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Structure-property relationships in the lanthanide-substituted $\text{PbBi}_2\text{Nb}_2\text{O}_9$ Aurivillius phase synthesized by the molten salt method

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ABSTRACT

Samples of $\text{PbBi}_2\text{Nb}_2\text{O}_9$, $\text{PbBi}_{1.5}\text{La}_{0.5}\text{Nb}_2\text{O}_9$, and $\text{PbBi}_{1.5}\text{Nd}_{0.5}\text{Nb}_2\text{O}_9$ have been prepared by the molten salt method. The structure, morphology, and electrical properties were investigated. All samples are single-phase and crystallize in an orthorhombic structure with $A2_1am$ symmetry. Neutron diffraction data indicate that the Ln^{3+} cations prefer to occupy the perovskite A-site, whereas Pb/Bi occupy the perovskite A-site and the Bi_2O_2 layer. Changes in unit cell volume are observed on substitution and are attributed to the ionic radii of the Ln^{3+} cations and also correlated to changes in the B-O bond distances in the BO_6 octahedra, which are also observed in IR spectra. SEM images reveal anisotropic plate-like grains, which increase in size with the presence of Ln^{3+} ions. The ferroelectric transition temperature (T_c) decreases with decreasing degree of BO_6 distortion as the influence of the $6s^2$ lone pair of Bi^{3+} is diminished. Relaxor ferroelectric behavior is observed with Ln^{3+} substitution, driven by the disorder of the A-site cations. The room temperature ferroelectric polarization increases with Ln^{3+} substitution, ascribed to the decreased dielectric loss.

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1. Introduction

The ferroelectric Aurivillius phases have received continued attention over the past few decades because of potential uses in non-volatile ferroelectric random access memory, energy storage, piezoelectric device applications, and high-temperature ferroelectric devices [1–4]. The crystal structure of Aurivillius phases can be described as an m -perovskite layer $[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}$ sandwiched between bismuth oxide $[\text{Bi}_2\text{O}_2]^{2+}$ layers along the c -axis. The integer m represents the number of BO_6 octahedra in the perovskite slab, which can accommodate various A-site and B-site cations, where A is a mono-, di-, or trivalent cation (or a combination thereof suited to dodecahedral coordination) and B is a transition metal cation suited to octahedral coordination [5].

Lead bismuth niobate, $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (PBNO), is a typical double-layer ($m = 2$) Aurivillius phase exhibiting a high dielectric constant together with a high ferroelectric Curie temperature (T_c) of 830 K [6]. The ferroelectric properties are due to the $6s^2$ lone pair electrons

associated with Pb^{2+} and Bi^{3+} , which induce a highly distorted structure. However, the spontaneous polarization is relatively low with a high coercive field, hindering possible application in the field of piezoelectric devices and energy storage [3,7].

Recently, efforts have been made to enhance its electrical properties by chemical modification of the A- or B-site cations, or both simultaneously, which can manipulate the structure as well as the properties. Due to the large range of A-site ionic radii that can be incorporated in the structure, the substitution of A-site cations is a feasible way to obtain more distorted BO_6 octahedra and hence enhance the ferroelectricity [8]. It has also been demonstrated that the substitution of Ln^{3+} for Bi^{3+} suppresses the oxygen vacancy concentration as well as leakage currents, consequently improving the ferroelectric properties [9,10]. Substitution also results in cation disorder, which can give rise to relaxor behavior and greater potential for use in various electronic devices [11].

Most studies have reported on the substitution of Ln^{3+} for Bi^{3+} in double-layer Aurivillius compound $\text{SrBi}_2\text{Nb}_2\text{O}_9$, which is likely to lower T_c [12–14]. However, the detailed structural changes that occur on substitution, including the cation distribution, which is strongly correlated to the reduced T_c , has thus far been less investigated. Since ferroelectricity can be realized by structural

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features such as atomic displacements and tilting of the BO_6 octahedra [15], it is important to determine precisely the positions of each atom, especially the light oxygen atoms.

