

Synchrotron X-Ray Diffraction Study of BaPb_{1-x}Sn_xO₃ Solid Solution

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The structures of BaPb_{1-x}Sn_xO₃ ($x = 0, 0.025, 0.05$ and 0.075) have been established from high resolution synchrotron X-ray powder diffraction. These solid solutions are all isostructural and the structures have been refined in the orthorhombic space group, Imma. In all cases the BaO octahedral layers are separated by Pb/SnO₆ layers. As expected on size arguments, the cell parameters decrease as the amounts of Sn increases due the size effects of the dopant cation.

Keywords: Barium plumbate, Synchrotron XRD, Rietveld, Rietica.

INTRODUCTION

The compound BaPbO₃ has been investigated extensively since 70 years ago. Originally, BaPbO₃ has been reported as a cubic perovskite [1] but then the structure has been corrected to orthorhombic distorted perovskite structure with space group Pnma [2]. Subsequent studies confirmed that BaPbO₃ is actually monoclinic at room temperature with space group I2/m [3]. Recent structural investigations suggested that BaPbO₃ possesses orthorhombic structure with space group Imma at room temperature [4]. Upon cooling BaPbO₃, down to 15 K, it exhibited a structural transition from orthorhombic, Imma structure to monoclinic, C2/m structure [4]. On the other hand, investigations by Fu *et al.* [5] did not give evidence such a low temperature phase transition, but confirmed several structural phase transitions at higher temperatures.

Since then there has been several investigations concentrated around Ba-Pb-O system with different stoichiometries and substitutions. BaPbO₃ has been studied in term of technological importances. The BaPbO₃ has become the base material for several superconductors like BaPb_{1-x}Bi_xO₃ ($T_c \sim 12$ K) [6] and BaPb_{1-x}Sb_xO₃ ($T_c \sim 3.5$ K) [7]. BaPbO₃ demonstrates great potential in improving the characteristics of Pb[Zr_xTi_{1-x}]O₃ (PZT) films. BaPbO₃ improves the microstructure, crystallinity and ferroelectric properties and reduces the leakage current of PZT films [8]. BaPbO₃ is also a useful material in applications such as ceramic electrodes, conductive pastes, anticorrosion pigments and sintered resistors [9,10].

The driving mechanism of BaPbO₃ metallicity is not very clear in the literature. It was attributed to oxygen vacancies by

Franz *et al.* [11] and to unfilled *d* bands of Pb⁴⁺ by Hsieh and Fu [12]. BaPbO₃ structure can be thought of as BaO layers separated by PbO₂ layers. Transport in BaPbO₃ is mainly determined by the PbO₂ layer whereas the BaO layer contributes to the structural stability. Since the PbO₂ is metallic [13] the PbO₂ layer seems to be responsible for the metallic behaviour of BaPbO₃. The metallic property arise from the overlap of the Pb-6*s* band with the non-bonding O-2*p* states [14-16]. The behaviour of PbO₂ layer in BaPbO₃ is analogous to the Cu-O layer in yttrium barium copper oxide superconductor [17].

The substitutions, which are based on ionic radii considerations, may drive the metallic properties of BaPbO₃ towards a semiconductor by creating either oxygen vacancies and/or allowing partial reduction of Pb⁴⁺ to Pb²⁺ there by stabilizing the unusual 3+ intermediate valency for Pb in the lattice [8-10,12,18,19]. Another reason is that the partial substitution of Pb by Ba in BaPbO₃ system would tend to produce some amount of Pb²⁺ and provides carrier generation [20].

The metal doped compound of BaM_{1-x}Sn_xO₃ (M = Zr and Ti) has been studied as the high potent electro-caloric effect and photocatalysts [21,22]. The similarity of the ionic size and the properties of Pb⁴⁺ and Sn⁴⁺ make the possibility of for one ion to replacing another position in the lattice. The purpose of the present investigation was to examine the crystal structure of solid solution of BaPb_{1-x}Sn_xO₃ ($x = 0, 0.025, 0.05, 0.075$ and 0.1) at room temperature and to look for whether the Sn alter the structure, based on the high resolution synchrotron X-ray diffraction data. This technique provides high resolution as well as high sensitivity to oxygen atoms and has been proved to be very powerful in solving ambiguous structure problem of oxide perovskites [23].

