Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Solid State Chemistry 178 (2005) 2363–2367
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

X-ray and neutron powder diffraction study of the double perovskites Ba_2LnSbO_6 (Ln = La, Pr, Nd and Sm)

W.T. Fu*, D.J.W. IJdo

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Received 10 March 2005; received in revised form 10 May 2005; accepted 20 May 2005

Abstract

The crystal structures of Ba_2LnSbO_6 (Ln = La, Pr, Nd and Sm) at room temperature have been investigated by profile analysis of the Rietveld method using either combined X-ray and neutron powder diffraction data or X-ray powder diffraction data. It has been shown that the structure of Ba_2LnSbO_6 with Ln = La, Pr and Nd are neither monoclinic nor cubic as were previously reported. They are rhombohedral with the space group $R\bar{3}$. The distortion from cubic symmetry is due to the rotation of the LnO_6/SbO_6 octahedra about the primitive cubic $[111]_p$-axis. On the other hand, the structure of Ba_2SmSbO_6 is found to be cubic. All compounds contain an ordered arrangement of LnO_6 and SbO_6 octahedra.

Keywords: Perovskites; X-ray powder diffraction; Neutron powder diffraction; Crystal structure

1. Introduction

Ternary compounds of the formula ABX_3 often crystallise in the perovskite structure. Depending on the tolerance factor, $t = (r_A + r_B)/\sqrt{2}(r_B + r_X)$, where r_A, r_B and r_X are the constituent ionic radii, a perovskite may adopt either the simple cubic structure ($t \approx 1$), space group $Pm\bar{3}m$, or a distorted one ($t > 1$ or $t < 1$), with lower symmetry. For the majority of perovskites known so far, the distortions from the ideally cubic structure were found to be due to the tilting of the BX_6 octahedra. Glazer [1,2] classified the tilting patterns in terms of independent tilts of the rigid octahedra around the pseudo-cubic axes, and obtained 23 possible tilt systems with the corresponding space groups. Woodward [3,4] re-examined the Glazer's tilt systems and found that in six of the tilt systems it is not possible to maintain perfectly rigid octahedra; small distortions of octahedra should occur. Recently, Howard and Stokes [5] undertook a group-theoretical analysis of the Glazer's tilt system and derived 15 possible space groups.

The double perovskites, $A_2BB'X_6$, are derived from the ABX_3 perovskites when half of the octahedrally coordinated B-cations are replaced by the suitable B'-cations. If an ordered arrangement between B and B' occurs, the symmetry and the size are changed. One may define the tolerance factor for $A_2BB'X_6$ double perovskites as $t = (r_A + r_B)/\sqrt{2}(\bar{r}_{(B,B')} + r_X)$, where $\bar{r}_{(B,B')}$ is the averaged ionic radii of the B and B'-cation. The ideal double perovskite has the cubic symmetry ($t \approx 1$), space group $Fm\bar{3}m$, with a unit cell edge double that of the cubic ABX_3 aristotype. If there is mismatch between the A–X and the averaged (B,B')–X bond lengths, i.e. $t > 1$ or $t < 1$, the structure of the double perovskites distorts from cubic symmetry. Just like the normal perovskites, the most commonly occurred distortions in $A_2BB'X_6$ are due to the tilting of the $BX_6/B'X_6$ octahedra. Woodward [3], based on the Glazer's description of the tilt systems, has considered the cation ordering and octahedral tilting occurring simultaneously and derived 13 possible space groups for double perovskites. Howard et al. [6] identified, using the group-theoretical analysis, 12 space

*Corresponding author. fax: +31 71 5274537.
E-mail address: w.fu@chem.leidenuniv.nl (W.T. Fu).

0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.05.021

groups under the same conditions of the octahedral tilting and the cation ordering.