In this work, we have synthesized the double-layer Aurivillius compound $PbBi_2Nb_2O_9$ and partially substituted lanthanide ions (Ln : La^{3+} and Nd^{3+}) using the molten-salt method, which has not previously been reported. The La^{3+} and Nd^{3+} ions were chosen to represent a larger and smaller cation compared to Bi^{3+} since the different size of the substituting ions is expected to lead to different types of structural distortion. We therefore synthesized compounds of composition $PbBi_2Nb_2O_9$, $PbBi_{1.5}La_{0.5}Nb_2O_9$, and $PbBi_{1.5}Nd_{0.5}Nb_2O_9$, abbreviated as PBNO, PBNO-La and PBNO-Nd, respectively. We perform neutron diffraction on these compounds and focus on the detailed structural changes, including compositional disorder, in order to further understand the correlation of the structure with the dielectric and ferroelectric properties.

2. Experimental procedures

The samples of PBNO, PBNO-La and PBNO-Nd were prepared by the molten salt method using K_2SO_4/Na_2SO_4 salt fluxes. High purity oxide precursors of PbO , Bi_2O_3 , La_2O_3 , Nd_2O_3 , and Nb_2O_5 (Aldrich, $\geq 99.99\%$) were weighed in stoichiometric proportions and ground in an agate mortar in ethanol. The oxide precursors then were ground together with a 1:1 molar ratio of K_2SO_4/Na_2SO_4 (Aldrich, $\geq 99\%$) salts with a molar ratio of 1:7 salt to oxide and placed in alumina crucibles. The mixtures were heated at a rate of 5 K/min to 1023 K, 1123 K, and 1223 K and held for 5 h at each temperature, with intermediate grinding steps. The final products were washed thoroughly with hot distilled water to remove the sulfate fluxes and dried at 383 K for 5 h. The crystalline phases were identified using X-ray powder diffraction (XRD; Shimadzu XRD 7000 operating with $Cu\ K\alpha$ radiation) at room temperature. Neutron powder diffraction (NPD) data were collected on the High-Resolution Powder Diffractometer (DN3) at the Center for Science and Technology of Advanced Materials, BATAN, Indonesia. The wavelength of the incident neutron beam was 1.8195 Å and data were collected for 11 h at room temperature. The unit cell parameters, site occupations, and atomic positions were refined by the Rietveld method from the NPD data using the RIETICA program [16]. FTIR spectra were obtained with a Perkin Elmer 1600 FTIR spectrophotometer at room

temperature. Scanning electron microscopy (SEM; FEI INSPECT S50) was used to investigate the microstructures of the samples. For electrical measurements, the final product was mixed with 5 wt% PVA as a binder and pressed to form a pellet. The pellet was slowly heated at 773 K for 3 h to burn out the binder and then continuously sintered at 1323 K for 5 h. The densities of the pellets were measured using the Archimedes method and the theoretical densities were obtained from the NPD analysis. Silver electrode paste (Aldrich, 99%) was coated on both surfaces of the sintered pellet and then heated at 383 K for 2 h. The temperature dependence of the dielectric constant and dielectric loss was measured over the frequency range 50 kHz to 1 MHz at temperatures between 300 K and 850 K using an LCR meter (Agilent E4980A). Room-temperature polarization loops were measured using a ferroelectric test system (TF Analyzer, AixACCT) at 1 Hz as a function of the applied electric field.

3. Results and discussion

Fig. 1 shows the XRD patterns of the PBNO, PBNO-La, and PBNO-Nd samples at room temperature. The XRD patterns are indexed according to a $PbBi_2Nb_2O_9$ standard diffraction pattern with the orthorhombic $A2_1am$ space group (ICSD-95920). All three XRD patterns show the typical peaks of the double-layered Aurivillius phase without any additional peaks, confirming the formation of single-phase products. The most intense diffraction peak (1 1 5) for all three samples is typical for double-layer Aurivillius phases ($m = 2$), which is in agreement with the fact that the most intense reflection is (1 1 $2m+1$) [17,18]. The XRD results thus demonstrate that the substitution of 25% molar ratio La^{3+} or Nd^{3+} for Bi^{3+} in $PbBi_2Nb_2O_9$ was successful.

It is observed in the enlarged XRD patterns in Fig. 1 that the 200/020 doublet of the PBNO sample at $2\theta = 32\text{--}33^\circ$ is typical for the $A2_1am$ orthorhombic crystal structure [19,20]. With Ln^{3+} substitution, these peaks almost merge to a single peak in both cases, which indicates that the structure becomes close to tetragonal [18,20]. This change in the degree of orthorhombicity can also be expected to affect the ferroelectric properties, as discussed further below. Additionally, the main XRD peaks slightly shift toward lower 2θ for PBNO-La and toward higher 2θ for PBNO-Nd, corresponding to changes in the lattice parameters [21].