EXPERIMENTAL

Polycrystalline of $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$ oxides were prepared by the solid state reaction of stoichiometric quantities of BaCO_3 (99.997 %, Aithaca), PbO_2 (99.999 %, Sigma-Aldrich) and SnO_2 (99.99 %, Sigma-Aldrich). The reagents were finely mixed in acetone slurry in an agate mortar and pestle before being heated in air at 750 °C for 4 h and thoroughly grinding and pelleting before being annealed at 950 °C for 48 h. The phase purity of the samples was confirmed using laboratory powder X-ray diffraction with CuK_α radiation. The microstructure of the samples was examined by scanning electron microscopy using a Jeol JCM-6000 SEM. The Ba:Pb:Sn ratios were measured using X-ray analysis and were in excellent agreement with the targeted stoichiometries for all compositions. Synchrotron X-ray powder diffraction data were collected using the powder diffractometer at BL-10 beamline of the Australian Synchrotron [24]. In all cases the samples were finely ground and placed in 0.3 mm diameter glass capillaries that were continuously rotated during the measurements. The wavelength was set at 0.82689 Å and the precise value of this was determined using NIST LaB6 standard reference material. The structures described here were refined by the Rietveld method as implemented in the program RIETICA [25]. The background was estimated by interpolating between, up to, 30 selected points. The peak shapes were modeled using a pseudo Voigt function, where the Gaussian component has widths given by the function $\text{FWHM}^2 = U \tan^2 \theta + V \tan \theta + W$ with refinable parameter U, V and W. The widths of the Lorentzian component varied as $\eta \sec \theta$ to model particle size effects and a peak asymmetry parameter was included. The scale factor, detector zero point, lattice parameters, atomic coordinates and isotropic atomic displacement parameters were refined together with the peak profile parameters.

The positions of the atoms are reported using the Wyckoff positions for the site occupied and these give the ideal occupation of sites by the atoms. The ideal atomic positions of BaPbO_3 orthorhombic with Imma space group which are used in initial refinements of $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$ include: Pb/Sn atoms are in position 4a, 0, 0, 0; Ba atoms are in the 4e, 0, $\frac{1}{4}$, z; the O1 atoms are in the 4e, 0, $\frac{1}{4}$, z and the O2 atoms are in the 8g, $\frac{1}{4}$, y, $\frac{1}{4}$. The Wyckoff position of Ba atoms is the same as that of the O1 atoms. This means that these atoms have the same symmetry position but not the same physical position.

RESULTS AND DISCUSSION

The products of the series $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$ were brown ($x = 0$) to light brown ($x = 0.1$) in colour and were stable in the atmosphere. The laboratory powder XRD analysis indicated that single phase compositions can be formed up to $x = 0.075$ (Fig. 1). Beyond this limit, $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$ performs an impurity of PbO_2 .

Rietveld refinement of synchrotron X-ray powder diffraction data of all sample, except the unstable refined data of $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0.1$), results the atomic coordinates of $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$ (Table-1). The plots of the observed, calculated and difference profiles for the Rietveld refinement are shown in Fig. 2. As the reported BaPbO_3 , the $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$ has an orthorhombic structure.

