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Double-layered Aurivillius-type ferroelectrics with magnetic moments

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ABSTRACT

We have synthesized the double-layer Aurivillius phase $\text{Bi}_2\text{LnNbTiO}_9$ where $\text{Ln} = \text{Nd-Gd, Bi}$. All compounds adopt the orthorhombic polar space group $A2_1am$. The magnetic Ln-ion occupies the cuboctahedral position in the middle of the perovskite double-layer, and thus controls the octahedral tilt of the perovskite block. This tilt modifies the ferroelectric displacement of the (Nb,Ti) towards the octahedral faces. This provides a mechanism to systematically modify the polarization. Mn-substitution on the (Nb,Ti) site for $\text{Ln} = \text{Bi}$ is homogeneous up to $x = 0.2$. The magnetic moments of Ln do not order down to 5 K.

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1. Introduction

Modern technology makes use of materials with extraordinary electrical and magnetic properties. The perovskite-type ceramics take a prominent position. Perovskites are built from corner sharing octahedra which form a three-dimensional structure.

They may contain most of the metals in different oxidation states and form solid solutions allowing to create materials with different properties. This allows to tune their functionality including magnetism or ferroelectricity. Related materials are layered perovskite-like compounds such as Ruddlesden–Popper [1], Aurivillius [2] or Dion–Jacobson phases [3]. Here, single or multiple perovskite blocks are separated by layers of ions or different blocks.

One of the interesting properties observed for perovskites is multiferroism. Multiferroics are materials in which two or all three of the properties ferroelectricity, ferromagnetism, and ferroelasticity occur in the same phase [4]. Due to practical reasons the meaning of the term ‘multiferroism’ has changed and now it often means simultaneous occurrence of ferroelectricity and any type of magnetic ordering (ferro-, antiferro- or ferrimagnetism). Specific device applications that have been suggested for such materials include multiple-state memory elements, electric-field-controlled

ferromagnetic resonance devices, and transducers with magnetically modulated piezoelectricity.

The first multiferroic compound, $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ was discovered in 1966 [5] but until now the number of multiferroics is very small. Theoretical analysis by Hill [6] shows that in the ABO_3 perovskites general demands for ferroelectricity and ferromagnetism are opposite: the electron configuration of the B ion should be d^0 for ferroelectrics and d^n ($n \neq 0$) for magnetic properties. Conventionally, there are two ways to solve this problem: one can either synthesize solid solutions of ferroelectric and magnetic phases or use subtle effects originating from the A ion. Recently various novel approaches have been suggested [7].

Layered perovskite-like oxides were not considered as possible multiferroics. However, most of the Aurivillius phases are ferroelectric and substitution of the non-magnetic ions by magnetic ones in these phases might lead to the formation of multiferroic compounds. The present article deals with two possible ways to prepare such compounds: the substitution of Bi^{3+} for Ln^{3+} and Ti^{4+} for Mn^{4+} in $\text{Bi}_3\text{NbTiO}_9$. The resulting compositions $\text{Bi}_2\text{LnNbTiO}_9$ and $\text{Bi}_3\text{NbTi}_{1-x}\text{Mn}_x\text{O}_9$ as well as mixed $\text{Bi}_2\text{LnNbTi}_{1-x}\text{Mn}_x\text{O}_9$ potentially show both ferroelectricity and magnetic ordering.

$\text{Bi}_2\text{LnNbTiO}_9$ phases were thoroughly investigated only for $\text{Ln} = \text{La}$ [8]. $\text{Bi}_2\text{NdNbTiO}_9$, $\text{Bi}_2\text{SmNbTiO}_9$ and $\text{Bi}_2\text{GdNbTiO}_9$ were synthesized in 2003 [9] but only their lattice parameters and ferroelectric properties were determined, while their magnetic properties and exact crystal structure, including site occupancies, remain unknown.

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Table 1Crystal data and structural parameters of Bi₂LnNbTiO₉ as refined from X-ray data.