Fig. 1. Room temperature X-ray diffraction patterns of pristine $PbBi_2Nb_2O_9$ and La, Nd-substituted samples.

Rietveld refinement of the NPD data was performed to investigate the structural parameters in detail. The initial refinements considered the structural model where $\text{PbBi}_2\text{Nb}_2\text{O}_9$ adopts the $A2_1am$ space group (ICSD-88479). All atoms occupy general Wyckoff positions 8b except for Bi(1) and O(1) in the perovskite layer which occupy 4a positions. Further to be noted, a result of the substitution of Ln^{3+} for Bi^{3+} is that there is insufficient Bi^{3+} to form the Bi_2O_2 layer, and consequently the other A-site cations (Pb^{2+} , La^{3+} or Nd^{3+}) should partially occupy the Bi-site. According to earlier studies, the occupation of the Bi_2O_2 layer by Ln^{3+} cations is not favored [19,22,23]. However, cations with a stereochemically active $6s^2$ lone pair similar to Bi^{3+} can possibly occupy this site [24]. Therefore, we assumed that Pb^{2+} can be incorporated into the Bi-site of the Bi_2O_2 layer, and the occupation by Ln^{3+} was assumed to be zero.

The refinement was initially performed with all Bi^{3+} cations occupying the A(2)-site of the Bi_2O_2 layer for PBNO. For the PBNO-La and PBNO-Nd samples, we performed refinements where all Ln^{3+} cations were confined to the A(1)-site of the perovskite layer with a 50% occupancy. The partial occupancy of the A(2)-site of the Bi_2O_2 layer by the Ln^{3+} cations was also considered but led to significantly worse fits. The positions of Nb and O atoms in the perovskite layer were refined while constraining the occupation to 1. Furthermore, the disorder of Pb^{2+} and Bi^{3+} cations in both layers should be considered in the refinement. The Pb/Bi disorder on both the A(1)-site of the perovskite layer and the A(2)-site of the Bi_2O_2 layer was refined by varying the occupancies manually, whereas the atomic positions were refined automatically. The final Rietveld fits of the NPD data are shown in Fig. 2(a). The detailed atomic positions and occupancies of the atoms are listed in Table 1.

The refinement results indicate that the Ln^{3+} ions only occupy the A(1)-site in the perovskite layer, together with Pb^{2+} and Bi^{3+} . The A(2)-site in the Bi_2O_2 layers is only occupied by Pb^{2+} and Bi^{3+} . This type of disorder is expected due to the preference of Ln^{3+} to occupy the A(1)-site of the perovskite layer rather than the A(2)-site of the Bi_2O_2 layer since the Ln^{3+} ions lack the necessary lone pair electrons

Table 1

Atomic coordinates and occupancies of all three samples obtained from Rietveld refinements using NPD data at room temperature.

Atom	Site	x	y	z	Occ
PBNO					
Pb(1)	4a	0	0.242(5)	0	0.880
Bi(1)	4a	0	0.242(5)	0	0.120
Bi(2)	8b	0.475(8)	0.744(4)	0.2013(4)	0.940
Pb(2)	8b	0.475(8)	0.744(4)	0.2013(4)	0.060
Nb(1)	8b	0.476(8)	0.764(5)	0.4117(5)	1
O(1)	4a	0.449(2)	0.191(7)	0	1
O(2)	8b	0.432(9)	0.800(5)	0.3405(7)	1
O(3)	8b	0.695(9)	0.0059(7)	0.25	1
O(4)	8b	0.661(9)	0.955(8)	0.0793(1)	1
O(5)	8b	0.728(10)	0.982(8)	0.5756(1)	1
PBNO-La					
Pb(1)	4a	0	0.246(9)	0	0.300
Bi(1)	4a	0	0.246(9)	0	0.200
La(1)	4a	0	0.246(9)	0	0.500
Bi(2)	8b	0.5057(12)	0.744(5)	0.1994(6)	0.700
Pb(2)	8b	0.5057(12)	0.744(5)	0.1994(6)	0.300
Nb(1)	8b	0.4643(8)	0.725(8)	0.4138(7)	1
O(1)	4a	0.444(7)	0.1950(13)	0	1
O(2)	8b	0.442(2)	0.7515(14)	0.3405(10)	1
O(3)	8b	0.7117(11)	0.0081(11)	0.25	1
O(4)	8b	0.6983(15)	0.958(9)	0.0795(17)	1
O(5)	8b	0.738(3)	0.993(3)	0.5727(17)	1
PBNO-Nd					
Pb(1)	4a	0	0.2330(16)	0	0.350
Bi(1)	4a	0	0.2330(16)	0	0.150
Nd(1)	4a	0	0.2330(16)	0	0.500
Bi(2)	8b	0.4953(16)	0.737(5)	0.2002(5)	0.675
Pb(2)	8b	0.4953(16)	0.737(5)	0.2002(5)	0.325
Nb(1)	8b	0.462(3)	0.730(6)	0.4147(6)	1
O(1)	4a	0.444(2)	0.196(16)	0	1
O(2)	8b	0.473(4)	0.766(8)	0.3444(9)	1
O(3)	8b	0.738(14)	0.0053(3)	0.25	1
O(4)	8b	0.6912(2)	0.9771(11)	0.0769(11)	1
O(5)	8b	0.723(2)	0.9733(17)	0.5644(11)	1

