisotropic displacement ellipsoids for all atoms drawn at the 68% level. As well as implausibly large displacements of O(1) and O(2) atoms, both octahedra of the tetragonal structure have highly variable bond-lengths not seen in hydroxide perovskites, and being due to the incorrect choice of space group $P4_2/n$.

Figure 1

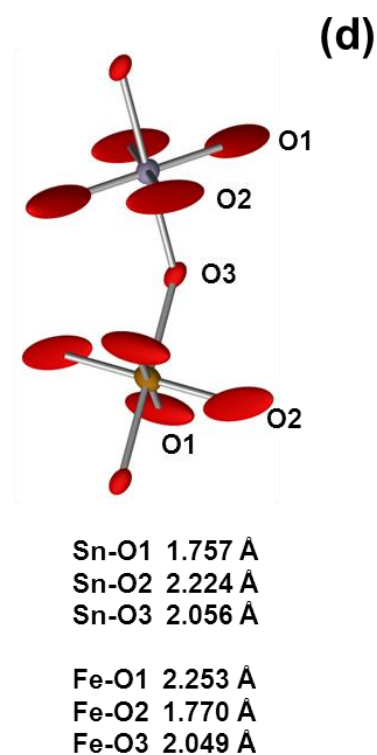
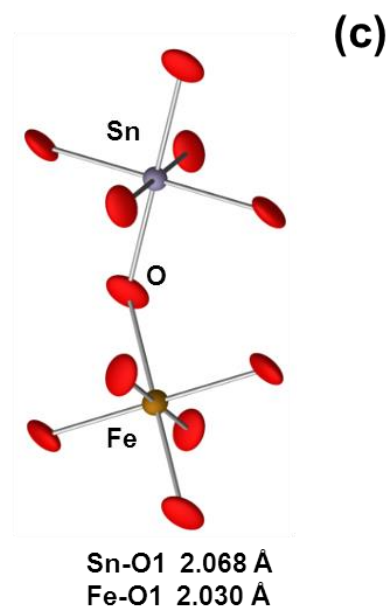
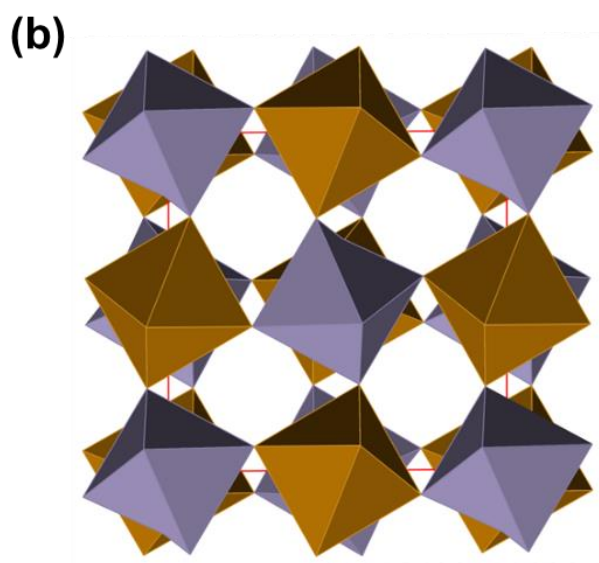
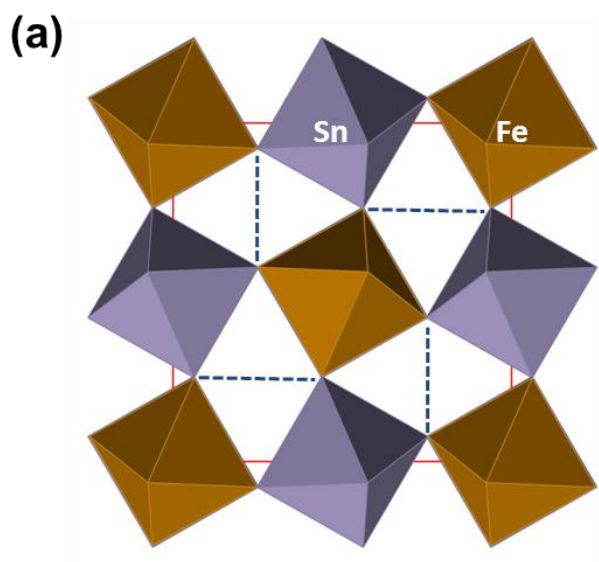


Table 1. Summary of data collection, structure refinement and polyhedral data for *Pn3* jeanbandyites.

