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Synthesis, structural analysis and dielectric properties of the double-layer Aurivillius compound $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$

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ABSTRACT

The double-layer Aurivillius phases $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3$, and 0.5) were synthesized by a molten salt method using a mixture of $\text{K}_2\text{SO}_4/\text{Na}_2\text{SO}_4$. The effect of composition on the structure, morphology and dielectric properties was investigated. X-ray diffraction showed that single-phase samples with a non-polar, orthorhombic $A2_1am$ structure were obtained for $x = 0, 0.1$ and 0.3 . The unit cell becomes more orthorhombic with increasing x as the degree of distortion of the BO_6 octahedra in the perovskite layer increases. Raman spectroscopy showed the typical modes of the orthorhombic double-layer Aurivillius structure and indicated that the La^{3+} ions prefer to occupy the perovskite A-site, Mn^{3+} occupies the B-site, and the Pb^{2+} ions are found in the Bi_2O_2 layer. The morphology of the samples was probed by scanning electron microscopy, which showed anisotropic, plate-like crystallites that increased in size with increasing x . The dielectric constant significantly increased with x , and the ferroelectric properties became more relaxor-like.

1. Introduction

In recent years, dielectric capacitors have received much attention as promising materials for energy storage applications due to their high dielectric constant over a wide temperature range, low dielectric loss, large remnant polarization, low coercive fields, high electrical energy densities, and outstanding fatigue endurance, which are competitive with batteries and other power storage systems [1–3]. Due to the rapid development of the electronics industry, energy storage systems with enhanced properties are urgently required. For instance, in battery-storage systems, the development of novel electrode materials with superior electrical conductivity and ion diffusivity has resulted in the improvement of recoverable energy density and storage efficiency [4,5]. On the other hand, the energy storage performance of dielectric capacitors can be enhanced by the development of ferroelectric materials with narrow hysteresis loops and high dielectric constants [6].

Aurivillius oxide compounds often exhibit excellent dielectric properties, making them potentially useful as such energy storage materials [6,7]. Aurivillius compounds are constructed by n perovskite-like

$(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ layers sandwiched between bismuth oxide layers $(\text{Bi}_2\text{O}_2)^{2+}$, stacked along the c -axis. Generally, the A-site cation is mono, di, or trivalent with a dodecahedral coordination (e.g., Na^+ , Ca^{2+} , Pb^{2+} , Ba^{2+} , Sr^{2+} , Ln^{3+}) and the B-site cation is a transition metal with an octahedral coordination (e.g., Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+}) [8]. The bismuth oxide layer plays an essential role as an insulator layer and the perovskite layers give rise to electrical polarization due to the presence of d^0 -cations and consequent BO_6 octahedral distortion [9,10].

The good dielectric constant and high Curie temperatures of lead-containing Aurivillius compounds have been extensively studied with regard to the lone-pair effect of the $6s^2$ -electrons of both Pb^{2+} and Bi^{3+} ions [11,12]. Double-layer $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (PBNO), which can alternatively be described as $(\text{Bi}_2\text{O}_2)^{2+}(\text{PbNb}_2\text{O}_7)^{2-}$, adopts a non-centrosymmetric crystal structure with the $A2_1am$ space group and exhibits spontaneous ferroelectric polarization with a high Curie temperature of $T_c = 557^\circ\text{C}$ and low dielectric loss [9]. The similar electronic structures of Pb^{2+} and Bi^{3+} allow a disordered distribution of both ions [13].

In order to improve these electrical properties of Aurivillius phases, the substitution of either A-site or B-site cations, or both

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simultaneously, has been a subject of intense research for many years. The substitution of lanthanides (*Ln*) on the A-site has been widely studied in order to improve the dielectric and piezoelectric properties, reduce dielectric loss and to induce a changeover from normal-ferroelectric to relaxor-ferroelectric behavior [2,14,15]. However, studies of *Ln* substitution for Bi^{3+} in double-layer Aurivillius compounds are still limited. The substitution of *Ln*: La^{3+} , Nd^{3+} , Sm^{3+} for Bi^{3+} has been studied for $\text{SrBi}_2\text{Nb}_2\text{O}_9$ [16–18], but not for $\text{PbBi}_2\text{Nb}_2\text{O}_9$.

