Synthesis and Structural Analysis of Aurivillius Phase, $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$

Zulhadjri*, Bilian Sahiga J.I., Wendari Tio Putra and Emriadi
Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Andalas, Padang, INDONESIA
*zulhadjri@fmipa.unand.ac.id

Abstract
Aurivillius phases represent a metal oxide compound that comprises perovskite-like layer $(A_{n-1}B_nO_{3n+1})^{2-}$ separated by a layer of bismuth oxide $(Bi_2O_2)^{2+}$. Most Aurivillius compounds are synthesized due to their ferroelectric properties with high phase transition temperature. Recently, a study on combination of ferroelectric and magnetic cations into perovskite layer of Aurivillius phase was carried out to obtain the magnetoelectric material. The magnetoelectric material with the formula $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ (x = 0, 0.2, 0.4 and 0.6) was prepared by a molten salt method using the mixture of sulfate salts K_2SO_4/Na_2SO_4 as the flux. The crystal structure and morphology of products were investigated by X-Ray Diffraction and SEM respectively.

Structural analysis with LeBail technique indicates that the products demonstrate a space group of $A2_1am$. The units cell of sample x = 0 are 5.4132(3) Å, 5.4093(2) Å, 40.6735(8) Å and 1191.00(7) $Å^3$ for a, b, c and V respectively. The value of cell volume crystals increased as the value of x increased. The particle morphology was analyzed by SEM and showed the plate-like grains which are characteristics for layers-structure Aurivillius phases. The dielectric constant values for the samples with $x \leq 0.2$ are relatively the same (~134) at 10 kHz and slightly higher for $x \geq 0.4$.

Keywords: Aurivillius phase, molten salts, magnetoelectric, dielectric, ferroelectric.

Introduction

Materials based on the Aurivillius type structure have attracted great attention in recent years, attributable to their sufficiently good dielectric properties and high ferroelectric–paraelectric phase transition temperature as to their advanced applications such as non-volatile ferroelectric memories, heat-resistant insulators and capacitors among others[1-3].

The general formula for Aurivillius type compounds is $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ where the A site can be occupied by large cations with dodecahedral coordination such as Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Bi^{3+}, Ln^{3+}, Na^+ or a mixture of these cations and the B site can be occupied by smaller cations with a higher charge such as Fe^{3+}, Mn^{3+},Ti^{4+}, Nb^{5+}, Ta^{5+}, W^{6+} or Mo^{6+} with octahedral coordination[1,4]. The structure of this compound can be described as intergrowth of fluorite-like $[Bi_2O_2]^{2+}$ layers and *n* perovskite-like layers $[A_{n-1}B_nO_{3n+1}]^{2-}$.

The ferroelectric properties of Aurivillius compounds were discovered by Smolenskii et al[5] in 1959. Most Aurivillius phases have high Curie temperatures T_c such as $Bi_4Ti_3O_{12}$ (675 °C), $PbBi_4Ti_4O_{15}$ (570 °C) and $Pb_2Bi_4Ti_5O_{18}$ (310 °C)[1,6]. For these compounds, the ferroelectricity is considered due to the presence of d^0 transition cation such as Ti^{4+} into the perovskite layer. The recent introduction of magnetic transition cations (d^n) into the perovskite layers within the Aurivillius phases has received significant interest, since this may result in a material that has both dielectric and magnetic properties known as magnetoelectric properties. Magnetic properties can appear by incorporating magnetically-active cations such as Mn^{3+} and Fe^{3+} into the B site in the perovskite blocks.

Several magnetoelectric materials based on the Aurivillius phase are: $Bi_5Ti_3FeO_{15}$, $Bi_6Ti_3Fe_2O_{18}$, $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$, $Pb_{2-x}Bi_{4+x}Ti_{5-x}Mn_xO_{18}$ and $Sr_{0.4}Bi_{0.6}Ti_{3.4}Mn_{0.6}O_{15}$[7-13]. However, these compounds do not show any long-range magnetic ordering.