The compounds of the formula Ba_2LnSbO_6 (Ln = lanthanides) have long been known since Blasse first reported Ba_2GdSbO_6 to be double cubic with 1:1 ordering of Gd(III) and Sb(V) ions [7]. Later on, the other compounds with heavier lanthanides were proved, by X-ray powder diffraction, to be double cubic [8], but the coordinates of the oxygen atoms were not given. Alonso et al. [9] have determined, using neutron powder diffraction data, the structure of Ba_2LnSbO_6 in the case of Ln = Ho and Y, and confirmed the cubic space group $Fm\bar{3}m$. For compounds with lighter lanthanides, the crystal structures seem to be less well characterised. Wittmann et al. [10] reported a monoclinic cell for Ba_2LnSbO_6 with Ln = La, Pr and Nd, and a primitive cubic cell for Ba_2SmSbO_6, respectively. However, Kurian et al [11] prepared Ba_2LnSbO_6 (Ln = Pr, Sm and Gd) as substrates for high-T_c superconducting $Ba_2YCu_3O_{7-\delta}$ and described them to be double cubic perovskites. But from their reported X-ray powder diffraction pattern of Ba_2PrSbO_6, the splitting of diffraction lines is clearly visible suggesting that its symmetry should be lower than cubic. We, therefore, carried out a structural study on the compounds Ba_2LnSbO_6 (Ln = La, Pr, Nd and Sm) and report their correct space groups and crystal structures in this paper.

2. Experimental

Samples of Ba_2LnSbO_6 (Ln = La, Pr, Nd, and Sm) were prepared from $BaCO_3$, La_2O_3, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, and Sb_2O_3 in alumina crucibles using the standard solid-state reaction in air. The hygroscopic La_2O_3 and Nd_2O_3 were preheated at 1000 °C for several hours before use. Due to the low melting point of Sb_2O_3, the mixtures were first heated at 800 °C overnight. The resultant powders were then sintered with a temperature step of 100 °C and 20 h at each step with regrinding. The final sintering temperature was 1300 °C. The samples were furnace cooled to room temperature.

X-ray diffraction patterns were collected with a Philips PW1050 diffractometer using Cu-$K\alpha$ radiation in steps of 0.02° (2θ) and 12 s counting time in the range of $10° < 2\theta < 116°$. The neutron powder diffraction data were collected at room temperature for Ba_2LnSbO_6 (~20 g), Ln = La and Pr, on the powder diffractometer of the High-Flux Reactor of NRG in Petten, with the neutron wavelength of 1.4258 Å and in steps of 0.05° (2θ). Vanadium can was used as sample holder. For neutron powder diffraction data, the absorption corrections were applied according to Weber [12].

Model refinement was performed by the Rietveld method using the Rietica computer program [13]. No anomalous scattering corrections were applied. A polynomial function with six parameters was used to fit the background. The profiles have been fitted using a Pseudo-Voigt function with peak asymmetric correction. The neutron scattering lengths used in the calculation are: $b_{(Ba)} = 5.06$, $b_{(La)} = 8.24$, $b_{(Pr)} = 4.58$, $b_{(Sb)} = 5.57$ and $b_{(O)} = 5.803$ fm.

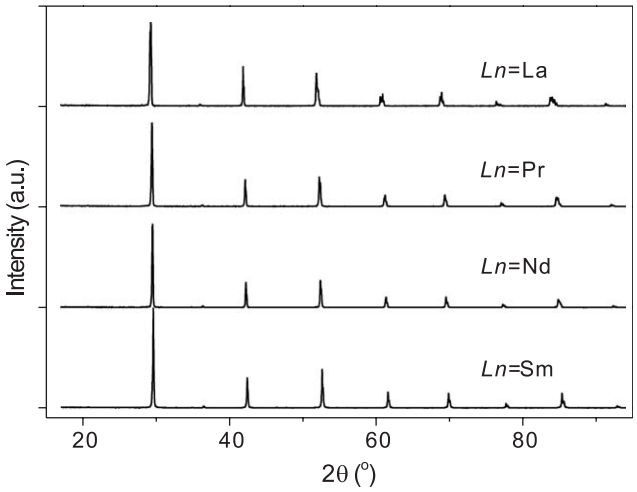

Fig. 1. X-ray powder diffraction patterns of Ba_2LnSbO_6 (Ln = La, Pr, Nd and Sm).