	Ion	Position	x	y	z	U _{iso}
Bi ₂ NdNbTiO ₉ a = 5.41892(5) b = 5.42058(5) c = 24.87409(26) R _{wp} = 9.40% R _p = 6.94%	Bi ³⁺	8b	0	0.7405(4)	0.69904(4)	0.02766(19)
	Nd ³⁺	4a	0.9919(13)	0.2558(8)	0	0.00581(34)
	Nb ⁵⁺	8b	0.0104(12)	0.2521(13)	0.58697(7)	0.0030(5)
	Ti ⁴⁺	8b	0.0104(12)	0.2521(13)	0.58697(7)	0.0030(5)
	O ²⁻	4a	0.068(4)	0.709(6)	0	0.01 [*]
	O ²⁻	8b	0.056(3)	0.261(5)	0.6570(4)	0.01 [*]
	O ²⁻	8b	0.244(12)	0.499(24)	0.2581(7)	0.01 [*]
	O ²⁻	8b	0.266(8)	0.484(6)	0.5684(5)	0.01 [*]
	O ²⁻	8b	0.324(4)	0.035(4)	0.5886(5)	0.01 [*]
	Bi ₂ SmNbTiO ₉ a = 5.40011(6) b = 5.40283(7) c = 24.86290(25) R _{wp} = 9.70% R _p = 7.14%	Bi ³⁺	8b	0	0.7388(4)	0.69902(4)
Sm ³⁺		4a	0.9970(23)	0.2521(8)	0	0.0022(3)
Nb ⁵⁺		8b	0.0067(21)	0.2461(12)	0.58709(7)	0.01 [*]
Ti ⁴⁺		8b	0.0067(21)	0.2461(12)	0.58709(7)	0.01 [*]
O ²⁻		4a	0.080(4)	0.724(7)	0	0.01 [*]
O ²⁻		8b	0.042(4)	0.283(4)	0.6563(4)	0.01 [*]
O ²⁻		8b	0.248(26)	0.500(11)	0.2542(9)	0.01 [*]
O ²⁻		8b	0.2342(9)	0.512(9)	0.5738(5)	0.01 [*]
O ²⁻		8b	0.331(4)	0.068(4)	0.5944(6)	0.01 [*]
Bi ₂ EuNbTiO ₉ a = 5.40124(27) b = 5.39046(27) c = 24.8568(12) R _{wp} = 9.32% R _p = 7.02%		Bi ³⁺	8b	0	0.7369(5)	0.69897(4)
	Eu ³⁺	4a	0.9796(20)	0.2527(10)	0	0.0022(9)
	Nb ⁵⁺	8b	0.0176(17)	0.2492(14)	0.58692(9)	0.0001(10)
	Ti ⁴⁺	8b	0.0176(17)	0.2492(14)	0.58692(9)	0.0001(10)
	O ²⁻	4a	0.052(8)	0.698(7)	0	0.01 [*]
	O ²⁻	8b	0.049(5)	0.278(5)	0.6566(5)	0.01 [*]
	O ²⁻	8b	0.250(13)	0.490(10)	0.2483(12)	0.01 [*]
	O ²⁻	8b	0.192(5)	0.508(7)	0.5679(6)	0.01 [*]
	O ²⁻	8b	0.291(7)	0.074(5)	0.5881(6)	0.01 [*]
	Bi ₂ GdNbTiO ₉ a = 5.38249(9) b = 5.39664(11) c = 24.8283(5) R _{wp} = 9.44% R _p = 7.28%	Bi ³⁺	8b	0	0.7361(4)	0.69875(4)
Gd ³⁺		4a	0.9980(18)	0.2519(11)	0	0.0023(4)
Nb ⁵⁺		8b	0.0184(13)	0.2506(15)	0.58688(9)	0.0026(7)
Ti ⁴⁺		8b	0.0184(13)	0.2506(15)	0.58688(9)	0.0026(7)
O ²⁻		4a	0.089(4)	0.733(9)	0	0.01 [*]
O ²⁻		8b	0.048(4)	0.279(6)	0.6572(5)	0.01 [*]
O ²⁻		8b	0.246(18)	0.504(31)	0.2546(12)	0.01 [*]
O ²⁻		8b	0.263(6)	0.443(5)	0.5662(6)	0.01 [*]
O ²⁻		8b	0.341(4)	0.043(4)	0.5897(7)	0.01 [*]

* Thermal parameters fixed during the refinement.