$CaBi_4Ti_4O_{15}$ (CBT) is a four-layered Aurivillius phase with a high Curie temperature i.e. around 790°C.[14,15] It is promising to be applied for high temperature materials. The modification of CBT can be carried out by doping with rare earth ions such as La^{3+}, Nd^{3+}, Er^{3+}, etc[16-18]. This doping is only effective to influence their electric properties. In this work, CBT was modified by doping using rare earth ion (Nd^{3+}) and magnetic ion (Mn^{3+}), with formula:

$Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$

(CBNTM) to form magnetoelectric materials. Doping Mn^{3+} as magnetic transition metal cations into CBT may result in magnetic properties. The use of Nd^{3+} cation with a smaller ionic radius (r = 1.27 Å)[19] to replace part of Bi^{3+} (r =1.45 Å)[20] is expected to improve its electrical properties. In this report, we only investigate the synthesis of forming a single phase of four-layer Aurivillius phases $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ and their dielectric properties. The single phase of Aurivillius was only found for x = 0, 0.2, 0.4 and 0.6.

Material and Methods

Polycrystalline $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ was synthesized using the molten salts technique. The raw materials used in this work are titanium(IV) oxide, manganese(III) oxide, bismuth(III) oxide, calcium carbonate and neodymium(III) oxide with high purity (Aldrich, ≥ 99.9%). These materials

were weighed in stoichiometric proportions with x = 0, 0.2, 0.4 and 0.6 and then mixed in an agate mortar. The mixture of sodium sulfate/potassium sulfate salts (1:1 molar ratio) was then ground together with the mixture of raw materials. The molar ratio of oxide compounds to the salt mixture was 1:7 which was excess in salts mixture.

The reactant mixtures were heated at temperatures of 750 °C, 850 °C and 900 °C for 5 h for each heating step. The products were washed several times using hot distilled water to remove the alkali salts and then dried at 110 °C for 24 h. The formation of phase oxide was confirmed by powder XRD (Simadzu XRD 7000). The Le Bail refinement of the X-ray data was performed using the RIETICA program[21]. The micro-structure characterization was carried out using scanning electron microscopy (SEM HITACHI S-3400).

For the dielectric constant measurement, the obtained powders were pressed into pellets with 1 cm in diameter and a thickness of about 0.1 cm. These pellets were then sintered at 800 °C for 8 h in air to form a ceramic. The ceramic pellets were coated with silver paste as electrodes. Dielectric properties were measured by using an LCR meter (Motech MT 4099) with a voltage of 1 V at room temperature at various frequencies.

Table 1
Unit cell parameters of $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ with x = 0.2, 0.4 and 0.6 were refined using the space group of $A2_1am$

Cell Parameter	$Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$			
	x = 0	x = 0.2	x = 0.4	x = 0,6
a (Å)	5.4132(3)	5.4136(2)	5.4172(3)	5.4185(3)
b (Å)	5.4093(2)	5.4103(1)	5.4129(2)	5.4148(4)
c (Å)	40.6735(8)	40.6740(7)	40.674(1)	40.779(3)
V (Å^3)	1191.00(7)	1191.31(7)	1192.67(8)	1196.5(1)
lb–al (Å)	0.0039	0.0033	0.0043	0.0037
c/a	7.514	7.513	7.508	7.526
Z	4	4	4	4
R_p (%)	3.04	2.86	2.95	3.00
R_{wp} (%)	3.82	3.65	3.81	3.99
χ^2	1.138	1.109	1.126	1.415

