ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis and Characterization of Four-Layer Aurivillius Phases $SrBi_3LaTi_4O_{15}$ Doped with Mn^{3+}.

Zulhadjri*, Erni Pakpahan, Sestry Misfadhila, and Syukri Arief.

Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Andalas, Kampus Limau Manis, Padang 25163, West Sumatera-Indonesia.

ABSTRACT

Synthesis of Aurivillius phases containing both dielectric and magnetic properties in one phase have received much interest since they are promising as multiferroic material. The present work, we describe the synthesis and structure analysis of four-layers Aurivillius phase $SrBi_3LaTi_4O_{15}$ doped with Mn^{3+} cation with formula $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ ($0 \le x \le 1$) containing both ferroelectric and magnetic cations. The synthesis was carried out by hydrothermal technique. The results of X-ray analysis revealed that the single phase of Aurivillius was shown by the sample with x = 0.6. The morphologies of the sample are plate-like aggregate crystals, typical of layered compounds belonging to the Aurivillius phase. Dielectric measurement show the small value of dielectric constant.

Keywords: Aurivillus phase, dielectric properties, hydrothermal

*Corresponding author

ISSN: 0975-8585

INTRODUCTION

Bismuth oxides layer-structured, namely Aurivillius compounds, have attracted much attention due to their ferroelectric properties which is potential to applicate in non-volatile random access memory and high temperature piezoelectric devices [1-3]. These compounds are described structuraly as intergrowths of fluorite-like $[Bi_2O_2]^{2+}$ layers with *n* perovskite-type layers $[A_{n-1}B_nO_{3n+1}]^{2-}$. The *A*-site could be occupied by mono-, di- or tri-valent cations or mixture of them having dodecahedral coordination, while *B*-site could be occupied by a transition element with octahedral coordination and *n* is an integer representing the number of sheets of corner-sharing BO_6 octahedra forming the ABO_3-type perovskite blocks [4,5].

Attempts to obtain a new Aurivillius phases have been investigated to study their ferroelectric properties, including *A*-site and *B*-site substitution. It was reported that substitution of *A*-site by lanthanoid ions can improve ferroeletric properties of $Bi_4Ti_3O_{12}$ [6,7]. On the other hand, the presence a magnetic transition metal cations (d^n) at the *B*-site mixture with d^0 transition cation may result in a material which has both ferroelectric and magnetic properties known as multiferroic (magnetoelectric) material. Recently, the cation of Mn^{3+} was doped into $PbBi_4Ti_4O_{15}$ and $Pb_2Bi_4Ti_5O_{18}$ [8,9]. Both of them do not show any long range magnetic ordering. Many efforts have been made to obtain the multiferroic materials based on the Aurivillius phases. The effort to to obtain the multiferroic materials based on the Aurivillius phases is a challenge and generate high interest.

$SrBi_4Ti_4O_{15}$ is a member of Aurivillius phase with n = 4. It has a high Curie temperature (*Tc* = 530 °C) [10]. The ferroelectric properties of this compound improve as doped by La^{3+} cation. Introducing a magnetic cation into the $SrBi_4Ti_4O_{15}$ doped La^{3+} may result in in a material which has both dielectric and magnetic properties known as magnetoelectric. In this paper, we report the synthesis and structure analysis of $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ prepared by hydrothermal technique. It was applied due to provide high homogeneity in the mixture of the precursors mainly different valency ions among Ti^{4+} and Mn^{3+}.

MATERIALS AND METHODS

Materials

The materials used in this research were $Bi(NO_3)_3.5H_2O$ (≥ 98,0 %, Sigma - Aldrich), $Sr(NO_3)_2$ (p.a ≥ 99,0 %, Merck), $Mn(NO_3)_2.4H_2O$ (98,5%, Merck), $La(NO_3)_3.6H_2O$ (Merck), $Ti(OC_3H_7)_4$ (97 %, Aldrich), NaOH, (Aldrich (99,9%)), and aquadest.

Instrumentation

The instruments used were *X*-ray diffraction (Simadzu XRD 7000), scanning electron microscopy (SEM JEOL JSM-6360LA).

