The effect of pressure and composition on Cu-bearing hydroxide perovskite

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Abstract

Hydroxide perovskite solid solutions along the $\text{Cu}_x\text{Zn}_{1-x}\text{Sn}(\text{OH})_6$ join have been investigated at ambient conditions. Two compositions, $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ (cubic) and $\text{CuSn}(\text{OH})_6$ (tetragonal), have also been studied at pressures up to 17 GPa. In both ambient and high-pressure experiments, samples were characterised using powder X-ray diffraction. Bulk compositions between $0 \leq X_{\text{Cu}} \leq 0.4$ are metrically cubic (space group $Pn\bar{3}$), whereas those with $X_{\text{Cu}} = 0.9$ and 1 produced single-phase tetragonal $\text{Cu}_{0.9}\text{Zn}_{0.1}\text{Sn}(\text{OH})_6$ and $\text{CuSn}(\text{OH})_6$ (space group $P4_2/n$). The products of syntheses with $0.5 \leq X_{\text{Cu}} \leq 0.8$ contain coexisting cubic and tetragonal phases. The cubic $\rightarrow$ tetragonal transformation is rationalised in terms of being driven by local strain associated with the accumulation of Cu-rich domains in the cubic phase. The high-pressure studies of cubic $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ and tetragonal $\text{CuSn}(\text{OH})_6$ phases showed contrasting behaviour. The compression curve of the cubic phase is smooth without inflexion or discontinuity to 17 GPa. The derived bulk modulus of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ is $K_0 = 75.8(4)$ GPa ($K' = 4$). For $\text{CuSn}(\text{OH})_6$, compression data cannot be fitted by a single equation-of-state over the entire pressure range to 17 GPa, as there is a clear discontinuity between 7 and 10 GPa that corresponds to an increase in compressibility at higher pressures. Compression data for $\text{CuSn}(\text{OH})_6$ to 7 GPa are: $K_0 = 59.7(9)$ GPa, $K_{a0} = 79(2)$ GPa, and $K_{c0} = 38.0(3)$ GPa ($K' = 4$ for all). It is shown that the strong Jahn–Teller distortion associated with the $\text{Cu}(\text{OH})_6$ octahedron is primarily responsible for the discontinuous and highly anisotropic compressional behaviour of the unit cell of $\text{CuSn}(\text{OH})_6$ hydroxide perovskite.

Keywords Hydroxide perovskite · Vismirnovite · Mushistonite · Jahn–Teller distortion · High pressure · Diamond-anvil cell · X-ray diffraction

Introduction

A comprehensive review of the crystal chemistry of hydroxide perovskites having stoichiometries $\square\text{AB}(\text{OH})_3$ and $\square\text{A}_2\text{BB}'(\text{OH})_6$ is given by Mitchell et al. (2017). The structure of hydroxide perovskite minerals and synthetic analogues (Fig. 1) consists of a framework of corner-linked $B(\text{OH})_6$ octahedra and a vacant A site. All oxygens in hydroxide perovskites are both H donors and acceptors. The octahedra can be occupied by homovalent cations giving the stoichiometry $B(\text{OH})_3$, where $B = \text{Fe}^{3+}$, Ga^{3+} , In^{3+} , or heterovalent with $\text{BB}'(\text{OH})_6$ where $B = \text{Na}$, Ca , Mg , Zn , Cu^{2+} ,

Fe^{2+} , Mn^{2+} , Nb^{5+} , and $B' = \text{Sn}^{4+}$, Si , Ge , and Sb . Heterovalent varieties have an ordered arrangement of alternating $B(\text{OH})_6$ and $B'(\text{OH})_6$ octahedra and hydroxide perovskites with $B^{2+}B^{4+}$ and $B^{1+}B^{5+}$ combinations having been observed in nature.

The absence of an A cation leads to a high degree of rotation of octahedra as the framework contracts around the vacant A site. Furthermore, the tilting angles of octahedra, as referred to the pseudo-cubic axes of the untilted $Pm\bar{3}m$ aristotype (Glazer 1972), have a very limited range of values of 14° – 17° and are almost independent of composition and space group. For example, the $Pn\bar{3}$ structures of $\text{CaSn}(\text{OH})_6$ (burtite), $\text{MnSn}(\text{OH})_6$ (wickmanite), and $\text{MgSn}(\text{OH})_6$ (schoenfliesite) have tilts of 14° – 17° , and the $P4_2/n$ structures of stottite (Welch and Wunder 2012) and tetrawickmanite (Lafuente et al. 2015) both have tilts of 17° about $[001]$ and 15° about $[100]/[010]$. $\text{MgSi}(\text{OH})_6$ with monoclinic space group $P2_1/n$ (Welch and Wunder, 2012) has tilts of 16° $[110]$, 14° $[1\bar{1}0]$, and 16° $[001]$. The very limited range of tilt angles shown by