Furthermore, substitution on the B-site with first-row transition metal cations (d^n) other than Ti^{4+} (d^0) has received considerable attention both in order to provide magnetic properties and also to enhance the electrical properties due to different ionic radii affecting the structural distortion of the BO_6 octahedra [19]. It was reported that the substitution of Mn^{3+} resulted in an increase in the dielectric and piezoelectric responses as well as introducing a magnetic moment [20,21]. Therefore, both A-site and B-site cation substitution is expected to be an effective strategy to improve the dielectric properties of the double-layer Aurivillius compound $\text{PbBi}_2\text{Nb}_2\text{O}_9$.

Most Aurivillius phases are synthesized using conventional solid-state reaction. However, for the strategy of combining d^0 and d^n cations in this work, the solid-state method is unsuitable as the ionic diffusion rate is lower and the reaction temperature required is higher, often causing the volatilization of Bi^{3+} and oxidation of Mn^{3+} and leading to the formation of impurity phases [10,22,23]. Therefore, methods that use a liquid-phase reaction medium such as the molten salt method are preferable. The synthesis of magnetic compounds using molten salts as the reaction medium gives many advantages such as low reaction temperatures, fast ionic diffusion, and shorter reaction times [10,24–26]. Based on this method, single-phase Aurivillius compounds containing mixed d^0 and d^n cations can easily be obtained.

To the best of our knowledge, the synthesis of $\text{PbBi}_2\text{Nb}_2\text{O}_9$ substituted by a combination of La^{3+} and Mn^{3+} using the molten salt method has not previously been reported. In this work, we synthesize compounds of composition $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3$ and 0.5) using $\text{K}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ as the flux medium. The substitution of Mn^{3+} for Nb^{5+} at the B-site is compensated by the substitution of Bi^{3+} for Pb^{2+} at the A-site to maintain overall charge neutrality. The effects of substitution level x on the structure, morphology and dielectric properties are investigated in this report.

2. Experimental procedures

The precursors PbO , Bi_2O_3 , La_2O_3 , Nb_2O_5 , and Mn_2O_3 (Aldrich, $\geq 99.9\%$) were weighed in stoichiometric molar ratios for the target compounds $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3$ and 0.5) and mixed in ethanol using an agate mortar for 2 h. A mixture of $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4$ (ratio 1:1) was added with a molar ratio of 1:7 salt to oxide. The precursor mixture was placed in an alumina crucible and heated continuously at a rate of $5^\circ\text{C}/\text{min}$ to 750°C , 850°C and 950°C for 5 h each. The final product was washed several times using hot distilled water to remove the alkali salt and then dried at 110°C for 5 h. The purity and crystal structure were assessed using X-ray diffraction (Shimadzu XRD 7000 with $\text{Cu K}\alpha$ radiation). The unit cell parameters were determined by the Le Bail refinement technique using the RIETICA program [27]. Raman spectroscopy was performed using a Bruker-Senterra spectrometer with a DPSS (diode pump solid state) laser ($\lambda = 532\text{ nm}$) in the spectral range $30\text{--}1200\text{ cm}^{-1}$ and FTIR spectroscopy was carried out using a Bruker Alpha spectrometer equipped with a single reflection ZnSe ATR, both at room temperature. The Raman spectra were corrected for the temperature factor using the Bose-Einstein equation and fitted using a Lorentzian model to obtain the peak positions, full widths at half maximum (FWHMs) and integrated intensities. Morphology and grain size were analyzed by scanning electron microscopy (SEM) using an INSPECT S50 microscope. For dielectric measurements, the product was pressed to form a pellet and sintered at 900°C for 5 h. Silver conductive paste (Aldrich, 99%) was