Fig. 2. (a) Observed, calculated and difference NPD profiles at room temperature. (b) Crystal structure models viewed along the [110] direction showing the occupation of each cation in the Bi_2O_2 and perovskite layers.

Table 2

Refined unit cell parameters, volume, orthorhombicity parameter and fit parameters of samples determined from NPD data at room temperature using the orthorhombic space group $A2_1am$.

	PBNO	PBNO-La	PBNO-Nd
Space group	$A2_1am$	$A2_1am$	$A2_1am$
Crystal class	Orthorhombic	Orthorhombic	Orthorhombic
a (Å)	5.4923(7)	5.4977(1)	5.4794(3)
b (Å)	5.4764(2)	5.4955(9)	5.4759(5)
c (Å)	25.4321(1)	25.4489(2)	25.3561(6)
V (Å ³)	764.974(8)	768.878(7)	760.801(1)
$(a-b)/(a+b)$	0.00145	0.00019	0.00032
Z	4	4	4
R_p	13.34	14.89	14.13
χ^2	1.667	1.517	1.475

[15,22]. Similar Pb/Bi disorder in $\text{PbBi}_2\text{Nb}_2\text{O}_9$ was previously reported by Ismunandar et al. [24]. The occupation of Bi^{3+} on the $A(1)$ -site of the perovskite layer is similar for all three samples: 12% for PBNO, 10% for PBNO-La, and 15% for PBNO-Nd. The slight increase of Bi^{3+} occupation in the perovskite layer for PBNO-Nd might be a result of the smaller Nd^{3+} cation decreasing the average size of the BO_6 octahedra, leading to a greater preference for the Bi^{3+} ions, which are slightly smaller than Pb^{2+} , to occupy this site, whereas in PBNO-La the larger La^{3+} cation tends to induce an increased occupation of larger Pb^{2+} ions in the perovskite layer. The crystal structures reflecting the occupation of each cation in the Bi_2O_2 and perovskite layers are shown in Fig. 2(b). According to the determined occupations listed in Table 1, the chemical formulae of the three compounds are perhaps more usefully written as $(\text{Bi}_{1.88}\text{Pb}_{0.12})\text{O}_2$ ($\text{Pb}_{0.88}\text{Bi}_{0.12})\text{Nb}_2\text{O}_7$ for PBNO, $(\text{Bi}_{1.4}\text{Pb}_{0.6})\text{O}_2$ ($\text{La}_{0.5}\text{Pb}_{0.4}\text{Bi}_{0.1})\text{Nb}_2\text{O}_7$ for PBNO-La and $(\text{Bi}_{1.35}\text{Pb}_{0.65})\text{O}_2$ ($\text{Nd}_{0.5}\text{Pb}_{0.35}\text{Bi}_{0.15})\text{Nb}_2\text{O}_7$ for PBNO-Nd.

The refined unit cell parameters are given in Table 2. The unit cell volume increases for PBNO-La and decreases for PBNO-Nd. This can be attributed to the larger ionic radius of La^{3+} (1.36 Å) and smaller ionic radius of Nd^{3+} (1.27 Å) compared to Bi^{3+} (1.31 Å) for 12-fold coordination [25,26]. As compared to pristine PBNO, the substitution of La^{3+} results in a significant increase of the b and c lattice parameters, whereas the substitution of Nd^{3+} significantly decreases the a and c lattice parameters. These changes imply a decrease in the degree of orthorhombic distortion in the ab -plane with Ln^{3+} substitution, by which the a and b lattice parameters approach each other [27,28]. The decreased degree of distortion can also be expressed in terms of the orthorhombicity ratio $((a-b)/(a+b))$ in Table 2.