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Fig. 1 Crystal structure of **a** tetragonal $P4_2/n$ and **b** cubic $Pn\bar{3}$ hydroxide perovskites relevant to the present study. Successive octahedra when viewed along the axes of the cubic aristotype have either the reverse or the same sense of rotation. **a** A reverse rotation along $[001]$ for the tetragonal $a^+ a^+ c^-$ tilt system of $P4_2/n$, and **b** the same sense for the cubic $a^+ a^+ a^+$ tilt system. The two different tilt systems have significantly different hydrogen-bonding topologies. Examples of hydrogen-bonded O–H...O bridges are shown as dashed red lines. A single B–O–B' angle is shown in green in **a**. **c** The acute angle formed by $[001]$ -Mn–O(3) in tetrawickmanite $\text{MnSn}(\text{OH})_6$, which corresponds to $[001]$ -Cu–O(apical) in mushistonite. The orange triangle is used to calculate the likely magnitude of the component of the Cu–O(apical) bond that is parallel to the c axis

diverse hydroxide perovskites strongly points to a major role for hydrogen bonding in these structures, i.e., the principal control on tilting is the strength of hydrogen bonds.

Hydrogen bonding is a key feature of these structures, and the connectivity of hydrogen-bonded networks correlates with tilt system (Mitchell et al. 2017). For example, hydroxide perovskites with cubic space groups $Pn\bar{3}$ and $Im\bar{3}$ (both having tilt system $a^+ a^+ a^+$) have isolated squares of O–H...O linkages without extended connectivity. Tetragonal hydroxide perovskites having space group $P4_2/n$ and the corresponding tilt system $a^+ a^+ c^-$, such as stottite $\text{FeGe}(\text{OH})_6$, have a combination of isolated squares and crankshafts (Welch and Wunder 2012). In tetragonal structures, all H atom sites of crankshafts are half-occupied, whereas the H site of the square is fully occupied (e.g., Lafuente et al. 2015; Welch and Kleppe 2016). All oxygens are both hydrogen-bond donors and acceptors. In the monoclinic synthetic high-pressure perovskite $\text{MgSi}(\text{OH})_6$ with tilt system $a^- a^- c^+$ (Wunder et al. 2011; Welch and Wunder 2012), the hydrogen-bonded topology comprises crankshafts in which the sites of all four non-equivalent H

atoms are half-occupied, and there are interleaved isolated zigzag chains in which the remaining H atom site is fully occupied. Correlations between space group and tilt system for hydroxide perovskites are summarised by Mitchell et al. (2017).

Hydroxide perovskites have potential technological importance and a range of properties that includes proton conduction (Jena et al. 2004), flame retardancy (Zhang et al. 2007), and photocatalytic activity (Fu et al. 2009). Natural occurrences are very rare, due to their low temperatures of formation and their reaction to other Sn-bearing phases (Mitchell 2002; Nefedov et al. 1977). Consequently, experimental studies have made extensive use of synthetic analogues, which are easily prepared following the method of Strunz and Contag (1960), although the products are typically very fine-grained and preclude study by single-crystal XRD.

The absence of the A cation makes it possible to study compositional and compressional effects of an octahedral framework related to perovskite. Studies of the compressibility of hydroxide perovskites (Ross et al. 2002; Welch and Crichton 2002; Welch et al. 2005) have shown that

the absence of *A* site cations results in much higher compressibilities compared with perovskites. Bulk moduli of hydroxide perovskites are typically in the range 70–80 GPa, compared with 150–200 GPa for perovskites, e.g., GdFeO_3 $K_0 = 182$ GPa (Ross et al. 2004) and CaSnO_3 $K_0 = 163$ GPa (Kung et al. 2001). Burtite– $\text{CaSn}(\text{OH})_6$ has an exceptionally low bulk modulus of 47 GPa (Welch and Crichton 2002).

Although several equation-of-state studies of hydroxide perovskites have been made, the mechanisms of compression are unknown in detail. The highly tilted frameworks of ambient hydroxide perovskites suggest that a change in compression mechanism could occur at modest pressures. This behaviour is unexplored in hydroxide perovskites at the atomic scale.