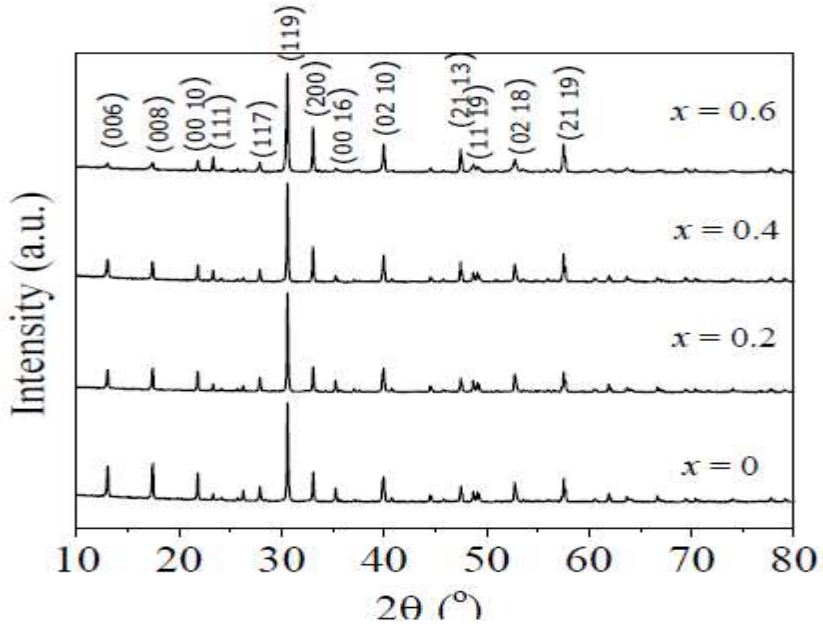

Figure 1: Powder X-ray diffraction patterns of $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ with x = 0.2, 0.4 and 0.6) were synthesized by molten salts method.