We now focus on the atomic displacements in the BO_6 octahedra of the perovskite layer since these are strongly correlated to the structural distortion and break inversion symmetry, giving rise to ferroelectricity. Selected bond angles and bond distances associated with the BO_6 octahedra are summarized in Table 3. The Nb(1) cation is displaced from the center of the octahedron along the a -axis as well as along both the b - and c -axes, resulting in different Nb-O bond distances. In addition, the shortest Nb-O bond and the average Nb-O distance increase for PBNO-La and decrease for PBNO-Nd compared to PBNO. This is consistent with our conclusion that the Ln^{3+} occupies the $A(1)$ -site in the perovskite layer, thus the changes in bond distances are related to the ionic radii of the Ln^{3+} ions.

The overall structural distortion also involves the tilting of the BO_6 octahedra, which is evidenced by the smaller than 180° bond angles listed in Table 3 and also visually depicted in Fig. 3. Octahedral tilting in Aurivillius phases with space group $A2_1am$ takes place around all three axes and was discussed by Aleksandrov and Bartolomé [29]; it involves a superposition of the tilt systems $(\varphi\varphi 0)$ ($\varphi\varphi 0$) and $(00\psi_z)$ ($00\psi_z$), where φ refers to out-of-phase tilting along the a - and b -axes of the parent $I4/mmm$ tetragonal structure, and ψ_z to in-phase tilting along the c -axis. It is therefore difficult to define an overall degree of tilting between our three samples, and we approximate the tilting by two

Table 3

Selected bond distances and bond angles associated with the BO_6 octahedra.

Bond	Bond distance (Å)		
	PBNO	PBNO-La	PBNO-Nd
Nb(1)–O(1)	2.2059(1)	2.2148(2)	2.1863(1)
Nb(1)–O(2)	1.8247(1)	1.8571(7)	1.7972(1)
Nb(1)–O(4 ₁)	2.1153(3)	1.9236(3)	2.0064(1)
Nb(1)–O(4 ₂)	1.9839(1)	1.8974(1)	1.7791(1)
Nb(1)–O(5 ₁)	1.8569(2)	2.1223(1)	1.9349(3)
Nb(1)–O(5 ₂)	1.9763(2)	2.0415(2)	2.1732(2)
Nb(1)–O average	1.993(8)	2.009(4)	1.979(4)
Bond	Bond Angle (°)		
	PBNO	PBNO-La	PBNO-Nd
O(2)–Nb(1)–O(1)	168.17(1)	176.79(1)	169.7(3)
O(4 ₁)–Nb(1)–O(5 ₁)	159.23(2)	163.16(3)	159.35(3)
O(4 ₂)–Nb(1)–O(5 ₂)	149.27(1)	158.42(3)	158.70(5)
Nb(1)–O(1)–Nb(1)	158.64(3)	171.67(2)	164.69(2)
Nb(1)–O(4)–Nb(1)	152.64(3)	157.02(5)	150.68(1)
Nb(1)–O(5)–Nb(1)	159.89(4)	161.52(1)	169.72(2)
BO_6 tilting along c -axis	10.68	4.17	7.66
BO_6 rotation around c -axis	11.87	10.35	9.9

parameters: tilting around the a -axis as quantified by the Nb–O(1)–Nb bond angle [30,31] (Fig. 3a), and tilting in the ab -plane as defined by the relative rotation angle between neighboring octahedra around the c -axis [18] (Fig. 3b). The BO_6 octahedra are considerably tilted around the a -axis by 10.68° in PBNO, as evidenced by the Nb(1)–O(1)–Nb(1) bond angle of 158.64(3)° in Fig. 3(a). The Ln^{3+} substitution causes a substantial decrease of this tilt angle; for PBNO-La and PBNO-Nd it is 4.17° [Nb(1)–O(1)–Nb(1) bond angle: 171.67(2)°] and 7.66° [Nb(1)–O(1)–Nb(1) bond angle: 164.68(2)°], respectively. The decreased degree of tilting implies reduced structural distortion, leading to closer values of the a and b lattice parameters and a decreased orthorhombicity ratio [28]. Additionally, there is also a slight reduction of the rotation angle of BO_6 octahedra around the c -axis with Ln substitution as observed in Fig. 3(b).