The objective of this investigation is to determine the effects of composition and pressure upon the structural state of the mushistonite–vismirnovite solid solution series, $\text{Cu}_x\text{Zn}_{1-x}\text{Sn}(\text{OH})_6$. Structure studies indicate that vismirnovite– $\text{ZnSn}(\text{OH})_6$ is cubic with SG $Pn\bar{3}$ (Cohen-Addad 1968), and mushistonite– $\text{CuSn}(\text{OH})_6$ is tetragonal $P4_2/nm$ (Morgerstern-Badarau 1976). The $Pn\bar{3}$ structure has tilt system $a^+ a^+ a^+$ (Glazer 1972) and is consistent with other cubic members of the schoenfliesite group, such as burtite, wickmanite, and schoenfliesite (Basciano and Peterson 1998). However, space group $P4_2/nm$ was shown to be very implausible for mushistonite by Welch and Kleppe (2016), as it involves a tilt system ($a^0 b^+ b^+$) with a zero tilt and a mirror plane bisecting the octahedra. Both features are improbable, because tilting of octahedra is expected for hydroxide perovskites, due to contraction around the empty *A* site and strong hydrogen bonding leads to further octahedral rotation. Furthermore, the topology of $P4_2/nm$ forces octahedra to become extremely distorted due to the bisecting mirror plane. Recent studies demonstrate that tetragonal hydroxide perovskites crystallize in space group $P4_2/n$ (Ross et al. 1988; Lafuente et al. 2015; Welch and Kleppe 2016) with tilt system $a^+ a^+ c^-$.

Unfortunately, crystals of natural or synthetic mushistonite of a quality suitable for structure determination by single-crystal XRD have not been available. Consequently, powder-diffraction data for synthetic analogues have to be tested against various space groups. Peak-splitting associated with lowering of metric symmetry from cubic to tetragonal is usually easily detected, although the correct choice of tetragonal space group from the powder-diffraction data is more challenging. However, the only tetragonal space group known for double hydroxide perovskites is $P4_2/n$, which is, therefore, the clear candidate for mushistonite.

Mushistonite is unique among tetragonal hydroxide perovskites in having a “prolate” cell metric with $c > a$. Tetrawickmanite, stottite, and $\text{Ga}(\text{OH})_3$ (soehngeite) have an “oblate” cell metric ($a > c$). Furthermore, the “eccentricity” of the metric ($c:a$) is 1.07 for mushistonite, whereas the value for the three other tetragonal phases is only 0.99. The strongly prolate

nature of the mushistonite unit cell points to a significant contribution from Jahn–Teller distortion of the $\text{Cu}(\text{OH})_6$ octahedron. Such a distortion in mushistonite is expected as it is a common feature of compounds with octahedrally coordinated transition metals having an odd number of *d*-electrons, such as $d^9 \text{Cu}^{2+}$. Consideration of the tetragonal ($P4_2/n$) structures of $\text{MnSn}(\text{OH})_6$, $\text{FeGe}(\text{OH})_6$, and $\text{Ga}(\text{OH})_3$ indicates that the acute angle between [001] and the $B\text{--O}(3)$ bond is $20^\circ\text{--}22^\circ$ for these structures (Fig. 1c). A simple trigonometric calculation shows that the component of the $B\text{--O}(3)$ bond that is parallel to [001] is 92% of the bond length for these structures. The prolate cell metric of $\text{CuSn}(\text{OH})_6$ suggests that the long $\text{Cu}\text{--O}(\text{apical})$ bond corresponds to that forming the [001]– $B\text{--O}(3)$ angle, and so is also likely to have a component parallel to [001] of at least 90%. Hence, the behaviour of the *c* parameter of $\text{CuSn}(\text{OH})_6$ is likely to be highly correlated with that of the $\text{Cu}\text{--O}(\text{apical})$ bond of the $\text{Cu}(\text{OH})_6$ octahedron.

Methods

Sample preparation

The samples of $\text{Cu}_x\text{Zn}_{1-x}\text{Sn}(\text{OH})_6$ with $x = 0, 0.04, 0.1, 0.2, \dots, 0.9$ and 1 were synthesised using the method of Strunz and Contag (1960). The reagents were 5 M aqueous solutions of $\text{K}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, CuCl_2 , and ZnCl_2 (Sigma-Aldrich). The synthesis reaction involved is as follows:

Solutions were mixed with magnetic stirrer at room temperature. Hydroxide perovskite was precipitated immediately. The well-crystallized precipitate was then washed repeatedly until all crystallized KCl was gone, as confirmed by powder-XRD.

Powder X-ray diffraction at ambient conditions

The powdered samples were loaded into circular well mount holders. Powder-diffraction data were collected in Bragg–Brentano geometry using a Panalytical X'Pert Pro MPD equipped with primary $\text{Ge}(111)$ monochromator, X'celerator position sensitive detector (opening angle of 2.122°), incident and diffracted-beam Soller slits (0.02°), and $1/4^\circ$ divergence and $1/2^\circ$ anti-scatter slits. X-ray tube operating conditions were 45 kV and 40 mA. Measurements were performed with $\text{Cu K}\alpha_1$ radiation in the range from 5 to $125^\circ 2\theta$, at a step size 0.02° , and an effective counting time of 100 s per step.