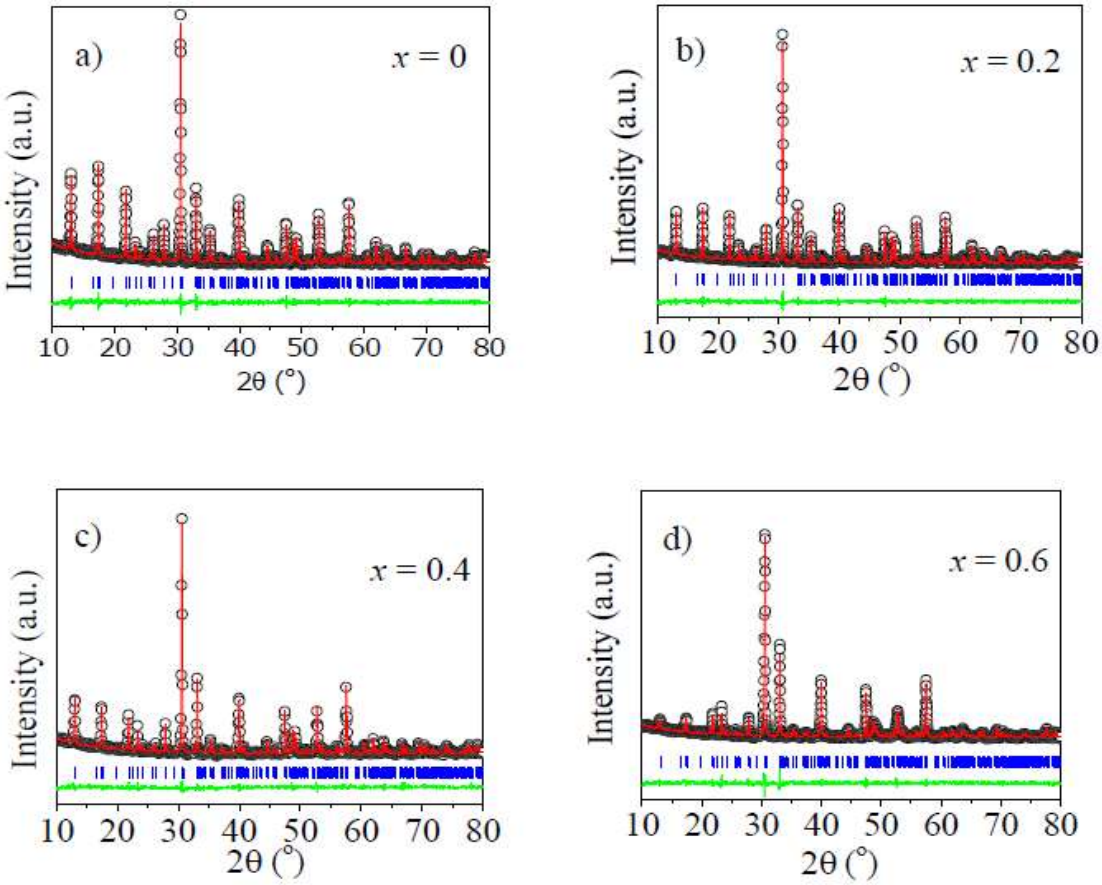

Figure 2: Le Bail plot of XRD powder of $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ with: a) x = 0, b) x = 0.2, c) x = 0.4 and d) x = 0.6. Observed XRD intensity (circle), calculated data (solid line) and the difference of patterns, y_{obs} - y_{cal} (solid line on the bottom curve). The tick marks represent the positions of allowed Bragg reflections in the phase of *$A2_1am$*.

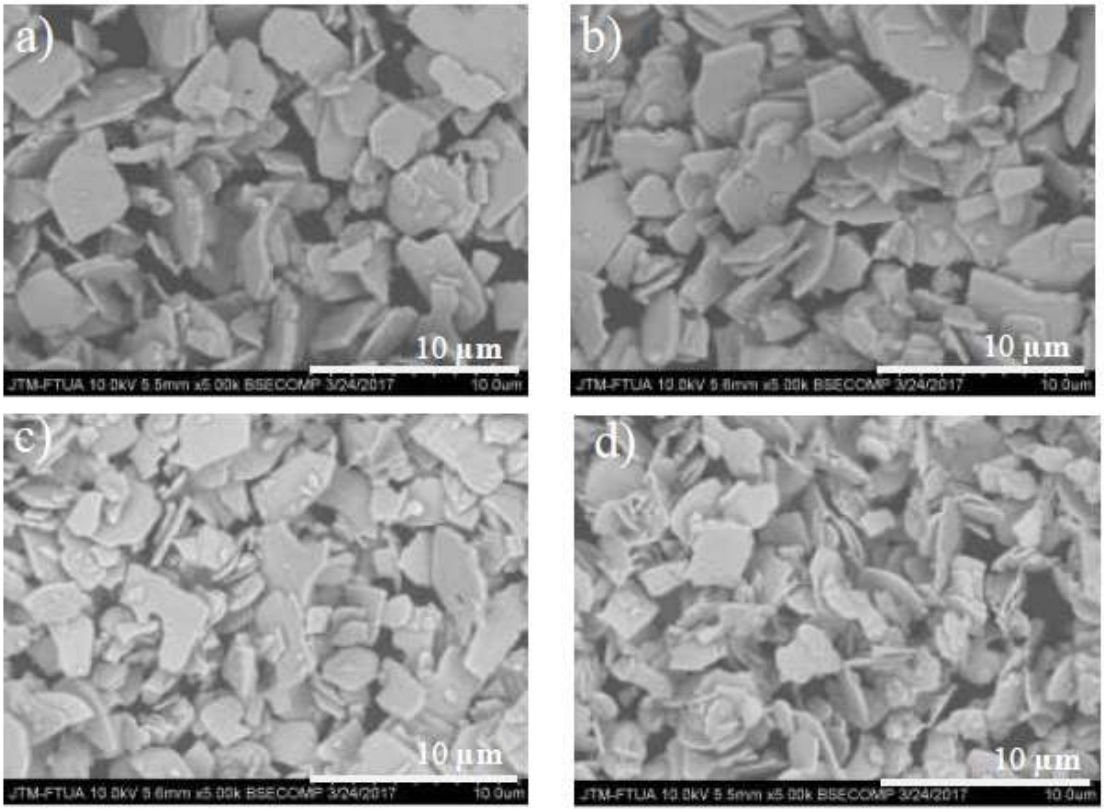

Figure 3: SEM micrographs of the of $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ with: a) x = 0, b) x = 0.2, c) x = 0.4 and d) x = 0.6