In the double-layer Aurivillius phases with $A2_1am$ symmetry, the atomic displacements along the a -axis are uncompensated and give rise to an electrical dipole moment. The atomic displacements along the b - and c -axes cancel out due to the presence of glide and mirror planes [18]. The atomic displacements along the a -axis with respect to the corresponding positions in centrosymmetric tetragonal symmetry ($I4/mmm$) can be calculated from the refined atomic coordinates (Table 1), from which the total polarization (P_s) can be determined using Shimakawa's formulation [32]:

$$P_s = \sum_i \frac{m_i \times \Delta x_i \times Q_i e}{V}$$

Here m_i is the site multiplicity, Δx_i is the atomic displacement of atom i along the a -axis, $Q_i e$ is the ionic charge for the i th constituent ion, and V is the unit cell volume. The total P_s is calculated from the contributions of both the perovskite layers and Bi_2O_2 layers, by setting the position of the $A(1)$ -site atom at the origin. The contribution of each ion to the total P_s is shown in Fig. 4. It is apparent that the calculated P_s decreases with Ln substitution; the values are 27.3, 15.9, and 17.2 $\mu\text{C}/\text{cm}^2$ respectively for PBNO, PBNO-La, and PBNO-Nd.

We note that the trend in P_s is also consistent with the decreased orthorhombicity and smaller octahedral tilt angles. Therefore, in our current samples, the two types of distortion associated with the atomic shifts and the octahedral tilts are likely related to each other. It has been established that the distortions are strongly affected by the stereochemically active $6s^2$ lone pair electrons of Bi^{3+} , which may favor an increase of P_s [8]. Consequently, the partial occupation of Ln^{3+} ions with no lone-pair electrons in the $A(1)$ -site perovskite layers decreases both the tilting angle of the BO_6 octahedra and the

Fig. 3. Crystal structures determined from NPD data. (a) Tilting of linked BO_6 octahedra from the c -axis. (b) Distortion of perovskite structure projected along the c -axis.

Fig. 4. Contribution to the total spontaneous polarization (P_s) of each ion determined from the atomic displacements along the a -axis.

Fig. 5. FTIR spectra of samples at room temperature.

atomic displacements. Moreover, the smaller ionic radius of Nd^{3+} compared to La^{3+} induces a greater degree of distortion, suggesting that the substitution of smaller cations could be more effective regarding the electrical properties [33].

The changes in local structure were investigated using FTIR spectroscopy at room temperature in the range 550–1200 cm^{-1} , corresponding to the internal modes of the BO_6 octahedra ($> 200\text{ cm}^{-1}$). The FTIR spectra in Fig. 5 show two vibration modes of PBNO at 573 and 820 cm^{-1} with assignments of asymmetric $B-O$ stretching and symmetric $B-O$ stretching of the BO_6 octahedra, respectively [34]. Both vibration modes of BO_6 should not change, since the Ln^{3+} ions do not substitute into the B -site of the perovskite layers. However, a slight shifting is observed in both modes as shown in Fig. 5, which is induced by the occupation of Ln^{3+} on the A -site of the perovskite layer [19,20], as revealed by neutron diffraction analysis. The substitution of larger La^{3+} results in a longer $Nb-O$ bond and thereby lowered bond strength,

shifting the vibration modes to lower wavenumbers of 565 and 813 cm^{-1} . Conversely, the substitution of smaller Nd^{3+} results in shifts toward higher wavenumbers of 579 and 826 cm^{-1} , since the $Nb-O$ bond is shorter and results in higher bond strength [21]. We note that the IR spectra do not show sulfate vibration modes around 970–995 cm^{-1} , which indicates that the salts used as the reaction media do not react with the products.

SEM micrographs of the powder samples are shown in Fig. 6. It is observed that the grain growth is highly anisotropic with plate-like grain morphologies, which is a characteristic feature of bismuth layer-structured compounds. The grain size of PBNO is in the range 1.08–1.97 μm and is reduced in size with Ln^{3+} substitution, to the range 0.55–0.88 μm for PBNO-La and 0.72–1.24 μm for PBNO-Nd. The Ln^{3+} ions are known to suppress grain growth, which is attributed to their low diffusivity [17]. In contrast, Bi^{3+} is reported to have high ionic mobility and can stimulate grain growth, thus grain growth will be inhibited with reduced Bi^{3+} content.