Synchrotron powder X-ray diffraction at high-pressure conditions

High-pressure measurements on cubic $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ and tetragonal $\text{CuSn}(\text{OH})_6$ were obtained using a diamond-anvil cell (DAC) fitted with rhenium gasket pre-indented to a thickness of 40 μm and drilled with a 150 μm sample hole. Liquid neon was used as the pressure-transmitting medium (Hemley et al. 1989), and the maximum pressure used was 17 GPa, which is its quasi-hydrostatic limit. Powdered samples of two key compositions, $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ (cubic, $Pn\bar{3}$) and $\text{CuSn}(\text{OH})_6$ (tetragonal, $P4_2/n$), were loaded into the DAC with a ruby sphere for pressure calibration using the ruby-fluorescence method (Mao et al. 1986). Diffraction experiments were collected on beamline I15 at the Diamond Light Source (UK) from 10^{-4} to 30 GPa at 298 K. Experiments were performed with a monochromatic beam ($\lambda = 0.30996$ Å) collimated to 30 μm in diameter. A MAR345 image plate detector (MarResearch) was used with a sample-to-detector distance of 450 mm and exposure times of 15–25 min. The sample-to-detector distance was calibrated with silicon powder and LaB_6 . The powder-diffraction images have been integrated with Fit2d.

Rietveld refinement

All XRD powder data were refined using GSAS (Larson and Von Dreele 2004), and refined parameters were background, peak profiles, unit cell, oxygen position, and isotropic displacement factors (U_{iso}). The B and B' sites lie at 000 and $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, respectively, and so only their U_{iso} values were refined. Starting models for Rietveld refinements were the cubic $Pn\bar{3}$ structure of vismirnovite (Cohen-Addad 1968), and the tetragonal $P4_2/n$ structure of tetrawickmanite (Lafuente et al. 2015). The latter structure model was preferred over that reported for mushistonite by Morgernstern-Badarau (1976) for which the Sn octahedron shows a very unreasonable distortion due to an incorrect choice of space group ($P4_2/nmm$). Low intense diffraction peaks from the rhenium gasket and the neon pressure transmission medium were observed in some experiments. Here, structures for rhenium (Swanson and Fuyat 1953; Duffy et al. 1999) and neon (Hemley et al. 1989) were included in the refinements.

Results

XRD at ambient conditions

The solid products of all experiments were hydroxide perovskite and KCl. The latter was completely removed by

washing as described above. Figure 2 shows XRD powder patterns for the Cu–Zn series. One-phase fields of cubic and tetragonal $\text{Cu}_x\text{Zn}_{1-x}\text{Sn}(\text{OH})_6$ occur within the compositional ranges $X_{\text{Cu}} = 0–0.4$ and $0.9–1$, respectively. Bulk compositions $0.5 \leq X_{\text{Cu}} \leq 0.8$ produced coexisting cubic and tetragonal phases.

Variations of lattice parameters with composition are shown in Fig. 3. A very minor change can be observed for the cubic phase with increasing Cu content ($0 \leq X_{\text{Cu}} \leq 0.4$). However, for $X_{\text{Cu}} > 0.4$, there is a significant increase in metric anisotropy for the tetragonal phase with cell parameter a_{tet} decreasing and c_{tet} increasing. Bond length and bond angles of the cubic phase are shown in Fig. 4 and listed in Table 1. The most significant changes from $X_{\text{Cu}} = 0$ to 0.4 are an increase in Cu/Zn–O bond lengths and a decrease in bond angles $B\text{--}O\text{--}B'$ ($B = \text{Cu, Zn}$, $B' = \text{Sn}$). No bond-length data are presented for the tetragonal phase due to low precision of refined oxygen positions; U_{iso} values had to be refined as an overall value.

High-pressure behaviour of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ and $\text{CuSn}(\text{OH})_6$

Crystal structures of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ and $\text{CuSn}(\text{OH})_6$ from laboratory XRD refinements were taken as starting models for Rietveld refinement using the GSAS program. Peak profiles, unit cell parameters, oxygen coordinates, and isotropic displacement factors were refined. A fixed U_{iso} of 0.004 Å² for the Cu/Zn site (the refined value for the ambient out-of-cell data set) had to be used for the cubic structure due to a persistent non-positive-definite value being obtained otherwise. Furthermore, an overall U_{iso} value for oxygen had to be refined for the $\text{CuSn}(\text{OH})_6$ due to U_{iso} for two of the three oxygens becoming non-positive-definite. The constraints on oxygen displacement parameters lead to some uncertainty in the refined positions of these atoms, and so no bond-length data are presented for $\text{CuSn}(\text{OH})_6$.