Results and Discussion

The X-ray diffraction (XRD) patterns of $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ powders with x = 0, 0.2, 0.4 and 0.6 are shown in figure 1. These patterns matched well with the XRD patterns of the four-layered Aurivillius phase, as reported by Zulhadjri et al[11], Kennedy et al[22] and Tellier et al[23] with an orthorhombic structure and space group of $A2_1am$. The samples with x = 0.8 and 1 observed an additional phase besides the four-layered Aurivillius phase. The XRD patterns in figure 1 exhibit a decreasing preferred orientation in the (00*l*) direction with an increase in x. This indicates that the ceramic grains were oriented along the c axes and decrease with an increase in x.

The X-ray data of the samples of the Aurivillius phase $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ with x = 0, 0.2, 0.4 and 0.6 were refined by the Le Bail technique using $A2_1am$ space group[23]. The fitting results of refinement are shown in figure 2. The profiles of Le Bail refinement are in agreement between the models applied with the sample data. The lattice parameters and the volume of unit cells are shown in table 1. The lattice parameters (*a*, *b* and *c*) and the volume of unit cells of the samples increase as x increases. The unit cell volume increases as the Mn-concentration increases. This is expected, since the cationic radius of Ca^{2+} (1.34 Å)[19] is smaller than Bi^{3+} (1.45 Å)[20] with a coordination number (CN) of 12; while the ionic radii of Ti^{4+} (0.605 Å)[19] is smaller than Mn^{3+} (0.645 Å)[19] with CN = 6. This indicates that the Mn^{3+} cation can be introduced to form single phase of Aurivillius and maximum is up to x = 0.6.