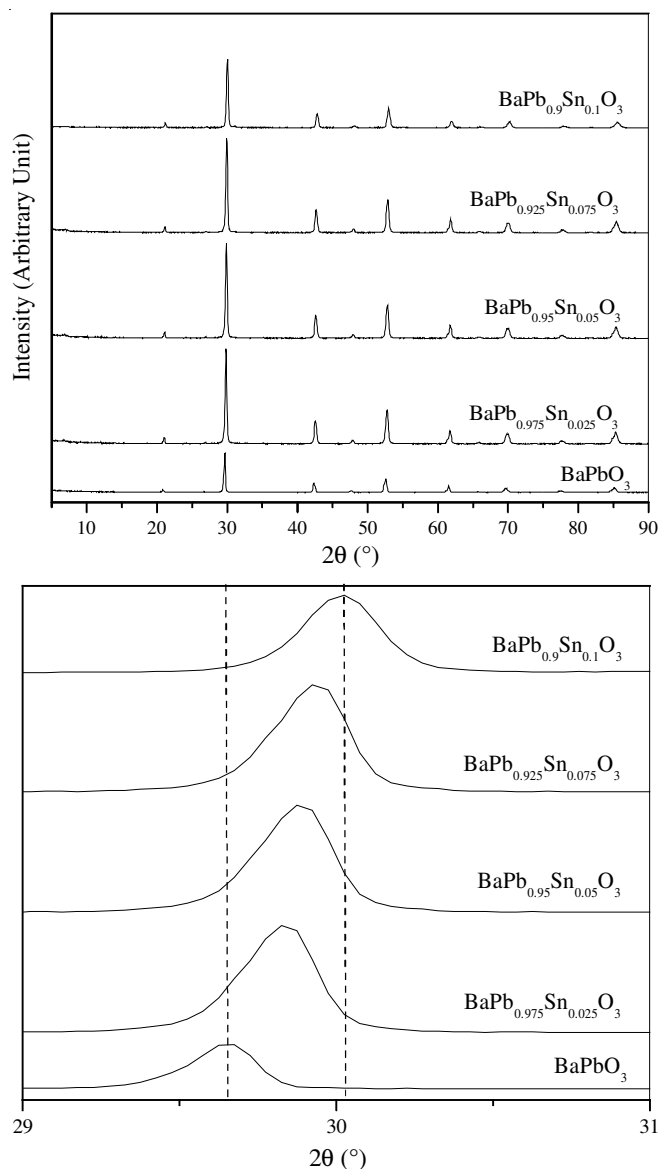


Fig. 1. Powder X-ray diffraction patterns of $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$

The observed synchrotron X-ray pattern is consistent with space group Imma and so the perovskite $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$ is orthorhombic with space group Imma. The stability of the perovskite $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$ is described by the tolerance factor $t = r_A +$

$$\frac{r_0}{\sqrt{2(r_B + r_0)}} \text{ where } r_A \text{ and } r_B \text{ are the ionic radii of the A and B}$$

cations in twelve- and six-fold coordination, respectively and r_0 is that oxygen in six-fold coordination. The crystallization of BaPbO_3 in orthorhombic structure is thus due to $t = 0.9787$. Due to the close ionic radii match, Pb^{4+} (0.775 Å) is expected to be replaced by Sn^{4+} (0.69 Å). In $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$, the t value is in between 0.9787 ($x = 0$) to 1.0030 ($x = 0.075$) which is reasonable indication for orthorhombic structure. A systematic variation of the orthorhombic cell parameters of $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$ are observed and listed in Table-2. The lattice parameters obtained are in good agreement with the previously reported data for BaPbO_3 [4]. The lattice parameters decrease as the Sn cation in the lattice increases due the size effects of the dopant cation (Fig. 3).