Representative high-pressure powder-diffraction patterns for the two phases are shown in Fig. 5, and typical results of Rietveld refinement of high-pressure patterns for both phases are shown in Fig. 6. Unit cell parameters for the high-pressure experiments are given in Table 2. Normalised volume and axial data as functions of pressure are shown in Figs. 7 and 8, respectively. Structural data are given in Tables 3 and 4.

On compression, the P – V data for the cubic $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ decrease smoothly to 17 GPa, with no indication of an inflexion or discontinuity. A fit to a second-order Birch–Murnaghan equation-of-state (BMEOS) for the compression data gives $K_0 = 75.8(4)$ GPa. A very similar fit was obtained to third-order, which gives $K_0 = 75(1)$

Fig. 2 Powder-XRD patterns of $\text{Cu}_x\text{Zn}_{1-x}\text{Sn}(\text{OH})_6$. Synthesis products were cubic within the compositional range $X_{\text{Cu}}=0-0.4$ and tetragonal in the range $0.9-1$. Bulk compositions $0.5 \leq X_{\text{Cu}} \leq 0.8$ produced coexisting cubic and tetragonal phases

Fig. 3 Lattice parameters of $\text{Cu}_x\text{Zn}_{1-x}\text{Sn}(\text{OH})_6$ solid solutions

GPa and $K'_0 = 4.0(2)$, indicating that a second-order model describes the P – V data sufficiently. The decompression data for $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ lie on the compression trend.

Variations with pressure of bond angles and bond lengths of the cubic phase are shown in Figs. 9 and 10, respectively. The (Zn,Cu)–O–Sn bond angle decreases markedly on compression to 7 GPa and remains approximately constant at 131° between 8 and 17 GPa. Within the small standard errors on their values, the lengths of (Zn,Cu)–O and Sn–O bonds decrease linearly to 17 GPa, although there is a suggestion of a steepening of the trend for the (Zn,Cu)–O bond at ~ 8 GPa.

Above 7 GPa, the compression curve of $\text{CuSn}(\text{OH})_6$ cannot be fitted by a single equation-of-state. The non-conformity between the trends below and above 7 GPa is seen as a slight steepening of the compression curve from 10 to 17 GPa. The axial compression curves also register this discontinuity. Furthermore, the discontinuity in the a parameter appears to show a change between two linear

Fig. 4 Bond length and bond angles of cubic $Cu_xZn_{1-x}Sn(OH)_6$

trends in which there is decrease in the compressibility at 10–17 GPa (Fig. 8). In contrast, the trend of the c parameter at 10–17 GPa shows a steepening that implies an increased compressibility.

Normalised P – V data to 7 GPa for $CuSn(OH)_6$ were fitted to a second-order BMEOS (Fig. 7), which gives $K_0 = 59.7(9)$ GPa. A third-order fit gives a similar value of $K_0 = 59(2)$ GPa with $K' = 4.6(3)$. Second-order fits of the axial data to 7 GPa (Fig. 8) give $K_{a0} = 79(2)$ GPa and $K_{c0} = 38.0(3)$ GPa. However, the fit to the a parameter data lies slightly below the data points, which vary almost linearly over this pressure range. Figures 7, 8 also show that the decompression curves of $CuSn(OH)_6$ are very different from that obtained on compression, and that this effect is primarily due to the behaviour of the c parameter. This clear difference between compression and decompression curves implies that there is hysteresis in $CuSn(OH)_6$ that is not seen in the cubic $Cu_{0.4}Zn_{0.6}Sn(OH)_6$ phase. The decompression data for the c parameter fall well below the corresponding compression curve. Furthermore, the value of the ambient c parameter recovered on decompression is 7.989(6) Å compared with the initial value of 8.1010(7) Å.