Fig. 6. SEM micrographs of the powder samples. (a) PBNO, (b) PBNO-La, (c) PBNO-Nd.

Fig. 7 shows the temperature dependence of the dielectric constant and dielectric loss of pelletized samples measured in the range 50 kHz to 1 MHz, which best reflects the intrinsic polarizability [35]. The density of the pellets was determined as 7.73 g/cm³, 7.57 g/cm³, and 7.64 g/cm³ for PBNO, PBNO-La, and PBNO-Nd respectively, which in each case is greater than 93% of the theoretical density and indicates that the molten salt method produces dense grains [21]. A

single dielectric peak is observed for all the samples, which corresponds to the phase transition from the ferroelectric to paraelectric phase (T_c). The T_c decreases from 828 K for PBNO to 508 K for PBNO-La and 613 K for PBNO-Nd. The decrease in T_c with Ln^{3+} substitution is consistent with the reduction in the degree of octahedral tilting and calculated P_s value, as discussed in the neutron diffraction analysis above. In addition, the T_c of PBNO-Nd is higher than that of

Fig. 7. Variation of dielectric constant (ϵ) and dielectric loss ($\tan \delta$) as a function of temperature and at different frequencies.

Table 4

Variation of electrical properties of samples measured at 1 MHz.

Sample	ε_{RT}	T_c (K)	ε_m	$\tan \delta (T_m)$	$(a-b)/(a+b)$	γ	ΔT (K)
PBNO	146	828	1740	0.297	0.00145	1.27	0
PBNO-La	198	508	257	0.077	0.00019	1.63	5
PBNO-Nd	206	613	324	0.039	0.00024	1.65	5

PBNO-La as the ionic radius of Nd^{3+} is smaller than La^{3+} , and T_c is known to increase with decreasing A-site ionic radius [31].

At T_c a significant decrease in dielectric constant (ε_m) and dielectric loss ($\tan \delta$) is observed with Ln^{3+} substitution, as shown in Table 4. The magnitude of ε_m is correlated to the grain size; decreasing grain size inhibits the movement of domain walls, contributing to the decrease in magnitude. The significant reduction of dielectric loss with Ln^{3+} substitution is attributed to the suppression of intrinsic oxygen vacancies that are created due to bismuth volatilization at high temperatures [8,9]. We also suggest that the trend in dielectric loss is also consistent with the trend in grain size. Smaller grains with more grain boundaries will tend to inhibit charge transport, resulting in lower dielectric loss [36,37].

Relaxor-ferroelectric behavior is initially observed in the PBNO-La and PBNO-Nd samples and is characterized by the broadened phase transition peaks and the frequency-dispersive behavior in Fig. 7(b) and (c) [6]. The dielectric peaks of both samples in the frequency range 50 kHz to 1 MHz shift slightly by ~ 5 K (ΔT), which can be attributed to the contribution of ferroelectric nano-domain motion. This relaxor behavior can also be evaluated by the degree of diffuseness (γ) calculated from the modified Curie-Weiss law equation [11]:

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C}$$

Here ε_m is the dielectric maximum at the transition temperature T_m , C is a Curie-type constant, and γ is the degree of diffuseness. A normal ferroelectric is known to follow $\gamma=1$, whereas for a relaxor the behavior follows $\gamma=2$. The γ value is fitted from plots of $\ln(1/\varepsilon_r - 1/\varepsilon_m)$ versus $\ln(T-T_m)$ in Fig. 8. The increased γ values for PBNO-La and PBNO-Nd indicate a changeover from normal ferroelectric to relaxor behavior, which leads to an increase in ΔT as listed in Table 4. This is induced by the increased disorder of the A-site cations (Pb/Bi/La or Nd) in the perovskite layer as well as the disordered A-site cations (Pb/Bi) in the Bi_2O_2 layer, as explained in the neutron

Fig. 8. Modified Curie-Weiss fitted lines to quantify the relaxor ferroelectric behavior. **Fig. 9.** P - E hysteresis loops measured at room temperature and 1 Hz frequency.

diffraction analysis above. The disorder leads to the breaking of long-range ferroelectric order into polar nanoregions, which is manifested by relaxor behavior.