TABLE-1
ATOMIC COORDINATES OF BaPb_{1-x}Sn_xO₃

Compounds	Atomic coordinates and atomic displacement parameters	Atom				
		Ba	Pb	Sn	O(1)	O(2)
BaPbO ₃	x (Å)	0	0	-	0	0.25
	y (Å)	0.25	0	-	0.25	0.030(1)
	z (Å)	0.501(1)	0	-	0.045(2)	0.25
	B _{iso} (Å ²)	0.11(1)	0.13(1)	-	0.0(2)	0.5(2)
	N	0.25	0.25	-	0.25	0.5
BaPb _{0.975} Sn _{0.025} O ₃	x (Å)	0	0	0	0	0.25
	y (Å)	0.25	0	0	0.25	-0.026(1)
	z (Å)	0.489(4)	0	0	-0.0(2)	0.25
	B _{iso} (Å ²)	0.57(2)	0.72(2)	3.5(2)	8.1(9)	0.6(2)
	N	0.25	0.2432	0.0068	0.25	0.5
BaPb _{0.95} Sn _{0.05} O ₃	x (Å)	0	0	0	0	0.25
	y (Å)	0.25	0	0	0.25	-0.021(2)
	z (Å)	0.480(3)	0	0	0.005(9)	0.25
	B _{iso} (Å ²)	0.99(2)	1.22(2)	3.87(5)	5.5(8)	0.0(2)
	N	0.25	0.2375	0.0125	0.25	0.5
BaPb _{0.925} Sn _{0.075} O ₃	x (Å)	0	0	0	0	0.25
	y (Å)	0.25	0	0	0.25	0.025(1)
	z (Å)	0.4880(3)	0	0	0.00(2)	0.25
	B _{iso} (Å ²)	0.78(2)	1.33(2)	3.03(5)	7.4(8)	0.3(2)
	N	0.25	0.2313	0.0188	0.25	0.50

TABLE-2
LATTICE PARAMETERS OF BaPb_{1-x}Sn_xO₃

Compounds	a (Å)	b (Å)	c (Å)	V (Å ³)	R _p	R _{wp}	R _{exp}	χ ²
BaPbO ₃	6.03394(3)	8.5178(4)	6.0721(3)	312.083(3)	4.42	6.19	2.14	8.40
BaPb _{0.975} Sn _{0.025} O ₃	6.03086(8)	8.5129(10)	6.0656(7)	311.445(7)	6.04	7.03	2.06	11.60
BaPb _{0.95} Sn _{0.05} O ₃	6.02501(9)	8.5072(1)	6.0584(9)	310.529(8)	9.77	11.57	1.88	37.78
BaPb _{0.925} Sn _{0.075} O ₃	6.02141(7)	8.5029(10)	6.0530(7)	309.913(6)	6.36	7.60	2.03	13.99

Various bond lengths and bond angles obtained from the Rietveld fitting of the synchrotron XRD data are shown in Table-3. The orthorhombic distortion observed in BaPb_{1-x}Sn_xO₃ as in BaPbO₃ (space group Imma) is similar to distortion for PrAlO₃ [26]. It is interesting to note that the lattice parameters a and c differ only from the second decimal place onwards and the Pb/Sn–O1 and Pb/Sn–O2 bond lengths are also of similar magnitude in BaPbO₃ but are little shorter in BaPb_{1-x}Sn_xO₃ (Table-3). The short Pb/Sn–O bonds are attributed the stronger interionic attraction due to the smaller ionic size of dopant. The interionic bond contraction affects the size Pb/SnO₆ octahedral (Fig. 4). The Pb/Sn–O1–Pb/Sn bond angle is about 165.5° in BaPbO₃ and is about 180° in BaPb_{1-x}Sn_xO₃. The closer Pb/Sn–O distances, the stronger ionic interaction due more rigid and regular Pb/SnO₆ octahedral.

The space group Imma is relatively rare for the ABO₃ perovskite [27]. Most orthorhombic perovskite structures are described in Pnma [4]. The structure shows the titling of the BO₆ octahedral, Imma having two equal out-of-phase tilts (a⁻b⁺b⁺). The structure of BaPbO₃ at room temperature is a