3. Results

X-ray diffraction patterns of Ba_2LnSbO_6 at room temperature are shown in Fig. 1. They all show strong lines characteristic of a primitive cubic cell. However, many of the diffraction lines are visibly split for Ln = La, Pr and Nd, indicating that the symmetry is lower than cubic (see also Fig. 2). In addition, a few very weak additional lines, indicative of the presence of a supercell in these compounds, are also visible. Due to quite small difference in the scattering power to X-ray between Ln and Sb atoms, all superlattice diffraction lines due to their ordering are of low intensity. However, the cation ordering is clearly revealed by neutron powder diffraction data (Fig. 3). To identify the possible space groups for Ba_2LnSbO_6, we have examined both the occurrence of the superlattice diffraction lines and the splitting of diffraction peaks corresponding to the basic cubic perovskite cell. As can be seen from both X-ray (Fig. 1) and neutron (Fig. 3) powder diffraction patterns, all observed superlattice diffraction lines are indexed in terms of a double cubic cell all with odd indices. This suggests that only out-of-phase tilting of the octahedra, if it exists, is possible. Considering further that the octahedral tilting occurs around one of the principle axes of the basic cubic perovskite cell,[1]

[1]We found, from our X-ray diffraction data, no evidence to suggest the triclinic symmetry, such as $F\bar{1}$ (tilt system ($a^-b^-c^-$)) or $I\bar{1}$ (tilt system ($a^0b^-c^-$)), for Ba_2LnSbO_6.

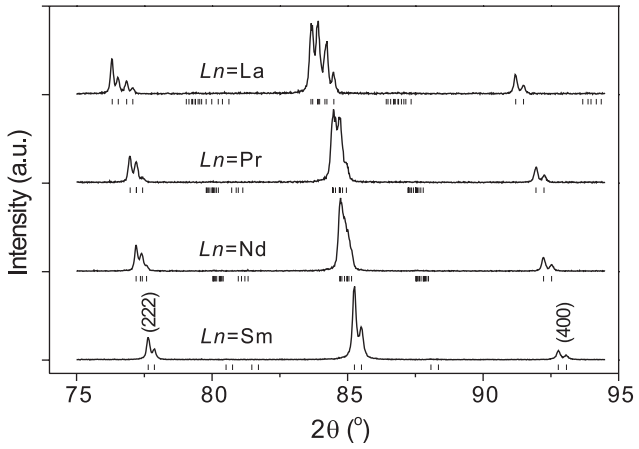

Fig. 2. An enlarged section of the diffraction patterns of Ba_2LnSbO_6 showing the basic (222) and (400) reflections. The tick marks below are the calculated positions of the allowed Bragg's reflections using the refined lattice parameters in the space groups $R\bar{3}$ (Ln = La, Pr, and Nd) and $Fm\bar{3}m$ (Ln = Sm), respectively. Note that the basic (222) reflection splits in the rhombohedral cell in the (400) and (444) reflections.

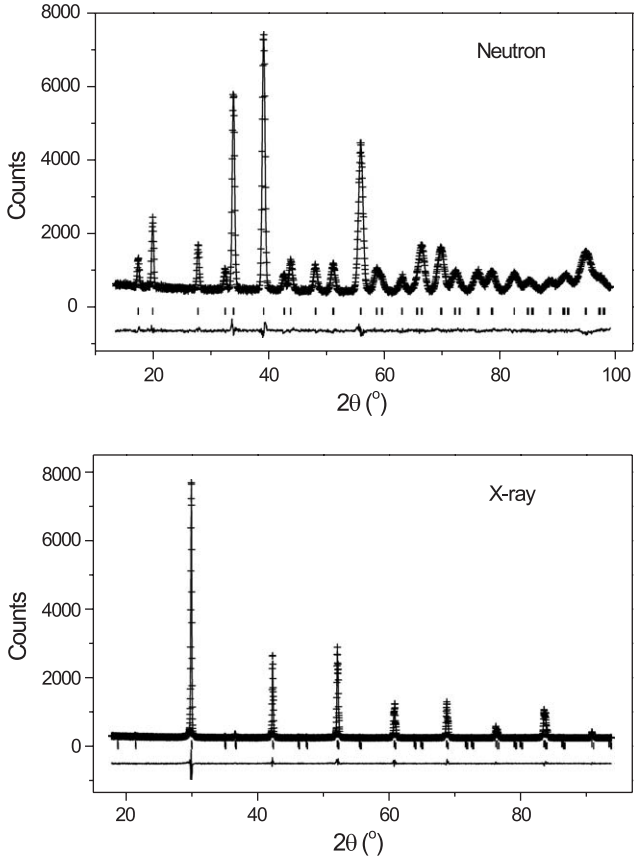

Fig. 3. Observed (crosses) and calculated (full line) profiles of both neutron and X-ray powder diffraction for Ba_2PrSbO_6. Tick marks below the profiles indicate the positions of the Bragg reflections. A difference curve (observed-calculated) is shown at the bottom of the plots.