Fig. 1. XRD Patterns of $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3, 0.5$) ceramics, indexed according to the standard double-layer Aurivillius structure of $\text{PbBi}_2\text{Nb}_2\text{O}_9$. The black dots for the $x = 0.5$ sample indicate peaks from an impurity pyrochlore phase.

applied to both surfaces of the sintered pellet as the electrodes and heated at 110°C for 2 h. Capacitance and dielectric loss measurements were carried out using a precision LCR-meter (Agilent 4980A) with an amplitude of 1 V in the frequency range 100 Hz to 1 MHz as a function of temperature ($30\text{--}500^\circ\text{C}$).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the products at room temperature. All XRD patterns could be indexed using the $\text{PbBi}_2\text{Nb}_2\text{O}_9$ standard diffraction pattern with the orthorhombic $A2_1am$ space group (ICSD 95920) [28]. Single-phase $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ samples were obtained for $x = 0, 0.1$ and 0.3 , whereas for $x = 0.5$ an unidentified impurity phase was observed.

The XRD data thus demonstrate that the substitution of 25% molar ratio La^{3+} for Bi^{3+} in $\text{PbBi}_2\text{Nb}_2\text{O}_9$ was successful. In addition, up to 15% of the Nb^{5+} can be simultaneously substituted by Mn^{3+} if the $\text{Pb}:\text{Bi}$ ratio is adjusted accordingly. We have previously reported that up to 15% of Ti^{4+} on the B-site of $\text{Pb}_{1-x}\text{Bi}_{4+x}\text{Ti}_{4-x}\text{Mn}_x\text{O}_{15}$ can be replaced by Mn^{3+} using the molten salt method [10]. As observed in Fig. 1, the two most intense peaks (115 and 200) shift toward higher 2θ with increasing x , corresponding to a decrease in the unit cell volume. The unit cells of the single-phase samples were refined using the structural parameters of the $A2_1am$ $\text{PbBi}_2\text{Nb}_2\text{O}_9$ phase reported by Miura et al. as the initial model [28]. Fig. 2 shows Le Bail fits to the XRD patterns of all the single-phase samples ($x = 0, 0.1, 0.3$). The good fits demonstrate that the substitution of La^{3+} and Mn^{3+} ions does not change the parent structure of $\text{PbBi}_2\text{Nb}_2\text{O}_9$.

The effects of increasing x on the lattice parameters and cell volume are summarized in Table 1. The a lattice parameter is relatively constant, whereas the b and c lattice parameters decrease with the cell volume as x increases. This is consistent with the larger ionic radius of Pb^{2+} ($1.29\text{ \AA}$) compared to Bi^{3+} ($1.17\text{ \AA}$) for 8-fold coordination, and with the similar ionic radii of Mn^{3+} ($0.645\text{ \AA}$) and Nb^{5+} ($0.640\text{ \AA}$) for 6-fold coordination [29]. The significant decrease in the c lattice parameter corresponds to a decrease in size of the BO_6 octahedra caused by the increasing proportion of smaller Bi^{3+} on the A-site according to the nominal formula [12,30]. Furthermore, the reduction of octahedral size may distort the lattice in the ab -plane, by which the structure becomes more orthorhombic with increasing x as quantified by the orthorhombicity ratio $(a-b)/(a+b)$.

The changes in local structure were investigated using Raman Spectroscopy at room temperature in the range $30\text{--}1200\text{ cm}^{-1}$ [31]. The Raman spectra in Fig. 3 show phonon modes characteristic of the

Fig. 2. XRD patterns fitted using the Le Bail method for single-phase $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ samples ($x = 0, 0.1$ and 0.3): experimental XRD data (open circles), calculated data (red line), and difference patterns (green line). The tick marks indicate the positions of allowed Bragg reflections in the space group $A2_1am$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Refined unit cell parameters of single-phase Aurivillius samples $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3$).