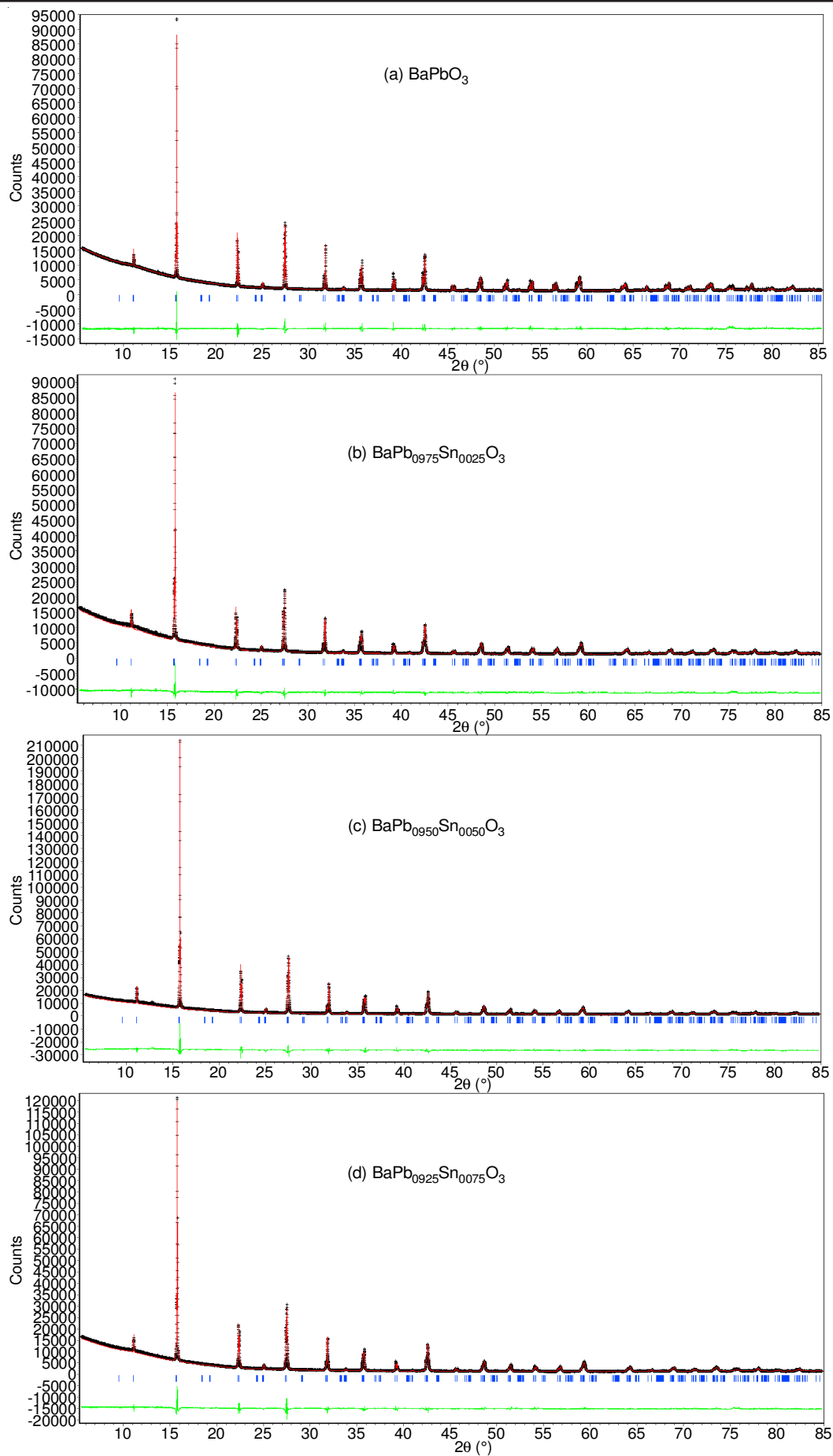
simple case of two-tilt system with equal tilting magnitude. The same space group has also been found in mixed perovskite BaPb_{1-x}Sn_xO₃, as well as in BaBi_{1-x}Pb_xO₃ (0.1 ≤ x ≤ 0.65) [28], BaPb_{0.8}Ti_{0.2}O_{2.8} [29] and BaBi_{0.8}In_{0.2}O₃ [30]. In BaPb_{1-x}Sn_xO₃, the Pb/SnO₆ octahedra tilt about 8.66° at room temperature. The shape of octahedral is slightly compressed, but the difference of Pb/Sn–O bond distances is rather small (Table-3). The Pb/Sn–O bond distance averaged values, 2.1492 Å, is in good agreement with sum of Shannon's ionic radii (2.175 Å) [31]. The octahedral tilting causes, on the other hand, somewhat larger changes of the Ba–O bondlengths, ranging from 2.734 to 3.300 Å. The averaged values, being 3.023, is again compatible with the sum of the corresponding ionic radii (3.01 Å) [31].