Table 1 Structural parameters of cubic $Cu_xZn_{1-x}Sn(OH)_6$ refined in $Pn\bar{3}$

X_{Cu}	a (Å)	x	y	z	U_{iso} Cu/Zn (Å ²)	U_{iso} Sn (Å ²)	U_{iso} O (Å ²)	Cu/Zn–O (Å)	Sn–O (Å)	Cu/Zn–O–Sn (°)	R_p	R_{wp}
0.0	7.76598(18)	–	0.069(2)	0.067(3)	0.248(1)	0.004(1)	0.042(4)	2.066(12)	2.096(12)	138.0(6)	0.0896	0.1308
0.04	7.76161(33)	–	0.068(3)	0.066(3)	0.248(2)	0.002(1)	0.037(5)	2.061(12)	2.089(15)	138.5(7)	0.1041	0.1485
0.1	7.7564(3)	–	0.066(3)	0.067(3)	0.248(2)	0.002(1)	0.042(5)	2.055(12)	2.091(12)	138.6(7)	0.1030	0.1484
0.2	7.75929(27)	–	0.069(2)	0.069(3)	0.248(2)	0.004(1)	0.039(5)	2.066(12)	2.098(15)	137.4(7)	0.1060	0.1528
0.3	7.75387(36)	–	0.069(3)	0.069(3)	0.249(2)	0.004(1)	0.039(5)	2.086(12)	2.078(12)	137.2(7)	0.1014	0.1456
0.4	7.75184(39)	–	0.071(3)	0.071(3)	0.250(2)	0.004(2)	0.048(6)	2.086(15)	2.088(15)	136.4(9)	0.1105	0.1539

Fig. 5 Representative high-pressure PXRD patterns of **a** cubic $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ and **b** tetragonal $\text{CuSn}(\text{OH})_6$. ↓ sign indicates decompression data

Fig. 6 Rietveld refinement of **a** cubic $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ at 13.8 GPa and **b** tetragonal $\text{CuSn}(\text{OH})_6$ at 14.1 GPa

Discussion

Structural trends of $\text{Cu}_x\text{Zn}_{1-x}\text{Sn}(\text{OH})_6$ solid solutions at ambient conditions

Incorporation of Cu into $\text{Cu}_x\text{Zn}_{1-x}\text{Sn}(\text{OH})_6$ hydroxide perovskite in the range $0 \leq X_{\text{Cu}} \leq 0.4$ results in only a minor change of the cubic cell parameter. There is a decrease in $B\text{--}O\text{--}B'$ angle and an increase in $B\text{--}O$ bond lengths ($B = \text{Cu}$,

Table 2 Unit cell parameters of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ and $\text{CuSn}(\text{OH})_6$ with pressure

<i>P</i> (GPa)	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
$\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ pressure increase			
0.0001	7.75184(4)		465.82(7)
5.2	7.59757(5)		438.56(8)
6.1	7.57278(5)		434.28(10)
6.8	7.55427(7)		431.10(12)
8.4	7.51842(7)		424.99(12)
10.4	7.47380(8)		417.47(14)
12.3	7.43340(9)		410.74(16)
13.8	7.40403(10)		405.89(17)
15.2	7.37905(11)		401.79(19)
16.6	7.35235(12)		397.45(20)
$\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ pressure decrease			
0.0001	7.76884(9)		468.89(17)
2.0	7.68339(10)		453.59(19)
5.9	7.57058(15)		433.90(26)
10.4	7.47685(18)		417.98(30)
$\text{CuSn}(\text{OH})_6$ pressure increase			
0.0001	7.57394(5)	8.1010(7)	464.71(62)
1.1	7.54582(12)	8.0258(15)	456.98(21)
2.2	7.51846(13)	7.9641(15)	450.19(23)
2.9	7.50080(16)	7.9255(19)	445.90(28)
3.8	7.47412(17)	7.8735(20)	439.83(31)
4.8	7.44900(22)	7.8295(26)	434.44(39)
5.9	7.41780(24)	7.7774(27)	427.94(40)
6.8	7.39156(29)	7.7423(33)	423.00(49)
10.1	7.33454(33)	7.6275(36)	410.33(54)
14.1	7.26987(24)	7.4675(26)	394.67(38)
17.0	7.22794(26)	7.3921(28)	386.18(41)
$\text{CuSn}(\text{OH})_6$ pressure decrease			
0.0001	7.57249(54)	7.9893(59)	458.13(92)
5.0	7.48005(34)	7.6284(33)	426.82(53)
14.0	7.28825(36)	7.4046(38)	393.32(53)

Fig. 7 Normalised plots of the variation of the unit cell volume with pressure for $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ and $\text{CuSn}(\text{OH})_6$. Filled circles are data collected on compression and open symbols for data collected on decompression. Lines are EOSBM2 fits to compression data. $\text{CuSn}(\text{OH})_6$ shows a change in compression behaviour above 7 GPa. The dashed black line is the P – V curve of burtite- $\text{CaSn}(\text{OH})_6$ (Welch and Crichton 2002) and the dotted black line is the P – V curve for vismironite- $\text{ZnSn}(\text{OH})_6$ from Welch and Crichton (unpublished data)