Procedure

Synthesis of the four-layers Aurivillius phases $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ were done by using $Bi(NO_3)_3.5H_2O$, $Sr(NO_3)_2$, $Mn(NO_3)_2.4H_2O$, $La(NO_3)_3.6H_2O$, $Ti(OC_3H_7)_4$ as the precursors. All precursors were balanced with stoichiometric quantities (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) and dissolved by 60 mL of NaOH 3 M. The solution was stirred for 2 hours and then insert into autoclaf. The samples were heated at temperature of 240 ^oC for 72 hours. The precipitate was obtained by filtration and washed by aquadest for several times to remove the base residue. Further, the products were heated at temperature 110 ^oC for 6 hours and calcined at temperature 550 ^oC for 5 hours. Then, the products were sintered at temperature 900 ^oC for 4 hours. The formation of phase oxide was confirmed by powder XRD (Simadzu XRD 7000). The LeBail refinement of the X-ray data was performed using the RIETICA program. The surface morphology of products was characterized by scanning electron microscopy (SEM) using JEOL, JSM-6360LA instrument.

For the measurement of the dielectric constant, the powders were pressed into pellets and heated at 800 °C for 12 hours to form a ceramic. The ceramic pellets coated with silver paste as electrodes. Dielectric properties were measured by using LCR meter (Hioki 3532-50 type) with a voltage of 1 V in the room temperature at various frequencies

ISSN: 0975-8585

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ powders with x = 0, 0.2, 0.4, 0.6, 0.8 and 1 prepared by hydrothermal technique are given in Figure 1. In general, these patterns matched with the XRD pattern of the four-layers Aurivillius phase as reported in [8,11] with an orthorhombic structure and space group $A2_1am$ indicated by appearance of the peaks with the high intensity around 2θ = 13.02°, 17.27°, 21.60°, 23.34°, 24.16°, 25.74°,26.19°, 27.89°, 30.45°, 33.02°, 39.20°, 39.63°, 47.27°, 47.92°, 52.00°, 57.22°. The single phase of the four layers Auriillius was only observed for the x = 0.6. The samples with x < 0.6 showed additional phase identified as perovskite phase indicated by 2θ around 32.53° [12]. It decreased with increasing of x. Meanwhile for the samples with x ≥ 0.8, the four layers Auriillius mixed with the three layers Aurivillius ($Bi_4Ti_3O_{12}$) [13] indicated by appearance of the peak around 2θ = 10.81° and $Bi_2Mn_4O_{10}$ phase [14] indicated by appearance of the peaks around 2θ =15.30°, 28.56°, and 33.55°.

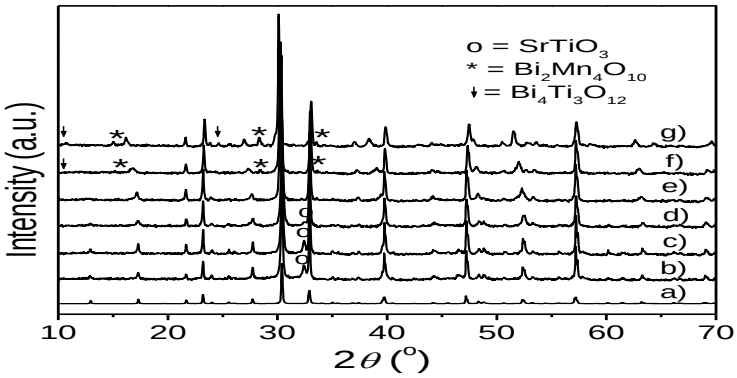

Figure 1: X-Ray Diffraction (XRD) patterns of Aurivillius phases $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ were synthesized by hydrothermal technique. a) $SrBi_4Ti_4O_{15}$ [11], b) x = 0, c) x =0.2, d) x = 0.4, e) x = 0.6, f) x = 0.8, g) x = 1.

X-ray data of the single phase of four layers Aurivillius $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ with x = 0.6 was refined by Lebail technique using $A2_1am$ space group [8] and the fitting results of refinement are shown in Figure 2. It can be seen that the profile are in agreement between the models applied with the data of the sample. The cell parameters of sample x = 0.6 refined by Lebail technique are given in Table 1. The ratio of lattice constants b/a is 0.9990 indicating the orthorombic of the sample very small and closer to tetragonal structure. The direction of the orthorhombic for this sample is along the a axis of the cell.