i.e. $[001]_p$, $[110]_p$ and $[111]_p$-axis, the structure of Ba_2LnSbO_6 would have one of the following possible space groups: $I4/m$ ($a^0a^0c^-$), $I2/m$ ($a^0b^-b^-$) and $R\bar{3}$ ($a^-a^-a^-$) including the one without tilting, $Fm\bar{3}m$ ($a^0a^0a^0$) [3,6]. Close inspection of the main peak splitting has ruled out both $I4/m$ and $I2/m$ as possible space groups (Fig. 2). For example, the basic (400) would split into two in both $I4/m$ and $I2/m$, but it clearly remains as one single peak; only splitting due to $K\alpha_1$ and $K\alpha_2$ radiations is resolved. Further examination of the basic (222) reflection showed a structural change from rhombohedral to cubic through La → Sm. For instance, the basic (222) diffraction line of Ba_2LaSbO_6 splits into two, which are indexed as (400) and (444), as is expected for the space group $R\bar{3}$. The degree of splitting becomes progressively smaller for Ln = Pr and Nd, and the splitting is no more visible for Ln = Sm. In fact, all diffraction lines of Ba_2SmSbO_6 showed no splitting except that being due to $K\alpha_1$ and $K\alpha_2$ radiations. Consequently, the likely space groups of Ba_2LnSbO_6 are $R\bar{3}$ for Ln = La, Pr and Nd and $Fm\bar{3}m$ for Ln = Sm, respectively.

The Rietveld refinements were carried out in the space groups $R\bar{3}$ and $Fm\bar{3}m$ to model the structures of Ba_2LnSbO_6. Considering that the neutron diffraction is more sensitive to the octahedral tilting and the cation ordering and that the X-ray diffraction provides more information on the symmetry of the lattice and the positions of the heavier cations, the structure of Ba_2LnSbO_6 with Ln = La and Pr were refined from the combined neutron and X-ray powder diffraction data [14]. For compounds with Ln = Nd and Sm, no neutron diffraction data were available; only X-ray powder diffraction data were used in the calculations. In all cases, Rietveld refinements yielded satisfactory results. The refined structural and thermal parameters are summarised in Table 1. Table 2 lists some selected inter atomic distances. The plots of the observed and calculated profiles of both neutron and X-ray diffraction of Ba_2PrSbO_6 are shown in Fig. 3.

4. Discussion

The crystal structures of Ba_2LnSbO_6 (Ln = La, Pr, Nd and Sm) are easily derived from the simple cubic aristotype by ordering the octahedral cations in a 1:1 ordering scheme (Fig. 4). In Ba_2LnSbO_6 (Ln = La, Pr, Nd), the LnO_6 and SbO_6 octahedra are tilted around the three-fold $[111]_p$-axis, resulting in rhombohedral symmetry. In Ba_2SmSbO_6, no octahedral tilting is observed. Such a structural change is expected given the systematic change of the match between the Ba–O and the averaged (Ln,Sb)–O (Ln = lanthanide) bond lengths. The tolerance factor of Ba_2LaSbO_6 is $t = 0.96$, indicating that the Ba atoms are somewhat smaller to fit in the cavity

Table 1
Refined atomic positions and thermal parameters of Ba_2LnSbO_6 (Ln = La, Pr, Nd and Sm) in the space groups $R\bar{3}$ and $Fm\bar{3}m$