	$\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$		
	$x = 0$	$x = 0.1$	$x = 0.3$
Space group	$A2_1am$	$A2_1am$	$A2_1am$
Crystal class	Orthorhombic	Orthorhombic	Orthorhombic
$a(\text{\AA})$	5.5185 (9)	5.5187 (4)	5.5190 (4)
$b(\text{\AA})$	5.5066 (6)	5.5015 (2)	5.4904 (3)
$c(\text{\AA})$	25.5372 (9)	25.4070 (0)	25.1576 (8)
$V(\text{\AA}^3)$	776.049 (9)	771.385 (1)	762.327 (2)
$(a-b)/(a+b)$	0.00108	0.00156	0.00259
Z	4	4	4
R_p (%)	3.090	3.193	3.219
R_{wp} (%)	3.940	4.386	4.225
χ^2	1.130	1.885	1.560

Fig. 3. Raman spectra of single-phase Aurivillius samples $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3$) at room temperature. Peak fits using a Lorentzian model are also shown.

double-layer Aurivillius structure. The assignments of the modes, corresponding to the internal modes of BO_6 octahedra ($> 200 \text{ cm}^{-1}$) and to modes associated with the A-site and the Bi_2O_2 layer ($< 200 \text{ cm}^{-1}$), are listed in Table 2 and are in good agreement with earlier reports

Table 2

Assignment of Raman modes of single-phase Aurivillius samples $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3$).

Peak position (cm^{-1})	Assignment
~ 64	Bi^{3+} in Bi_2O_2 layer
~ 96	Translational modes of O-A-O bonding
~ 168	A-site ion in perovskite layer
~ 215	BO_6 bending and tilting
~ 565	Asymmetric BO_6 stretching
~ 714	B-O vibration modes
~ 858	Symmetric BO_6 stretching

Fig. 4. Composition dependence of wavenumber and FWHM of selected Raman modes. (a) Internal modes associated with BO_6 octahedra. (b) Modes associated with the A-site and the Bi_2O_2 layer.

[31–34]. Although the overall appearance of the Raman spectra remains similar with increasing x , both some of the internal BO_6 modes and low wavenumber modes are shifted and become broader as shown in Fig. 4.

The lowest frequency mode is associated with the vibration of Bi^{3+} in the rigid Bi_2O_2 layer and does not show any significant shift from 64 cm^{-1} with increasing x . For $x = 0$ and 0.1 , the Bi^{3+} composition in $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ is insufficient to form the Bi_2O_2 layer without partial occupancy of the Bi site by Pb^{2+} or La^{3+} , while for $x = 0.3$ the Bi^{3+} composition is sufficient. It is reported that occupation of the Bi_2O_2 layer by other cations is not favored since it can destroy the structure [35]. The Bi_2O_2 layers are comprised of a square planar net of bismuth cations, each coordinated to four oxygen anions forming a BiO_4 tetragonal pyramid. The substitution of this bismuth is preferable for cations having a stereochemically active lone pair of electrons, which is the essential common property between Bi^{3+} and the doping cations. It

Fig. 5. FTIR spectra of single-phase Aurivillius samples $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3$) at room temperature.

is this distorted environment that is thought to limit cation substitution in this layer [16,36]. It is also reported that the presence of La^{3+} in the Bi_2O_2 layer causes a shift of the 64 cm^{-1} mode to lower wavenumbers [33,37]. It is found that the frequency of this mode does not change with x in the current study; we suggest that the Bi^{3+} vacancies in the Bi_2O_2 layer are occupied by Pb^{2+} ions, while the La^{3+} ions prefer to occupy the A-site of the perovskite layer. The preference of Pb^{2+} to occupy the Bi_2O_2 layer is due to the similar characteristics of Pb^{2+} and Bi^{3+} ions, which both possess $6s^2$ lone pair electrons. This result is in agreement with earlier studies which also show that the Pb and Bi will have a similar preference for the disorder in both the perovskite layers and the Bi_2O_2 layers [13,38,39]. This is also consistent with the observation that the A-site mode at 95 cm^{-1} does not shift as the $\text{Pb}^{2+}/$

Bi^{3+} ratio is varied, since these cations have similar masses. The increase in FWHM of the peaks at 64 cm^{-1} and 95 cm^{-1} suggests that the degree of disorder increases in both the Bi_2O_2 and perovskite layers as the $\text{Pb}^{2+}/\text{Bi}^{3+}$ ratio increases.