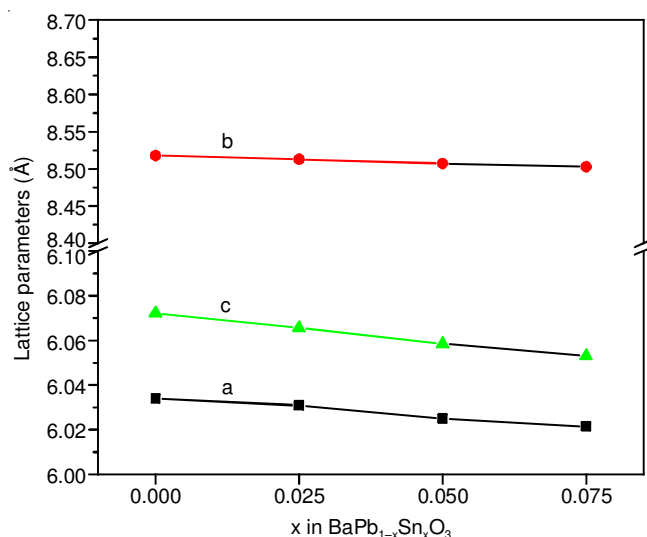
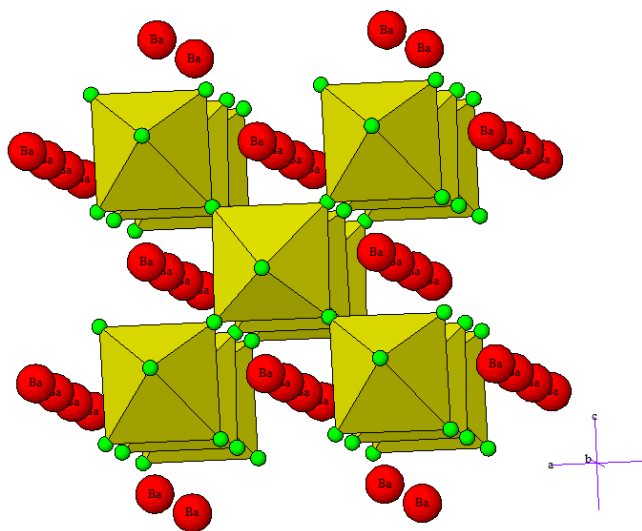
Conclusion

We have investigated the crystal structure of BaPb_{1-x}Sn_xO₃ (x = 0, 0.025, 0.05 and 0.075) at room temperature based on the data collected by using a very high-resolution synchrotron XRD. Data refinement results in a proposed structural model.

TABLE-3
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) FOR BaPb_{1-x}Sn_xO₃

Compounds	Pb/Sn–O(1) (Å)	Pb/Sn–O(2) (Å)	Ba–O(1) (Å)			Ba–O(2) (Å)		Pb/Sn–O(1)–Pb/Sn (°)
BaPbO ₃	2.147(2) x2	2.155(1) x4	2.77(1)	3.30(1)	3.023(1) x2	3.200(8) x4	2.849(7) x4	165.5(7)
BaPb _{0.975} Sn _{0.025} O ₃	2.12847(4) x2	2.1494(9) x4	2.97(13)	3.1(1)	3.016(3) x2	3.143(6) x4	2.904(6) x4	180.0(6)
BaPb _{0.95} Sn _{0.05} O ₃	2.1270(8) x2	2.1439(11) x2	2.88(5)	3.18(5)	3.014(2)	3.089(10) x4	2.954(8) x4	178(2)
BaPb _{0.925} Sn _{0.075} O ₃	2.126(1) x2	2.1450(9) x4	2.98(10)	3.08(10)	3.012(3) x2	3.131(7) x4	2.906(6) x4	179(3)