Ba_2LaSbO_6 ($R\bar{3}$)		Ba_2PrSbO_6 ($R\bar{3}$)		Ba_2NdSbO_6 ($R\bar{3}$)		Ba_2SmSbO_6 ($Fm\bar{3}m$)	
a (Å)	6.0825(1)	a (Å)	6.0549(1)	a (Å)	6.04003(9)	a (Å)	8.50908(8)
α (°)	60.292(1)	α (°)	60.124(2)	α (°)	60.086(1)		
Ba	2c (x,x,x)	Ba	2c (x,x,x)	Ba	2c (x,x,x)	Ba	8c (0.25,0.25,0.25)
x	0.2513(2)	x	0.2509(3)	x	0.2501(4)	B(Å)^2	0.56(2)
B(Å)^2	0.38(2)	B(Å)^2	0.26(2)	B(Å)^2	0.47(2)		
La	1a (0,0,0)	Pr	1a (0,0,0)	Nd	1a (0,0,0)	Sm	4a (0,0,0)
B(Å)^2	0.02(4)	B(Å)^2	0.17(7)	B(Å)^2	0.15(2)	B(Å)^2	0.54(7)
Sb	1b (0.5,0.5,0.5)	Sb	1b (0.5,0.5,0.5)	Sb	1b (0.5,0.5,0.5)	Sb	4b (0.5,0.5,0.5)
B(Å)^2	0.15(5)	B(Å)^2	0.01(1)	B(Å)^2	0.15(2)	B(Å)^2	0.13(8)
O	6f (x,y,z)	O	6f (x,y,z)	O	6f (x,y,z)	O	24e (x,0,0)
x	−0.2771(7)	x	−0.2860(6)	x	−0.279(4)	x	0.258(2)
y	0.2307(2)	y	0.2393(4)	y	0.240(5)	B(Å)^2	1.1(1)
z	0.3097(2)	z	0.2925(7)	z	0.276(4)		
B(Å)^2	0.96(2)	B(Å)^2	0.94(2)	B(Å)^2	1.0(1)		
R_{wp} = 4.02%[a] (17.90%)[b]		R_{wp} = 4.16%[a] (16.96%)[b]		R_{wp} = 16.42%[b]		R_{wp} = 16.53%[b]	
R_p = 2.82%[a] (11.72%)[b]		R_p = 3.29%[a] (10.88%)[b]		R_p = 10.45%[b]		R_p = 10.31%[b]	
R_B = 1.28%[a] (3.24%)[b]		R_B = 1.61%[a] (6.30%)[b]		R_B = 2.54%[b]		R_B = 4.24%[b]	
χ^2 = 3.62[a] (2.23)[b]		χ^2 = 1.96[a] (2.14)[b]		χ^2 = 2.70		χ^2 = 3.06	

[a] R-factor of neutron diffraction data.
[b] R-factor of X-ray diffraction data.

Table 2
Selected interatomic distances (Å) and the tilting angle of the octahedra (°)

	Ba_2LaSbO_6	Ba_2PrSbO_6	Ba_2NdSbO_6	Ba_2SmSbO_6
Ln–O	2.342(1) 6 ×	2.290(3) 6 ×	2.22(3) 6 ×	2.20(2) 6 ×
Sb–O	1.996(1) 6 ×	2.015(4) 6 ×	2.07(4) 6 ×	2.06(2) 6 ×
Ba–O	2.819(1) 3 ×	2.877(2) 3 ×	2.90(4) 3 ×	3.0092(5) 12 ×
	2.996(5) 3 ×	2.902(6) 3 ×	2.92(1) 3 ×	
	3.113(5) 3 ×	3.167(6) 3 ×	3.14(1) 3 ×	
	3.342(1) 3 ×	3.200(2) 3 ×	3.15(4) 3 ×	
φ (°)	7.8	5.3	3.6	0

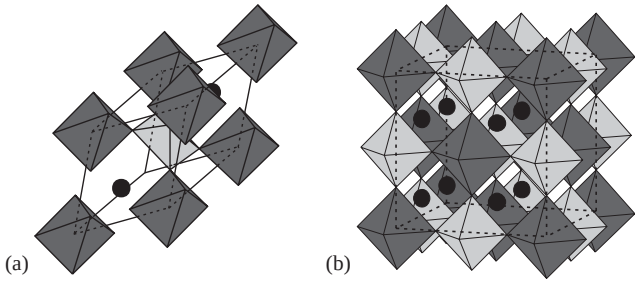

Fig. 4. Schematic representation of the crystal structures of rhombohedral Ba_2LnSbO_6 (Ln = La, Pr, and Nd) (a) and cubic Ba_2SmSbO_6 (b), showing the LnO_6 (dark shaded) and SbO_6 (light shaded) octahedra and the Ba atoms (black).