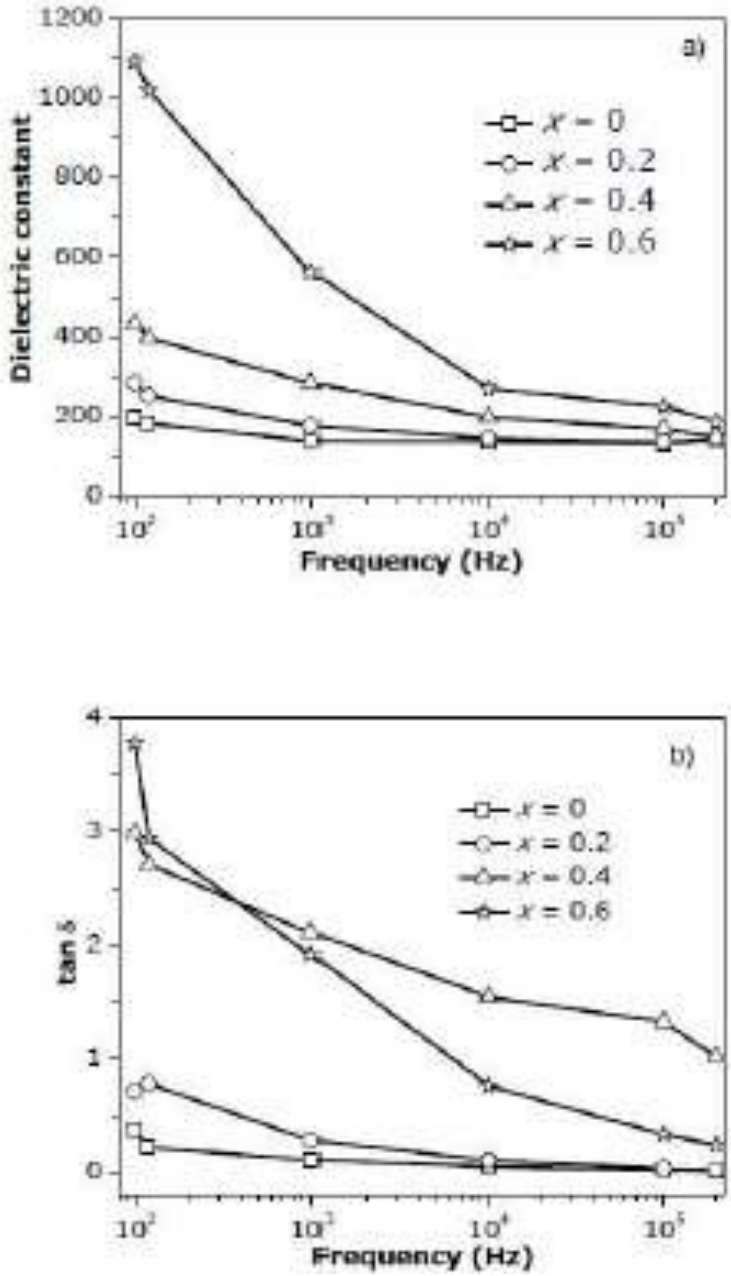

Figure 4: Frequency dependence of: a) dielectric constant and b) dielectric loss of $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ with x = 0, 0.2, 0.4 and 0.6 was measured at room temperature

The value ratio of l*b*–*a*l for all samples is around 0.004 and this value is lower than the $CaBi_4Ti_4O_{15}$ (0.021)[23] indicating the orthorhombicity of the samples is very small and nearer to tetragonal as doped with both Nd^{3+} and Mn^{3+}.

The morphologies of samples $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ with x = 0, 0.2, 0.4 and 0.6 were observed by SEM as shown in figure 3. It can be seen that the profile for all products are plate-like aggregate crystals, typical of layered compounds belonging to the Aurivillius phase.

The frequency dependence of the dielectric constant and dielectric loss measured at room temperature for $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ with x = 0.2, 0.4 and 0.6 is shown in figure 4. At a low frequency, the dielectric constant for all samples (figure 4a) has a high value. The same phenomenon is also exhibited for $Pb_{1-x}Bi_{4+x}Ti_{4-x}Mn_xO_{15}$[11] and $Sr_{0.4}Bi_{0.6}Ti_{3.4}Mn_{0.6}O_{15}$[13], likely due to the interface of two electrically different regions of space charge (interfacial) polarization[24].

The intrinsic dielectric constant is observed at a high frequency. At 10 kHz, the values of dielectric constants of x = 0 and 0.2 are ~134 and slightly high for x = 0.4 with a value of 171 and x = 0.6 with a value of 227. The high dielectric constants for x=0.4 and x=0.6 indicate that the conductivity of these samples increases as observed in dielectric loss. Therefore, the value of the dielectric constant is related to the depletion layer thickness and Schottky type carrier injection at the interface between the electrodes and the samples.

The value of dielectric loss (figure 4b) was found to be higher for the sample with a high value of x, or high Mn^{3+} concentration. The higher dielectric loss for the sample with a high value of x is predicted to be due to the appearance of Mn^{4+} which is the same valence as Ti^{4+}. The increase in x or content of Mn^{4+} in the sample increases the conductivity of the sample attributed to double exchange interaction between Mn^{3+} and Mn^{4+} and leading to an increase in dielectric loss[25].

Conclusion

The Aurivillius phase of $Ca_{1-x}Bi_{3+x}NdTi_{4-x}Mn_xO_{15}$ with x = 0, 0.2, 0.4 and 0.6 was synthesized by the molten-salt technique. Single phase Aurivillius compounds were found for all samples with a space group $A2_1am$. The dielectric constants value for the samples with $x \leq 0.2$ is relatively the same (~134) at 10 kHz and slightly higher for $x \geq 0.4$. This is due to the depletion layer thickness and Schottky type carrier. The dielectric loss of the samples increased as x increased which is attributed to the double exchange interaction between Mn^{3+} and Mn^{4+}, leading to a more conductive sample.

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