Since all three samples show a peak in the dielectric constant suggesting the onset of ferroelectricity, polarization-electric field (P - E) hysteresis loops were performed at room temperature at a frequency of 1 Hz, as shown in Fig. 9. The P - E loops are unsaturated, implying that the domains are not fully aligned at the highest electric fields of 160 kV/cm. Although unsaturated, all three samples exhibit ferroelectric behavior, as indicated by the increase of both the remnant polarization (P_r) and saturated polarization (P_s) in non-linear fashion as the electric field increases [23,38].

The P - E loop of pristine PBNO suggests that this sample exhibits capacitor behavior rather than ferroelectric behavior, as there is no obvious switching peak in the I - E curve (inset to Fig. 8a). For the PBNO-La and PBNO-Nd samples, the P - E hysteresis loops are accompanied by ferroelectric domain switching, as apparent in the insets to Fig. 9(b) and (c), indicating improved ferroelectric properties. These phenomena initially appear to be in conflict with the decreased values of P_s calculated from the structural distortion, as discussed above. We assume that the ferroelectric domains of pristine PBNO are frozen and cannot be reoriented in the external fields applied, since the measurement was performed at RT (300 K), well below the high T_c (828 K), whereas the T_c of PBNO-La (508 K) and PBNO-Nd (603 K) are closer to the measurement temperature, making it easier to align the ferroelectric domains in these two samples. It has been reported that the switching polarization increases with increasing temperature and electric field [39]. A tendency towards well-saturated P - E loops was observed previously for the double-layer Aurivillius phase $\text{Sr}_{1-x}(\text{K}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_2\text{Nb}_2\text{O}_9$, where a higher measurement temperature of 180 °C was used [40]. Thus, we suggest that the P_s and P_r of the PBNO sample will increase and show a well-defined loop at elevated temperatures, as well as exhibiting a higher dielectric constant with increasing temperature as shown in Fig. 7. We also assume that the lower measured P_s values for all three samples compared to the calculated values is due to the unsaturated polarization in the room temperature measurements.

Due to the easier alignment of the ferroelectric domains, the P_r increases to 0.79 $\mu\text{C}/\text{cm}^2$ for PBNO-La and 2.06 $\mu\text{C}/\text{cm}^2$ for PBNO-Nd as compared to 0.47 $\mu\text{C}/\text{cm}^2$ for pristine PBNO at an applied field of 160 kV/cm. This trend is consistent with the magnitude of the room-temperature dielectric constant (ϵ_{RT}), listed in Table 4. The higher P_r values and ϵ_{RT} are attributed to the reduction of oxygen vacancies as well as dielectric loss, since charge transport is inhibited in the Ln -substituted materials [36].

4. Conclusions

The double-layer Aurivillius phase $\text{PbBi}_2\text{Nb}_2\text{O}_9$ was prepared by the molten-salt method with partial substitution of lanthanide ions (Ln : La^{3+} , Nd^{3+}) for Bi^{3+} ions. X-ray diffraction confirmed that all the samples are single-phase and adopt non-centrosymmetric orthorhombic $A2_1am$ symmetry. The Ln^{3+} ions inhibit grain growth, reducing the size of the grains with plate-like morphology. Neutron diffraction data indicated that the Ln^{3+} ions occupy the A-site of the perovskite layer and that Pb^{2+} and Bi^{3+} ions occupy the A-site of both the perovskite and Bi_2O_2 layers. With Ln^{3+} substitution, the degree of orthorhombicity decreases and the BO_6 octahedral distortion decreases, which are related to the decreased ferroelectric transition temperatures (T_c). This is also consistent with a decrease in the overall ferroelectric distortion as the effect of the $6s^2$ lone pair electrons of Bi^{3+} is diminished. Relaxor-ferroelectric behavior is induced with Ln^{3+} substitution since the degree of disorder of the A-site cations on both the perovskite and Bi_2O_2 layers increases. The remnant polarization (P_r) at room temperature is significantly increased for PBNO-Nd and PBNO-La, which is attributed to the higher

dielectric constant at room temperature and decreased dielectric loss.

CRediT authorship contribution statement

Tio P. Wendari: Investigation, Methodology, Visualization, Writing - original draft. **Syukri Arief:** Conceptualization, Writing - review & editing. **Nandang Mufti:** Conceptualization, Validation. **Andon Insani:** Resources, Methodology. **Jacob Baas:** Investigation, Formal analysis. **Graeme R. Blake:** Resources, Validation, Writing - review & editing. **Zulhadjri:** Supervision, Conceptualization, Validation, and Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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