formed by the LaO_6 and SbO_6 octahedra. The tilting of octahedra reduces the size of cavity by reducing some of the Ba–O distances. As the ionic radius of the lanthanide diminishes from La to Nd, the mismatch between Ba–O and the averaged (Ln,Sb)–O bond-lengths decreases. This can also be seen from the magnitude of the averaged tilting angle (φ) calculated from the coordinates of the oxygen atom using the formula [15] : $\tan(\varphi) = \sqrt{3}(z - y)$ (rad). For Ln = La, Pr and Nd, the tilting angles are 7.8°, 5.3° and 3.6° , respectively, being in agreement with the increasing of the tolerance factors, 0.96, 0.97 and 0.971, respectively. It is also noticed that several known ordered perovskites that do adopt the rhombohedral space group $R\bar{3}$, e.g. Ba_2BiSbO_6 (t = 0.961) [16], Ba_2YbBiO_6 (t = 0.961) [17], Ba_2LaIrO_6 (t = 0.967) [18], Ba_2BiTaO_6 (t = 0.952) [19], all have the comparable values of the tolerance factor. With further decreasing the size of lanthanide, e.g. Ln = Sm, no bond length mismatch apparently exists, and the ordered perovskites have the double cubic structure as were also confirmed previously for Ln = Gd [7], Ho and Y [9].

Our results are in agreement with the earlier finding of Wittmann et al. [10] that the compounds with Ln = La, Pr, and Nd are non-cubic, but differ with their description as monoclinic. As was mentioned above, octahedral tilting around the twofold $[110]_p$-axis would result in monoclinic symmetry with the space group $I2/m$. In this space group, however, the basic (h00)-type would split into two, which is clearly not the case. On the other hand, we confirmed the cubic structure of Ba_2SmSbO_6 as was reported by Kurian et al. [11], but their description of Ba_2PrSbO_6 being also double cubic is now wrong.

It is interesting to note that the calculated tolerance factor of Ba_2SmSbO_6 (t = 0.977) deviates quite a bit from unity. It has nevertheless the cubic symmetry

without any octahedral tilt. As compared to the cubic ABX_3 aristotype, in which the only variable parameter is the cell length, the structure of double cubic $A_2BB'X_6$ has an additionally adjustable parameter, i.e. the position of X-anion in-between the B and B' cations, so that the relative sizes of B and B' could be adjusted. It may, therefore, release, at certain extent, the mismatch between the A–X bond length and the averaged (B,B')–X bond length in double perovskite structure. In fact, in Ba_2LnSbO_6 the Ln–O bond lengths are all smaller (Table 2) than the sum of the corresponding ionic radii [20]. For example, the bond lengths of La–O and Pr–O are found to be 2.342 Å and 2.290 Å as were compared to the calculated values of 2.432 and 2.390, respectively. On the other hand, the observed Sb–O bond lengths are quite compatible with that from the sum of ionic radii (2.00 Å). The same feature has also been found in the cubic perovskites Ba_2HoSbO_6 and Ba_2YSbO_6 [9] as well as in the rhombohedral Ba_2BiSbO_6 [16]. Given that Ba_2SmSbO_6 ($t = 0.977$) is a double cubic perovskite, it is expected that other $Ba_2B(III)B'(V)O_6$-type perovskites with comparable values of the tolerance factor should also adopt the double cubic structure. Indeed, our recent investigations on Ba_2NdIrO_6 ($t = 0.978$), Ba_2PrRuO_6 ($t = 0.977$), Ba_2NdRuO_6 ($t = 0.979$), Ba_2NdIrO_6 ($t = 0.978$) and Ba_2HoNbO_6 ($t = 0.981$) showed that they all have cubic symmetry at room temperature. The detailed results on these perovskites will be published elsewhere. Finally, we want to mention that the compound Ba_2LnSbO_6 with $Ln = Ce$ does not exist. In this case, Ce is tetravalent leading to a cation-deficient perovskite of the formula $Ba_2Ce_{0.75}SbO_6$, space group $I4/mmm$ [21], with complete ordering of Ce, Sb and vacancies.