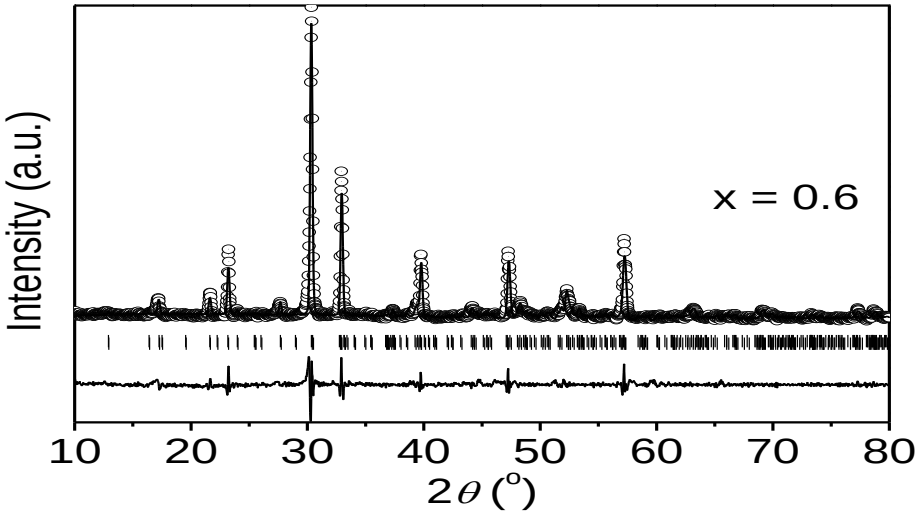

Figure 2: Le Bail plot of XRD powder of $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ with x = 0.6 synthesized by hydrothermal technique. Observed XRD intensity (circle), calculated data (solid line), and the difference of patterns, y_{obs} - y_{cal} (solid line on the bottom curve). The tick marks represent the positions of allowed Bragg reflections in the phase of $A2_1am$.

ISSN: 0975-8585

Table 1: Cell Parameters of $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ with $x = 0.6$ refined from XRD using the space group $A2_1am$.

Cell Parameters	Sample
a (Å)	5.4461(4)
b (Å)	5.4405(5)
c (Å)	41.0336(5)
V (Å^3)	1215.8(2)
b/*a*	0.9990
Z	4
R_p (%)	4.11
R_{wp}(%)	5.52
χ^2	2.219

The morphologies of samples $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ with x = 0.6 were observed by SEM as shown in Figure 3. It can be seen that the profile products are a plate-like aggregate crystals, typical of layered compounds belonging to the Aurivillius phase.

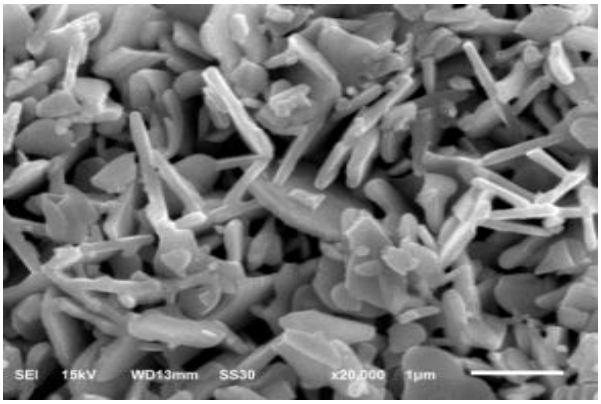

Figure 3: SEM micrographs of $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ with x = 0.6 synthesized by hydrothermal technique.

The frequency dependence of the dielectric constant at room temperature for $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ with x = 0.6 is shown in Figure 4. At low frequency the dielectric constant has a high value and decreases with increasing frequency and become constant for frequency ≥ 10 kHz. It is known that increasing of dielectric constant with decreasing frequency can be caused by the interface of two electrically different regions of space charge (interfacial) polarization [15]. The value of dielectric constant at 1 MHz is around 11. This value is relatively small for a ferroelectric compounds. The small of dielectric constant is predicted due to the appearance of Mn^{4+} which is same valence as Ti^{4+}. The Increasing of Mn^{4+} increases conductivity of the sample via double exchange interaction between Mn^{3+} and Mn^{4+} and leading to a decrease in dielectric constant [16].