Fig. 2. Plots of the observed, calculated and difference profiles for the Rietveld refinement of the $\text{BaPb}_{1-x}\text{Sn}_x\text{O}_3$

Fig. 3. Plot of the lattice parameters vs. x in BaPb_{1-x}Sn_xO₃Fig. 4. Crystal structure of orthorhombic BaPb_{1-x}Sn_xO₃

We firmly confirmed the orthorhombic, space group Imma, that provides the correct description of structure of BaPb_{1-x}Sn_xO₃.

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REFERENCES

- R. Weiss, *C.R. Acad. Sci.*, **246**, 3073 (1958).
- D.E. Cox and A.W. Sleight, *ERDA Energy Res. Abstr.*, **2**, 7623 (1977).
- D.T. Marx, P.G. Radaelli, J.D. Jorgensen, R.L. Hitterman, D.G. Hinks, S. Pei and B. Dabrowski, *Phys. Rev. B*, **46**, 1144 (1992); <https://doi.org/10.1103/PhysRevB.46.1144>.
- S.M. Moussa, B.J. Kennedy and T. Vogt, *Solid State Commun.*, **119**, 549 (2001); [https://doi.org/10.1016/S0038-1098\(01\)00265-4](https://doi.org/10.1016/S0038-1098(01)00265-4).
- W.T. Fu, D. Visser, K.S. Knight and D.J.W. IJdo, *J. Solid State Chem.*, **180**, 1559 (2007); <https://doi.org/10.1016/j.jssc.2007.03.009>.
- P. Giraldo-Gallo, H. Lee, Y. Zhang, M.J. Kramer, M.R. Beasley, T.H. Geballe and I.R. Fisher, *Phys. Rev. B*, **85**, 174503 (2012); <https://doi.org/10.1103/PhysRevB.85.174503>.
- M.J. Pacheco, F. Regalado, D. Santos, L. Ciriaco and A. Lopes, *J. Electrochem. Soc.*, **161**, H474 (2014); <https://doi.org/10.1149/2.0391409jes>.
- C.S. Liang, J.M. Wu and M.C. Chang, *Appl. Phys. Lett.*, **81**, 3624 (2002); <https://doi.org/10.1063/1.1520332>.
- M. Yasukawa and T. Kono, *J. Alloys Comp.*, **426**, 420 (2006); <https://doi.org/10.1016/j.jallcom.2006.03.098>.
- Y. Guo and H. Liu, *J. Power Sources*, **183**, 381 (2008); <https://doi.org/10.1016/j.jpowsour.2008.04.092>.
- A. Franz, D. Klimm, W. Schmitz, I. Haferkorn and K. Bente, *Cryst. Res. Technol.*, **46**, 906 (2011); <https://doi.org/10.1002/crat.201000207>.
- Y.H. Hsieh and S.L. Fu, *Ceram. Int.*, **18**, 289 (1992); [https://doi.org/10.1016/0272-8842\(92\)90076-P](https://doi.org/10.1016/0272-8842(92)90076-P).
- D.J. Payne, R.G. Egdell, W. Hao, J.S. Foord, A. Walsh and G.W. Watson, *Chem. Phys. Lett.*, **411**, 181 (2005); <https://doi.org/10.1016/j.cplett.2005.06.023>.
- D.J. Payne, G. Paolicelli, F. Offi, G. Panaccione, P. Lacovig, G. Beamson, A. Fondacaro, G. Monaco, G. Vanko and R.G. Egdell, *J. Electron Spectrosc. Relat. Phenom.*, **169**, 26 (2009); <https://doi.org/10.1016/j.elspec.2008.10.002>.