2. Experimental

All materials were synthesized from stoichiometric quantities of Bi₂O₃ (99.99%), TiO₂ (99.9%), MnO₂ (99.9%), and Ln₂O₃ (99.9%). Initial oxides were ground in an agate mortar, pelletized and heated in an alumina crucible. The Bi₂LnNbTiO₉ phases were synthesized by sequential heating at 900 and 1100 °C for 3 h at each temperature. The reaction mixture for Bi₃NbTi_{1-x}Mn_xO₉ melts and reacts with crucibles at high temperature so heating was performed at 900 °C for 5 h.

X-ray diffraction was performed on a Bruker D8 diffractometer using CuKα radiation. Rietveld refinement was performed with the GSAS suite of programs [10]. Powder diffraction patterns for the refinement were obtained in the range 2θ = 10–135° with 0.02° step. Step time was 9 s. Neutron diffraction experiments were performed in the Petersburg Nuclear Physics Institute, using the WWR-M reactor, beam line 9a. The wavelength of the monochromated neutron beam was 1.85 Å, the diffraction data were obtained for 2θ = 4–143° with 0.1° step.

3. Results and discussion

The synthesis of Bi₂LnNbTiO₉ was attempted for Ln = Nd, Sm, Eu, Gd, Dy, Ho, and Er. Pure Aurivillius phases were obtained for Ln = Nd–Gd while for smaller lanthanides impurities with pyrochlore and Bi₄Ti₃O₁₂ structures were observed. Previous investigations concerning the substitution of Bi³⁺ for Ln³⁺ in triple-layered Aurivillius Bi₄Ti₃O₁₂ [11] also displayed such a limit. The exact

composition of the impurity phases is difficult to determine: the Bi₄Ti₃O₁₂-phase might contain a certain amount of Ln on the Bi positions while the pyrochlore phases in such systems are strongly non-stoichiometric.

Rietveld refinement was carried out for Bi₂LnNbTiO₉ (Ln = Nd, Sm, Eu, Gd). Evaporation of Bi₂O₃ at high temperatures results in appearing of traces of pyrochlore-type impurities, so an interval corresponding to the strongest pyrochlore peak (approximately 28–28.6°) was excluded during all calculations. All compounds were refined in the space group A2₁am. As the position of the origin along the x axis is not defined in this space group, it was fixed by assuming that the x coordinate of the Bi³⁺ ion is equal to zero. The thermal factors of the oxygen atoms were fixed at the value 0.01 and not refined. The results are presented in Table 1. The structure of Bi₂NdNbTiO₉ is shown in Fig. 1. The refinement was also carried out using the centrosymmetric space group Pmcb that was proposed by Nalini et al. [8] for Bi₂LaNbTiO₉. However, in this case the results were not satisfactory for the following reasons. The y coordinates of (Nb,Ti) have an error twice larger than in case of the space group A2₁am. The thermal parameters of the oxygen ions are unacceptably large (U_{iso} = 0.8). Finally, the final profile factors were significantly larger (up to R_p = 10.93 for Bi₂SmNbTiO₉). This indicates that the non-centrosymmetric space group A2₁am describes the structure better than the centrosymmetric space group Pmcb.

The lattice parameters of Bi₂LnNbTiO₉ for Ln = Nd–Gd, compared with Ln = La, from Ref. [8] are shown in Fig. 2. The observed decrease in lattice parameters reflects the smaller ionic sizes in the lanthanide series.

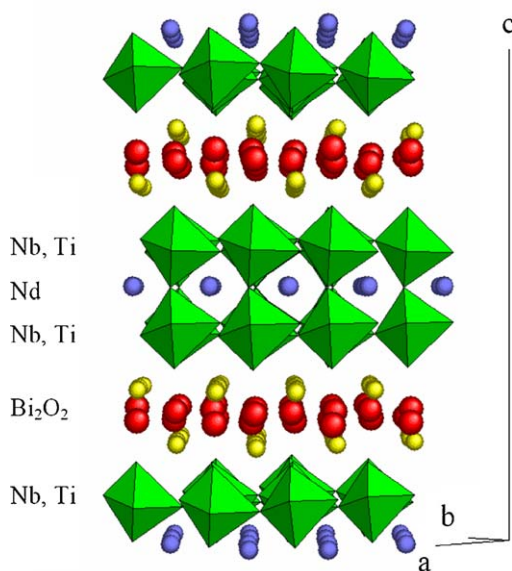


Fig. 1. Perspective drawing of $\text{Bi}_2\text{NdNbTiO}_9$ along the (1 1 0) direction.