	Hingston	Llallagua
$a, V (\text{\AA}, \text{\AA}^3)$	7.6427(2), 446.41(2)	7.658(2), 449.1(2)
Theta range	3.77–31.46	3.76–30.55
$h / k / l$ ranges	-10,+11/ ± 10 /-10,+11	± 10 / ± 10 / ± 10
Total unique reflections	254	235
Total unique reflections $I > 2\sigma(I)$	157	147
$R_{\text{int}} (m3)$	0.052	0.065
$R_1(\text{obs}), wR_2(\text{obs})$	0.027, 0.070	0.038, 0.085
$R_1(\text{all}), wR_2(\text{all})$	0.050, 0.079	0.059, 0.094
GoF	1.238	1.097
Residual max/min ($e/\text{\AA}^3$)	0.67, -0.41	0.86, -0.55
<i>B</i> site-scattering obs,calc ($e^- pfu$)	24.7, 22.1	25.0, 24.2
<i>B'</i> site-scattering obs,calc ($e^- pfu$)	48, 45.7	49.5, 42.4
Fe-O (\AA)	2.030(5)	2.040(7)
Sn-O (\AA)	2.068(5)	2.069(7)
Fe(OH) ₆ vol (\AA^3)	11.15	11.32
Sn(OH) ₆ vol (\AA^3)	11.79	11.80
<i>QE</i> Fe(OH) ₆ *	1.0003	1.0004
<i>QE</i> Sn(OH) ₆ *	1.0003	1.0003
<i>BAV</i> Fe(OH) ₆ (degr^2)*	1.14	1.28
<i>BAV</i> Fe(OH) ₆ (degr^2)*	0.94	1.12
Fe BVS (Fe ²⁺ -O) (<i>vu</i>)**	2.70	2.60
Fe BVS (Fe ³⁺ -O) (<i>vu</i>)**	2.93	2.82

**QE* = quadratic elongation, *BAV* = bond-angle variance (both after Robinson et al. 1971).

***BVS* = bond-valence sum of Fe. Bond-valences for the *B* site cation were calculated using the R_0 values for Fe²⁺-O (1.735 \AA) and Fe³⁺-O (1.765 \AA) given by Brown and Altermatt (1985), with $b = 0.37 \text{\AA}$.

Table 2. Atom coordinates, anisotropic and equivalent-isotropic displacement parameters (\AA^2) for Hingston (upper entries) and Llallagua (lower entries) jeanbandyites in space group $Pn\bar{3}$. Occupancies of B and B' sites were refined using the neutral atomic scattering factors of Fe and Sn, respectively, and are expressed in terms of fractions of those atoms present.

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Sn*	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0124(2)	U_{11}	U_{11}	0.0004(3)	U_{23}	U_{23}	0.0124(2)
	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0180(3)	U_{11}	U_{11}	-0.0006(3)	U_{23}	U_{23}	0.0180(3)
Fe*	$\frac{1}{2}$	$\frac{1}{2}$	0	0.0141(5)	U_{11}	U_{11}	-0.0012(6)	U_{23}	U_{23}	0.0141(5)
	$\frac{1}{2}$	$\frac{1}{2}$	0	0.0197(7)	U_{11}	U_{11}	-0.0021(8)	U_{23}	U_{23}	0.0197(7)
O	0.2527(7)	0.4251(7)	-0.0614(6)	0.021(2)	0.024(3)	0.038(3)	-0.005(2)	0.013(2)	-0.013(2)	0.027(1)
	0.2520(9)	0.4249(9)	-0.0618(9)	0.028(3)	0.025(3)	0.050(4)	-0.006(3)	0.031(3)	-0.016(3)	0.034(2)

* Site occupancies for Hingston/Llallagua jeanbandyites: Sn = 0.96(1)/0.99(2), Fe = 0.95(2)/0.96(2).