- D.J. Payne, R.G. Egdell, G. Paolicelli, F. Offi, G. Panaccione, P. Lacovig, G. Monaco, G. Vanko, A. Walsh, G.W. Watson, J. Guo, G. Beamson, P.-A. Glans, T. Learmonth and K.E. Smith, *Phys. Rev. B*, **75**, 153102 (2007); <https://doi.org/10.1103/PhysRevB.75.153102>.
- M. Heinemann, H.J. Terpstra, C. Haas and R.A. de Groot, *Phys. Rev. B*, **52**, 11740 (1995); <https://doi.org/10.1103/PhysRevB.52.11740>.
- M. Magnuson, T. Schmitt, V.N. Strocov, J. Schlappa, A.S. Kalabukhov and L.C. Duda, *Sci. Rep.*, **4**, 7017 (2015); <https://doi.org/10.1038/srep07017>.
- A.G. Mamalis, S.G. Ovchinnikov, M.I. Petrov, D.A. Balaev, K.A. Shaihtudinov, D.M. Gohfeld, S.A. Kharlamova and I.N. Voteya, *Physica C*, **364-365**, 174 (2001); [https://doi.org/10.1016/S0921-4534\(01\)00749-3](https://doi.org/10.1016/S0921-4534(01)00749-3).
- V.R.R. Medicherla, T. Shripathi and N.P. Lalla, *J. Phys. Condens. Matter*, **20**, 35219 (2008); <https://doi.org/10.1088/0953-8984/20/03/035219>.
- A.B. Velichenko, R. Amadelli, A. Benedetti, D.V. Girenko, S.V. Kovalyov and F.I. Danilov, *J. Electrochem. Soc.*, **149**, C445 (2002); <https://doi.org/10.1149/1.1495498>.
- H. Kaddoussi, Y. Gagou, A. Lahmar, J. Belhadi, B. Allouche, J.L. Dellis, M. Courty, H. Khemakhem and M. El Marssi, *Solid State Commun.*, **201**, 64 (2015); <https://doi.org/10.1016/j.ssc.2014.10.003>.
- Y. Yuan, Z. Zhao, J. Zheng, M. Yang, L. Qiu, Z. Li and Z. Zou, *J. Mater. Chem.*, **20**, 6772 (2010); <https://doi.org/10.1039/c0jm00455c>.
- W.T. Fu and D.J.W. IJdo, *J. Solid State Chem.*, **178**, 2363 (2005); <https://doi.org/10.1016/j.jssc.2005.05.021>.
- K.S. Wallwork, B.J. Kennedy and D. Wang, *AIP Conf. Proc.*, **879**, 879 (2007); <https://doi.org/10.1063/1.2436201>.
- C.J. Howard and B.A. Hunter, A Computer Program for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns, Lucas Heights Research Laboratories, New South Wales, Australia, pp. 1-27 (1998).
- R.P. Burbank, *J. Appl. Cryst.*, **3**, 112 (1970); <https://doi.org/10.1107/S0021889870005794>.
- J. Shi and L. Guo, *Progr. Nat. Sci.: Mater. Int.*, **22**, 592 (2012); <https://doi.org/10.1016/j.pnsc.2012.12.002>.
- D.E. Cox and A.W. Sleight, in ed: R.M. Moon, Proceedings of the Conference on Neutron Scattering, Gatlinburg, National Technical Information Service, Springfield, VA, USA, p. 45 (1976).
- J.E. Greedan, K.L. Willmer and H.F. Gibbs, *Eur. J. Solid State Chem.*, **29**, 505 (1992).
- W.T. Fua, M.J. Polderman and F.M. Mulder, *Mater. Res. Bull.*, **35**, 1205 (2000); [https://doi.org/10.1016/S0025-5408\(00\)00332-9](https://doi.org/10.1016/S0025-5408(00)00332-9).
- R.D. Shannon, *Acta Crystallogr. A*, **32**, 751 (1976); <https://doi.org/10.1107/S0567739476001551>.