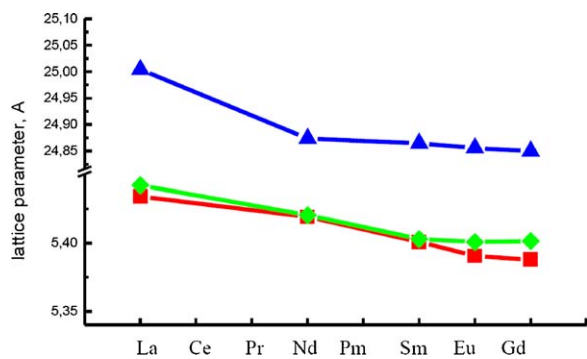


Fig. 2. Lattice parameters of $\text{Bi}_2\text{LnNbTiO}_9$. ■ (a); ◆ (b); ▲ (c).

In order to improve the calculated results with respect to the ferroelectric displacements, particularly to make all thermal parameters positive, the $\text{Bi}_2\text{NdNbTiO}_9$ structure was refined using both X-ray and neutron diffraction. It was not possible to measure neutron diffraction for other lanthanides due to the high neutron absorption. The Rietveld refinement results are given in Table 2 and Fig. 3. It is worth noting that while some oxygen coordinates are changed up to 10 standard deviations compared to the X-ray refinement results, the off-center distortion values (see below) correspond to each other much better. This means that the results for other lanthanides are probably equally reliable. The only significant difference in the results is that all atoms are shifted compared to the Bi atom along the x axis at about 0.11 \AA . This fact

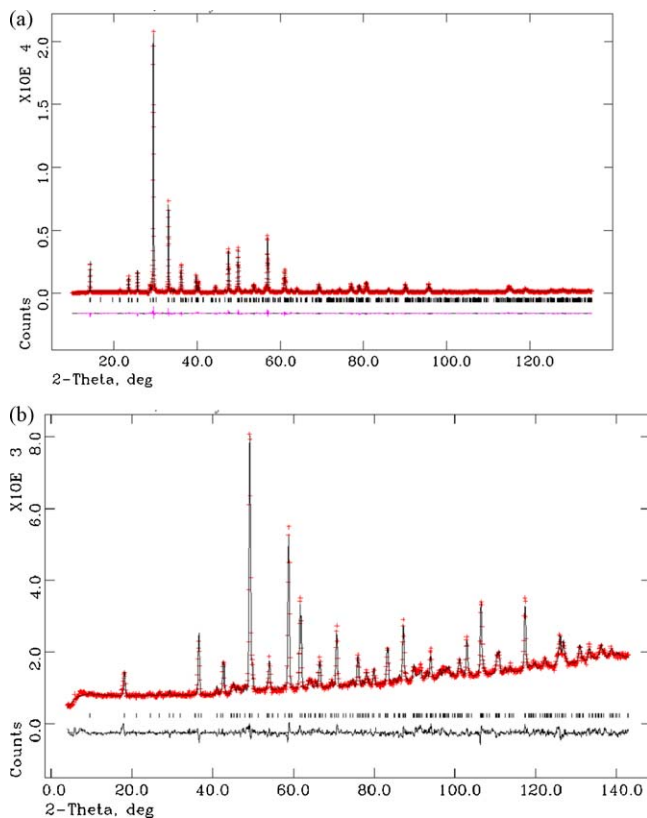


Fig. 3. Observed, refined and difference diffraction patterns of $\text{Bi}_2\text{NdNbTiO}_9$. (a) X-ray diffraction data; (b) neutron diffraction data.

can be explained by taking into account the strong covalent Bi–O interaction. As a result of such interaction, the mass center of the electron density of the Bi atom (determined by the X-ray diffraction) is shifted from the position of the Bi nucleus (determined by the neutron diffraction).