Fig. 8 Normalised plots of the variation of unit cell axes with pressure. Compression data have filled symbols and decompression data have open symbols. Lines are EOSBM2 fits to the data for $\text{CuSn}(\text{OH})_6$

Zn , $B' = \text{Sn}$) (Fig. 4; Table 1). At the local level, increasing distortion of the octahedral framework is expected with increasing Cu content due to Jahn–Teller distortion associated with $\text{Cu}(\text{OH})_6$ octahedra. For compositions $0 \leq X_{\text{Cu}} \leq 0.4$, an increasing proportion of $\text{Cu}(\text{OH})_6$ octahedra results in an increase of the average B – O bond length,

Fig. 9 Variations of (Zn,Cu) – O and Sn – O bond lengths of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ with pressure

while long-range cubic symmetry is retained. Structure expansion by lengthening of B – O bonds is compensated by increasing tilting of neighbouring octahedra (reflected in a decrease of the B – O – B' angle), leading to only a minor change in cell dimensions.

Higher Cu contents lead to the formation of CuSnCuSn quartets being more probable. It is conceivable that strain associated with aggregated Cu-rich domains (propagated Jahn–Teller distortion) results in critical behaviour and a change in overall symmetry $Pn\bar{3} \rightarrow P4_2/n$ for compositions with $X_{\text{Cu}} > 0.4$. Although precise bond-length data are unavailable for the tetragonal phase, it is reasonable to assume that the increase of unit cell parameter c is most likely correlated with increasing distortion of the long apical B – $\text{O}(3)$ bond, which is the major connector for $\text{Cu}(\text{OH})_6$ octahedra along the $[001]$ direction.

Structural trends of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ and $\text{CuSn}(\text{OH})_6$ as functions of pressure

Normalised P – V curves of cubic $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ and tetragonal $\text{CuSn}(\text{OH})_6$ are clearly separated (Fig. 7), with the latter being significantly more compressible.

Fig. 10 Variation of the (Zn,Cu)–O–Sn angle and volumes of octahedra of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ with pressure

The compression curve of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ decreases smoothly without inflexion or discontinuity, and compares closely with those curves of $\gamma\text{-Fe}(\text{OH})_3$ (Welch et al. 2005),

Table 3 $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ with pressure: structural and statistical parameters of the Rietveld refinement in $Pn\bar{3}$

P (GPa)	x	y	z	a (Å)	$U_{\text{iso}} \text{ O}$ (Å ²)	$U_{\text{iso}} \text{ Sn}$ (Å ²)	R_{wp}	R_p
Pressure increase								
5.2	−0.067(2)	0.085(2)	0.248(1)	7.59757(5)	0.017(4)	0.004(1)	0.0055	0.0037
6.1	−0.067(2)	0.087(2)	0.248(1)	7.57278(5)	0.016(4)	0.003(1)	0.0066	0.0043
6.8	−0.072(3)	0.087(3)	0.248(2)	7.55427(7)	0.019(5)	0.005(2)	0.0091	0.0061
8.4	−0.071(2)	0.088(2)	0.249(1)	7.51842(7)	0.005(4)	0.003(2)	0.0093	0.0054
10.4	−0.075(4)	0.081(4)	0.249(1)	7.47380(8)	0.022(5)	0.010(2)	0.0085	0.0050
12.3	−0.073(5)	0.088(3)	0.249(2)	7.43340(9)	0.016(5)	0.003(2)	0.0086	0.0050
13.8	−0.072(3)	0.087(3)	0.248(1)	7.40403(10)	0.033(5)	0.010(2)	0.0082	0.0047
15.2	−0.074(3)	0.087(3)	0.247(1)	7.37905(11)	0.036(5)	0.007(2)	0.0089	0.0048
16.6	−0.072(3)	0.086(3)	0.247(2)	7.35235(12)	0.061(7)	0.010(2)	0.0085	0.0046
Pressure decrease								
0.0001	−0.060(5)	0.077(5)	0.246(2)	7.76854(10)	0.029(7)	0.011(2)	0.0086	0.0049
2.0	−0.058(4)	0.082(4)	0.245(2)	7.68339(11)	0.029(6)	0.007(2)	0.0038	0.0029
5.9	−0.071(5)	0.083(4)	0.243(2)	7.57058(15)	0.023(8)	0.005(2)	0.0052	0.0040
10.4	−0.074(4)	0.090(4)	0.245(2)	7.47685(18)	0.027(8)	0.009(3)	0.0042	0.0035
Ambient Lab XRD								
0.0001	−0.071(3)	0.071(3)	0.250(2)	7.75184(39)	0.048(6)	0.012(1)	0.1105	0.1539