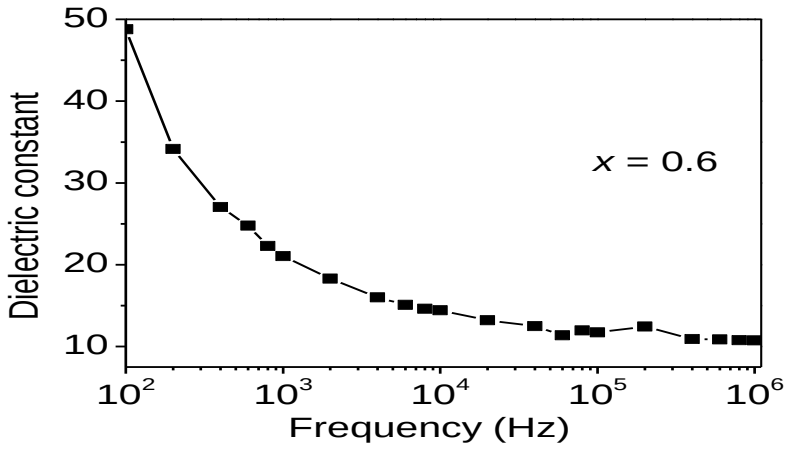

Figure 4: Frequency dependence of dielectric constant of $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ with x = 0.6 synthesized by hydrothermal technique.

ISSN: 0975-8585

CONCLUSIONS

The four layers Aurivillius compounds of $Sr_{1-x}Bi_{3+x}LaTi_{4-x}Mn_xO_{15}$ (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) have been prepared by hydrothermal technique. Single phase Aurivillius compound with space group $A2_1am$ was found for the sample with x = 0.6. The sample with $x < 0.6$ showed the four layers Aurivillius mixture with perovskite phase. Meanwhile, the samples with $x \geq 0.8$ contained impurities identified as $Bi_4Ti_3O_{12}$ and $Bi_2Mn_4O_{10}$ phases. The dielectric constant value of the sample with x = 0.6 is small might be related with double exchange interaction between Mn^{3+} and Mn^{4+} in the sample.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from Dirjen Dikti Kementerian Pendidikan dan Kebudayaan Republik Indonesia for Fundamental Research no kontrak 003/UN.16/PL/D-FD/I/2014. We acknowledge to Pusat Sains and Teknologi Bahan Maju (PSTBM)-BATAN Indonesia for using LCR meter instrument and Dr. Nandang Mufti (Universitas Negeri Malang, Indonesia) for discussion.

REFERENCES

[1] Scott JF, Paz de Araujo CA. Science 1989; 246: 1400-1405.
[2] Auciello O, Scott JF, Ramesh R. Phys Today 1998; 51: 22-27.
[3] Simoes AZ, Aguiar EC, Riccardi CS, Moura F, Longo E, Varela JA. J Alloys Comp 2009; 477: 85-89.
[4] Aurivillius B. Arkiv För Kemi. 1949; 1: 463-480.
[5] Subbarao EC. J Phys Chem Solids 1962; 23: 665-676.
[6] Santos VB, M'Peko JC, Mir M, Mastelaro VR, Hernandes AC. J European Ceram Soc 2009; 29: 751-756.
[7] Kim KT, Kim CI. Mater Sci Eng B 2005: 118: 229–233.
[8] Zulhadjri, Prijamboedi B, Nugroho AA, Mufti N, Fajar A, Palstra TTM, Ismunandar. J Solid State Chem 2011; 184: 1318-1323.
[9] Zulhadjri, Prijamboedi B, Nugroho AA Mufti N, Ismunandar. ITB J Sci 2011; 43 A: 139-150.
[10] Nalini G, Guru Row TN. Bull Mater Sci 2002; 25: 275-281.
[11] Hervoches CH, Snedden A, Riggs R, Kilcoyne SH, Manuel P, Lightfoot P. J Solid State Chem 2002; 164: 280-291.
[12] Jauch W, Palmer A. Phys. Rev B 1999; 60: 2961-2963.
[13] Shrinagar A, Garg A, Prasad R, Auluck S. Acta Crystallographica A 2008; 64: 368-375.
[14] Niizeki N, Wachi M. Zeitschrift fuer Kristallographie 1968; 127: 173-187.
[15] Ni WQ, Zheng XH, Yu JC. J Mater Sci 2007; 42: 1037-1041.
[16] Blasco J, Ritter C, Garcia J, de Teresa JM, Perez-Cacho J, Ibarra MR. Phys Rev B 2000; 62: 5609-5618.