The possibility of the partial Bi–Nd disorder has been checked during the refinement. It was found that the cations are completely ordered in the $\text{Bi}_2\text{NdNbTiO}_9$ phase.

It is generally known that the ferroelectric properties of the Aurivillius-type structures are mainly determined by off-center distortion of the Ti/Nb ions inside the octahedra towards one of the faces [12]. While the component of the polarization vector perpendicular to the ab plane vanishes due to the mirror symmetry (inset Fig. 4), the in-plane components add up giving the total dipole moment. The magnitude of the off-center distortion is approximately the same for all double-layered Aurivillius phases but the ab component depends on the tilting angle of the octahedra. Another result of the tilting is the difference between the a and b parameters, and therefore this difference can be used to predict the magnitude of ferroelectric properties. In case of $\text{Bi}_2\text{LnNbTiO}_9$ one can see that the ferroelectric signature from the

Table 2

The structure of $\text{Bi}_2\text{NdNbTiO}_9$ refined using X-ray and neutron diffraction simultaneously.

	Ion	Position	x	y	z	U_{iso}
$a = 5.41867(22)$	Bi^{3+}	8b	0	0.7401(5)	0.69905(4)	0.0270(5)
$b = 5.42002(21)$	Nd^{3+}	4a	0.9884(26)	0.2526(10)	0	0.0064(8)
$c = 24.8736(5)$	Nb^{5+}	8b	0.0132(22)	0.2510(16)	0.58707(8)	0.0017(10)
$R_{\text{wp, X-ray}} = 9.53\%$	Ti^{4+}	8b	0.0132(22)	0.2510(16)	0.58707(8)	0.0017(10)
$R_{\text{p, X-ray}} = 7.06\%$	O^{2-}	4a	0.018(6)	0.697(4)	0	0.046(5)
$R_{\text{wp, neut}} = 4.57\%$	O^{2-}	8b	0.038(4)	0.2911(24)	0.65760(24)	0.0245(29)
$R_{\text{p, neut}} = 3.49\%$	O^{2-}	8b	0.243(5)	0.4932(22)	0.2504(4)	0.0093(14)
$R_{\text{wp, sum}} = 7.07\%$	O^{2-}	8b	0.246(5)	0.5194(26)	0.56880(28)	0.0192(23)
$R_{\text{p, sum}} = 4.97\%$	O^{2-}	8b	0.306(5)	0.0499(34)	0.5861(4)	0.055(4)

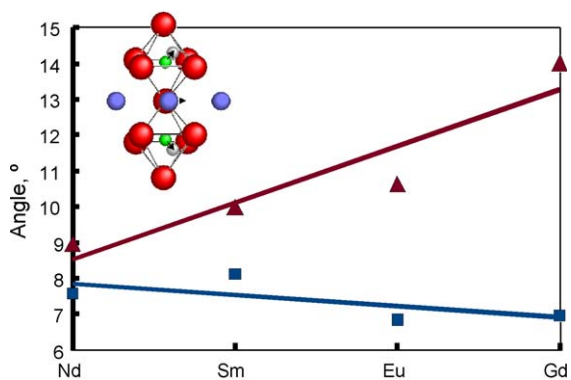


Fig. 4. Tilting angle in Bi₂LnNbTiO₉. ■, axial tilting; ▲, equatorial tilting.

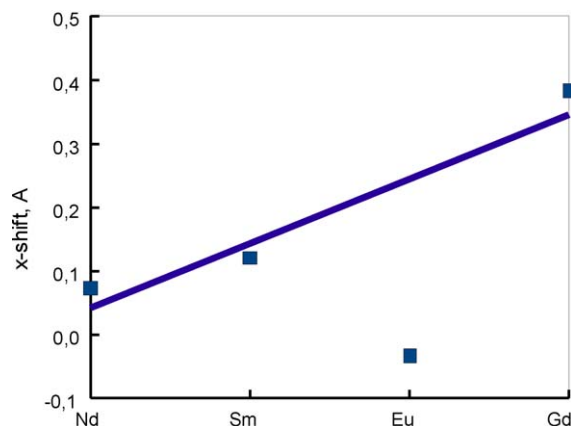


Fig. 5. Cationic shift along x axis in Bi₂LnNbTiO₉.

lattice parameters, $(b-a)$ could be observed for Bi₂EuNbTiO₉ and Bi₂GdNbTiO₉ rather than for Bi₂NdNbTiO₉ and Bi₂SmNbTiO₉ and thus the Curie temperature should increase with increasing atomic number of the lanthanide (Fig. 2).