More obvious changes are observed in the BO_6 internal modes ($> 200\text{ cm}^{-1}$) due to the changing ratio of Nb^{5+} to Mn^{3+} ions. A shift towards lower wavenumber is observed for the symmetric BO_6 stretching mode at 858 cm^{-1} with increasing x (increasing Mn^{3+} content). Furthermore, the B–O vibration mode at 714 cm^{-1} both shifts to 698 cm^{-1} and becomes broader with increasing x . The Lorentzian fitting curve in Fig. 3 shows the appearance of a new peak at 756 cm^{-1} for $x = 0.1$ and 0.3 , which confirms the presence of Mn^{3+} ions in the BO_6 octahedra [20]. The changes in both the BO_6 stretching and B–O vibration modes are probably induced by the two possible local environments of Mn^{3+} on the B-site. We suggest that the Mn^{3+} ions prefer to form a locally ordered Mn–O–Mn arrangement since the new mode at 756 cm^{-1} appears when Mn is introduced to the structure. Most of the Mn^{3+} ions will be arranged to form Nb–O–Mn bonds. Furthermore, the smaller chemical bond strength of the Mn–O bond (362 kJ/mol) compared with that of Nb–O (726.5 kJ/mol) results in the shifts of the 714 cm^{-1} and 858 cm^{-1} modes toward lower wavenumbers and an increase in FWHM values as shown in Fig. 4b [40]. Similar shifts were previously observed in the Raman spectra of Mn-substituted $\text{PbBi}_4\text{Ti}_4\text{O}_{15}$ [34]. We note that a partially ordered arrangement of Mn^{3+} in Aurivillius phases could give rise to magnetic ordering via Mn–O–Mn exchange interactions.

Similar peak shifts are also observed in the IR spectra as shown in Fig. 5. The BO_6 vibration modes are observed at $574, 750$ and 823 cm^{-1} , in similar fashion to the Raman spectra [41]. Neither the Raman nor FTIR spectra contain sulfate vibration modes around $970\text{--}995\text{ cm}^{-1}$, which indicates that the salts used as the reaction media do not react with the products [42].

The morphology of the products was analyzed using SEM as shown in Fig. 6. Plate-like grains are observed, which is typical morphology for

Fig. 6. SEM micrographs of single-phase Aurivillius samples $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.3$.

Fig. 7. Temperature dependence of the dielectric constant (ϵ_r) and loss ($\tan \delta$) of Aurivillius phases $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3$).

Fig. 8. Fits of dielectric properties of $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3$) using a modified Curie-Weiss law to quantify relaxor ferroelectric behavior.

Aurivillius phases. The average grain size significantly increases with x , from the range 1.5–1.7 μm for $x = 0$ to 2.2–2.5 μm for $x = 0.1$ and 2.7–3.1 μm for $x = 0.3$. This increase in grain size can be attributed to

the increase in Bi^{3+} content. It has previously been reported that the Bi^{3+} ion has a high ionic mobility and can stimulate grain growth [2].

Fig. 7 shows the temperature dependence of the dielectric constant and dielectric loss of our samples ($x = 0, 0.1$, and 0.3) measured in the range 50 kHz to 1 MHz. The peak in the dielectric constant at maximum temperature (T_m) is essentially independent of frequency for $x = 0$ and indicates the onset of ferroelectric order. The $x = 0.1$ and $x = 0.3$ samples exhibit a broader peak and significant frequency dispersion of the dielectric permittivity, which indicates a pronounced relaxor-ferroelectric characteristic with increasing x . The strongest frequency dispersion is found for $x = 0.3$ and thus the ferroelectric behavior of this sample is the most relaxor-like. The degree of diffuseness of the relaxor behavior can be described by a modified Curie-Weiss law [37]:

$$1/\epsilon_r - 1/\epsilon_m = (T - T_m)^\gamma / C$$

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, where $\gamma = 1$ for normal ferroelectrics and $\gamma = 2$ for relaxor-ferroelectrics. Fig. 8 shows linear fits to plots of $\ln(1/\epsilon_r - 1/\epsilon_m)$ versus $\ln(T - T_m)$ at 1 MHz. The fitted value of γ increases with x and the temperature relaxation ($T_{m(1\text{MHz})} - T_{m(50\text{kHz})}$) increases from 5 $^\circ\text{C}$ to 40 $^\circ\text{C}$ as listed in Table 3. Clearly, increasing the composition x in $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ leads to an increase in the degree of relaxor-behavior. This is likely due to the increased degree of disorder on both the A-site ($\text{Pb}^{2+}/$

Table 3Variation of electrical properties of single-phase Aurivillius samples $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ ($x = 0, 0.1, 0.3$) measured at 1 MHz.

Sample	ϵ_{RT}	$\tan \delta$ (RT)	T_m (°C)	ϵ_m	$\tan \delta$ (T_m)	Tolerance Factor (t)	γ	ΔT (°C) T_m (1MHz–50kHz)
$x = 0$	198.22	0.0656	235	257.36	0.07648	0.945	1.63	5
$x = 0.1$	203.02	0.0667	300	311.43	0.1758	0.944	1.78	20
$x = 0.3$	220.30	0.0985	360	476.14	1.079	0.940	2.14	40

Bi^{3+}) and B-site ($\text{Nb}^{5+}/\text{Mn}^{3+}$) in the Bi_2O_2 and perovskite layers, as explained in the Raman study above.

The dielectric peak at 1 MHz shows a significant increase in both magnitude and T_m as x increases, as shown in Table 3. The increase in dielectric properties (ϵ_m and T_m) can be attributed to the more distorted crystal structure, as evidenced by the increased orthorhombicity and the Raman peak shifts. The increase in structural distortion is consistent with the decrease in Goldschmidt tolerance factor (t) for the perovskite part of the structure in Table 3 [11,37]. We suggest that the disorder involving cations with different radii (size mismatch) gives rise to atomic displacements along the a and b axes, resulting in increased ionic polarizability [43]. Furthermore, the increasing occupancy of smaller Bi^{3+} on the A-site is expected to result in greater distortion of the BO_6 octahedra, which is known from previous studies to induce an increase in T_m [13,36]. It is also possible that the larger grain size for compositions with higher x results in a lower density of domain walls, thus the sample can be polarized more easily and the dielectric properties are enhanced [12,19]. The dielectric loss is found to increase with increasing x at both room temperature and at T_m . This is caused by the increase in electron concentration by the introduction of Mn^{3+} for Nb^{5+} [10]. Furthermore, the larger grain size and subsequently smaller number of grain boundaries allows better charge transport, contributing to the increase of dielectric loss [41].

4. Conclusion

The double-layer Aurivillius compound $\text{PbBi}_2\text{Nb}_2\text{O}_9$ has been synthesized by the molten salt method, partially substituting La^{3+} for Bi^{3+} and Mn^{3+} for Nb^{5+} . Single-phase samples of $\text{Pb}_{1-2x}\text{Bi}_{1.5+2x}\text{La}_{0.5}\text{Nb}_{2-x}\text{Mn}_x\text{O}_9$ were obtained for the compositions $x = 0, 0.1$ and 0.3 and show non-centrosymmetric orthorhombic symmetry with the $A2_1am$ space group. It was found that with increasing x , the cell volume decreases and the degree of orthorhombicity increases. Raman spectroscopy indicated that the La^{3+} ions occupy the A-site of the perovskite layer and the Mn^{3+} ions occupy the B-site. Plate-like grain morphology is observed for all samples and the grain size becomes larger with increasing x . Both the dielectric constant and T_m increase with x , which is consistent with the increased structural distortion and grain size.

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