In conclusion, we have studied the structures of the double perovskites Ba_2LnSbO_6 (Ln = La, Pr, Nd and Sm) at room temperature, using either the combined X-ray and neutron powder diffraction or X-ray powder diffraction techniques alone. They all contain the ordered arrangement of LnO_6 and SbO_6 octahedra but with different symmetries. In Ba_2LnSbO_6 whose tolerance factor deviates largely from the unity, the octahedra are tilted around the primitive $[111]_p$ -axis of the cubic aristotype, resulting in the space group $R\bar{3}$. Examples are Ln = La, Pr, and Nd. For smaller lanthanides, i.e. from Sm downwards, no octahedral tilting occurs, and Ba_2LnSbO_6 have the simple double cubic structure with the space group $Fm\bar{3}m$. For a number of $Ba_2B(III)B'(V)O_6$-type perovskites, it seems that the double cubic structure exists with the tolerance factor (t) of about above 0.98.

Acknowledgments

The authors are indebted to Mr. A. Bontenbal of NRG in Petten for the collection of the powder neutron diffraction data and to Dr. R.A.G. de Graaff for valuable discussions.

References

[1] A.M. Gazer, Acta Crystallogr. B 28 (1972) 3384.
[2] A.M. Gazer, Acta Crystallogr. A 31 (1975) 756.
[3] P.M. Woodward, Acta Crystallogr. B 53 (1997) 32.
[4] P.M. Woodward, Acta Crystallogr. B 53 (1997) 44.
[5] C.J. Howard, H.T. Stokes, Acta Crystallogr. B 54 (1998) 782.
[6] C.J. Howard, B.J. Kennedy, P.M. Woodward, Acta Crystallogr. B 59 (2003) 463.
[7] G. Blasse, J. Inorg. Nucl. Chem. 27 (1965) 993.
[8] P. Garcia-Casado, A. Mendiola, I. Rasines, Z. Anorg. Allg. Chem. 510 (1984) 194.
[9] J.A. Alonso, C. Cascales, P. Garcia-Casado, I. Rasines, J. Solid State Chem. 128 (1997) 247.
[10] U. von Wittmann, G. Rauser, S. Kemmler-Sack, Z. Anorg. Allg. Chem. 482 (1981) 143.
[11] J. Kurian, J. Koshi, P.R.S. Wariar, Y.P. Yadava, A.D. Damodaran, J. Solid State Chem. 116 (1995) 193.
[12] K. Weber, Acta Crystallogr. 23 (1967) 720.
[13] C.J. Howard, B.A. Hunter, A computer program for Rietveld analysis of X-ray and neutron powder diffraction patterns, Lucas Height Research Laboratories, 1998.
[14] R.B. Von Dreele, in: R.A. Young (Ed.), The Rietveld Method, Oxford University Press, Oxford, 1993 (Chapter 12).
[15] S. Pei, J.D. Jorgensen, B. Dabrovski, D.G. Hinks, D.R. Richards, A.W. Mitchell, J.M. Newsam, S.K. Sinha, D. Vaknin, A.J. Jacobson, Phys. Rev. B 41 (1990) 4126.
[16] W.T. Fu, Solid State Commun. 116 (2000) 461.
[17] W.T.A. Harrison, K.P. Reis, A.J. Jacobson, L.F. Schneemeyer, J.V. Waszczak, Chem. Mater. 7 (1995) 2161.
[18] W.T. Fu, D.J.W. IJdo, J. Alloys Compd. 394 (2005) L5–L8.
[19] K.S. Wallwork, B.J. Kennedy, Q. Zhou, Y. Lee, T. Vogt, J. Solid State Chem. 178 (2005) 207.
[20] R.D. Shannon, Acta Cryst. A 32 (1976) 751.
[21] D.J.W. IJdo, R.B. Helmholdt, Acta Cryst. C 49 (1993) 652.