There are three types of cation positions in the double-layered Aurivillius phases A₂A'B₂O₉. The B-cations possess octahedral coordination, the A'-cations are twelve-fold coordinated (cuboctahedra A'O₁₂) and the A-cations are usually regarded as eight-fold coordinated (tetragonal antiprism AO₈). All coordination polyhedra are distorted in the low-temperature structure. The most important changes are discussed in detail below.

The BO₆ octahedra (B = Ti, Nb) are remarkably different from the ones in the ideal tetragonal structure (Fig. 4, inset). Three types of the structure changes can be distinguished: the octahedron rotation and tilting, the off-center shift of the B ion and the distortion of the oxygen octahedron itself. The B cations move off center towards a face of the octahedra mostly along the xz direction. It is clear from the symmetry reasons that the x -component of this shift determines the ferroelectric displacement of the Aurivillius phases. Rotation of the BO₆ octahedra around z axis and tilting in the yz plane give an opposite contribution to the value of the x -component of the B ion shift and compensate each other with respect to a ferroelectric displacement.

The most intriguing is the distortion of the octahedra. The tilting angle can be determined by two ways. The first one is the angle between the z axis and the line connecting two axial oxygen ions. The second one is the angle between the xy plane and the equatorial plane of the octahedron. (In fact, the four equatorial ions are not exactly in the same plane, but different possible ways of the determination of the equatorial tilting do not affect the trend and

almost do not affect values.) While the axial tilting remains almost constant when the lanthanide changes, the equatorial one increases significantly when the ionic radius of the lanthanide is decreased (Fig. 4). This means that axial tilting is determined mostly by the covalent Bi–O interaction [12] that remains nearly constant, while the equatorial one depends on the geometrical factors.

The octahedra distortion acts in such way that the B ion has more freedom to shift along the x axis (see Table 3). This means that the compound should become more polar when the Ln radius is decreased. This does not hold for Bi₂EuNbTiO₉ where the direction of the shift is opposite, probably due to more subtle effects caused by the low spin state of Eu³⁺ ion (Fig. 5).

The LnO₁₂ cuboctahedra are also distorted due to the rotation of the BO₆ octahedra. The lanthanide ion is moved off center almost directly along x axis (Table 3). Due to the symmetry reasons the lanthanide ion remains in the plane formed by the "O1" ions. Like for B ions, the Ln ions shift increases along the row with the exception of Bi₂EuNbTiO₉.

It is interesting to note that the coordination polyhedra of the Bi³⁺ ions change as a result of the structure distortion. Selected Bi–O interatomic distances are shown in Table 4, including the distances between Bi³⁺ ion and two axial oxygen ions in BO₆ octahedra and the distance between Bi³⁺ ion and equatorial oxygen ion in BO₆ octahedra (note that all Bi–O distances are different). One can see that the coordination of Bi³⁺ changes from eight-fold in the idealized I4/mmm structure to nine-fold in the distorted A2₁am structure. The coordination polyhedron is a capped tetragonal antiprism (Fig. 6) that is typical for another class of layered structures, namely the Ruddlesden–Popper phases.

Table 3

Selected distortion parameters for Bi₂LnNbTiO₉.

	Bi ₂ NdNbTiO ₉	Bi ₂ SmNbTiO ₉	Bi ₂ EuNbTiO ₉	Bi ₂ GdNbTiO ₉
Equatorial tilting angle	8.96°	9.98°	10.65°	14.02°
Axial tilting angle	7.58°	8.12°	6.84°	6.95°
B ion shift along x axis (Å)	0.0730	0.1203	(–)0.0336	0.3838
Ln ion shift along x axis (Å)	0.0990	0.2344	0.1748	0.3106