U_{iso} of Cu–Zn site had to be fixed (taken from ambient refinement of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$, 0.004 Å²)

Table 4 Bond lengths and angles with pressure of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$

P (GPa)	Cu/Zn–O (Å)	Sn–O (Å)	Angle Cu/Zn–O–Sn (°)
Pressure increase			
0.0001 ^a	2.067(12)	2.093(12)	137.9(6)
5.2	2.054(7)	2.0811(8)	133.5(4)
6.1	2.0513(8)	2.0825(9)	132.7(4)
6.8	2.0542(10)	2.086(12)	131.6(5)
8.4	2.053(8)	2.0733(10)	131.3(5)
10.4	2.0363(8)	2.0471(10)	132.5(5)
12.3	2.0329(9)	2.051(12)	131.0(5)
13.8	2.017(9)	2.042(12)	131.6(5)
15.2	2.0092(9)	2.048(12)	130.8(5)
16.6	1.9925(10)	2.035(12)	131.8(5)
Pressure decrease			
0.0001	2.054(15)	2.117(15)	137.3(8)
2	2.037(12)	2.103(15)	136.2(7)
5.8	2.017(15)	2.116(18)	132.7(7)
10.4	2.023(15)	2.097(18)	130.3(7)

^a Ambient Lab XRD data

$\text{FeGe}(\text{OH})_6$ (Ross et al. 2002), $\text{In}(\text{OH})_3$, $\text{MgSn}(\text{OH})_6$, and $\text{ZnSn}(\text{OH})_6$ (Welch, unpublished data) given in Table 5. The similarity is exemplified in Fig. 7 by the compression curve for synthetic $\text{ZnSn}(\text{OH})_6$ [$K_0 = 73(1)$ GPa, $K'_0 = 4$]. Only burtite– $\text{CaSn}(\text{OH})_6$ has a significantly different bulk modulus [$K_0 = 47.4(4)$ GPa, $K'_0 = 4$, Welch and Crichton 2002]. With the single exception of burtite, the similar bulk moduli ($K_0 = 72$ –80 GPa) for a wide range of hydroxide perovskites

Table 5 Bulk moduli of hydroxide perovskites

Mineral/phase	Formula	Bulk modulus, K_0 (GPa)	K'_0	References
Burtite	$\text{CaSn}(\text{OH})_6$	47.4(4)	4	Welch and Crichton (2002)
Schoenfliesite	$\text{MgSn}(\text{OH})_6$	78(1)	4	Welch and Crichton ^a
3.65 Å phase	$\text{MgSi}(\text{OH})_6$	83(1)	4.9(2)	Mookherjee et al. (2015)
Dzhlindite	$\text{In}(\text{OH})_3$	80(2)	4	Welch and Crichton ^a
Bernalite	$\text{Fe}(\text{OH})_3$	78.2(4)	4	Welch et al. (2005)
Stottite	$\text{FeGe}(\text{OH})_6$	78.4(3)	6.2(1)	Ross et al. (2002)
Vismirnovite	$\text{ZnSn}(\text{OH})_6$	73.0(5)	4	Welch and Crichton ^a
Vismirnovite (Cu40)	$\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$	75.8(4)	4	This study
Mushistonite	$\text{CuSn}(\text{OH})_6$	59.7(9)	4	This study

^aUnpublished data

point to a compression behaviour that is largely independent of composition, symmetry, or tilt system.

The bulk modulus of the tetragonal $\text{CuSn}(\text{OH})_6$ is much lower than that of cubic $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$, and there is a strong compressional axial anisotropy: $K_{c0} = 38.0(3)$ GPa and $K_{a0} = 79(2)$ GPa. Furthermore, the axial modulus K_{c0} of $\text{CuSn}(\text{OH})_6$ is even lower than K_0 of burtite. At the atomic level, it would appear reasonable to attribute this strong compressional axial anisotropy to the presence of a long Cu–O bond that has a significant component (> 90%) parallel to [001], and arises from Jahn–Teller distortion of the $\text{Cu}(\text{OH})_6$ octahedron.

We interpret the trends in Cu/Zn–O and Sn–O bond lengths (Fig. 9), and Cu/Zn–O–Sn angle and octahedral volumes (Fig. 10) for $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Sn}(\text{OH})_6$ in terms of octahedral tilting as being the major mechanism to 7 GPa, but becoming less significant at higher pressures, whereas compression of octahedra continues almost linearly to 17 GPa. Furthermore, it is clear from the ambient and high-pressure studies presented here that Jahn–Teller distortion associated with Cu has a significant role in the crystal chemistry and physical behaviour of hydroxide perovskites.

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