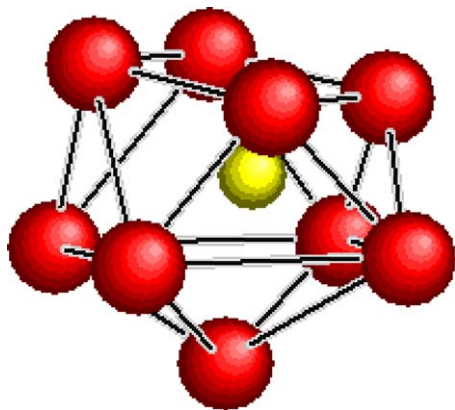
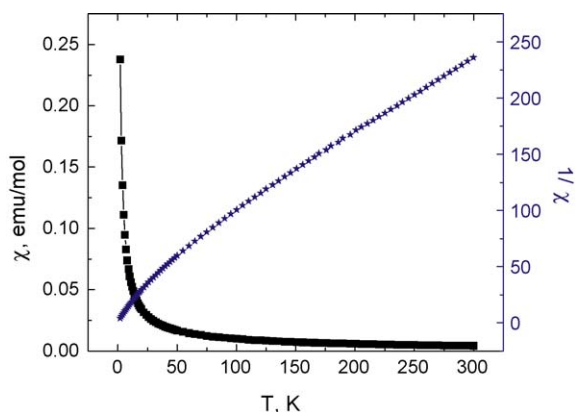
Table 4

Interatomic distances (Å) in the BiO₉ polyhedra in Bi₂LnNbTiO₉.

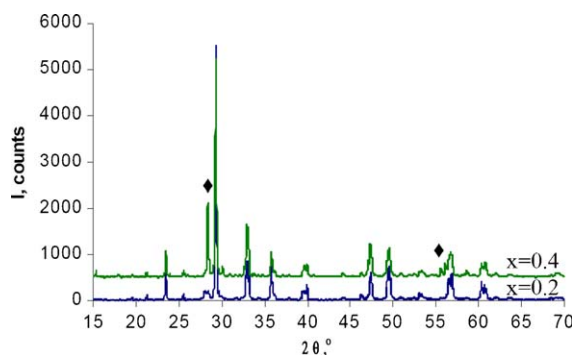
	Bi ₂ NdNbTiO ₉	Bi ₂ SmNbTiO ₉	Bi ₂ EuNbTiO ₉	Bi ₂ GdNbTiO ₉
Bi–O2 (1)	3.087	3.027	3.099	3.048
Bi–O2 (2)	3.222	3.194	3.177	3.104
Bi–O5	3.113	2.905	3.098	2.823

Table 5Crystal data and structural parameters of $\text{Bi}_3\text{NbTi}_{0.8}\text{Mn}_{0.2}\text{O}_9$.

	Atom	Site	x	y	z	U_{iso}
$\text{Bi}_3\text{NbTi}_{0.8}\text{Mn}_{0.2}\text{O}_9$	Bi^{3+}	8b	0	0.7311(4)	0.69898(4)	0.0228(6)
$A2_1am$ (No 36)	Bi^{3+}	4a	0.9924(16)	0.2576(7)	0	0.0259(7)
$a = 5.44605(22)$	Nb^{5+}	8b	0.0446(11)	0.2568(13)	0.58829(11)	0.0039(12)
$b = 5.40547(21)$	Ti^{4+}	8b	0.0446(11)	0.2568(13)	0.58829(11)	0.0039(12)
$c = 25.0999(10)$	Mn^{4+}	8b	0.0446(11)	0.2568(13)	0.58829(11)	0.0039(12)
$R_{\text{wp}} = 9.61\%$	O^{2-}	4a	0.070(5)	0.696(6)	0	0.01
$R_p = 6.51\%$	O^{2-}	8b	0.069(4)	0.290(4)	0.6556(6)	0.01
	O^{2-}	8b	0.262(9)	0.497(16)	0.2569(8)	0.01
	O^{2-}	8b	0.271(8)	0.530(6)	0.5715(6)	0.01
	O^{2-}	8b	0.372(4)	0.039(4)	0.5887(7)	0.01

**Fig. 6.** BiO_8 antiprism with an extra oxygen ion.**Fig. 7.** Temperature dependence of the magnetic susceptibility of $\text{Bi}_2\text{NdNbTiO}_9$.

The temperature dependence of the magnetic susceptibility of all materials follows the Curie law for independent moments (Fig. 7). The Curie constants correspond with the magnetic moments expected for the rare earth ions. The magnetic ions exhibit small

**Fig. 8.** Powder diffraction patterns of $\text{Bi}_3\text{NbTi}_{1-x}\text{Mn}_x\text{O}_9$. ◆, pyrochlore-type phase.

interactions because the (super)exchange interactions are small. This means that the coupling between magnetism and ferroelectricity is expected to be restricted to low temperatures.

4. $\text{Bi}_3\text{NbTi}_{1-x}\text{Mn}_x\text{O}_9$

In order to determine the possible degree of substitution of Ti by Mn in $\text{Bi}_3\text{NbTiO}_9$ the series of solid solutions $\text{Bi}_3\text{NbTi}_{1-x}\text{Mn}_x\text{O}_9$ was synthesized ($x = 0.1, 0.2, 0.3, 0.4, 0.6, 0.8,$ and 1). The pure Aurivillius phase was obtained for $x = 0.1$ and $x = 0.2$ while for $x \geq 0.3$ a pyrochlore phase appears (Fig. 8). In case of $\text{Bi}_2\text{LnNbTi}_{1-x}\text{Mn}_x\text{O}_9$ the highest possible degree of substitution remains the same but both pyrochlore and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ impurities appear.

The results of Rietveld refinement of $\text{Bi}_3\text{NbTi}_{0.8}\text{Mn}_{0.2}\text{O}_9$ are shown in Table 5. The structure does not change a lot compared to the structure of $\text{Bi}_3\text{NbTiO}_9$. The ferroelectric properties are expected to be approximately the same.

5. Conclusions

The double-layer Aurivillius phase $\text{Bi}_2\text{LnNbTiO}_9$ where Ln = Nd–Gd, Bi adopt the polar space group $A2_1am$ where the Ln ion occupies the position in the middle of the perovskite double layer. Within this series of compounds the net polarization can be changed, controlled by the octahedral distortion of the perovskite block, induced by the small ionic size of the Ln-ion. This distortion is driven both by chemical and geometrical factors: the former is more important for the axial oxygen ions, and the latter for the equatorial ions. The Ti ions can be only partially (≤ 0.2) be replaced by Mn^{4+} .

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References

- [1] S.N. Ruddlesden, P. Popper, Acta Crystallogr. 10 (1957) 538–539; S.N. Ruddlesden, P. Popper, Acta Crystallogr. 11 (1958) 54–55.
- [2] B. Aurivillius, Arki Kemi 1 (1949) 463–471; B. Aurivillius, Arki Kemi 1 (1949) 499–512; B. Aurivillius, Arki Kemi 2 (1950) 519–528.
- [3] M. Dion, M. Ganne, M. Tournoux, Mater. Res. Bull. 16 (1981) 1429–1435.
- [4] H. Schmid, Ferroelectrics 162 (1994) 317.
- [5] E. Ascher, H. Rieder, H. Schmid, H. Stössel, J. Appl. Phys. 37 (1966) 1404.
- [6] N.A. Hill, J. Phys. Chem. B 104 (2000) 6694–6709.
- [7] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, Y. Tokura, Nature 426 (2003) 55–58; B.B. Van Aken, T.T.M. Palstra, A. Filippetti, N.A. Spaldin, Nat. Mater. 3 (2004) 164–170; D.V. Efremov, J. van den Brink, D.I. Khomskii, Nat. Mater. 3 (2004) 853–856.
- [8] G. Nalini, G.N. Subbanna, T.N. Guru Row, Mater. Chem. Phys. 82 (2003) 663–671.
- [9] Y. Sugaya, K. Shoji, K. Sakata, Jpn. J. Appl. Phys. 42 (2003) 6086–6089.
- [10] A.C. Larson, R.B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR. 86-748, 2000.
- [11] R.A. Armstrong, R.E. Newnham, Mater. Res. Bull. 7 (1972) 1025–1034.
- [12] R.E. Newnham, R.W. Wolfe, J.F. Dorrian, Mater. Res. Bull. 6 (1971) 1029–1040.