

The Effect of Molar Ratio $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{NaCl}$ to Molten Salt Synthesis Method of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

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Abstract-

The plate-like morphology of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ get more attention from many researchers due to the effect of its morphology particle to some properties such as ferroelectric and photocatalyst. The molten salt synthesis is well known as the simple method to obtain the typical of particle morphology such as plate-like particle. The plate-like particle of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was successfully synthesized using molten salt synthesis method at various molar ratio $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{NaCl}$ of 1:4, 1:6, 1:8 and 1:10. X-ray diffraction data showed that single phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was successfully obtained. Based on scanning electron microscopy images, the higher of molar ratio $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{NaCl}$ results the bigger of plate-like particle size of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

Keywords—

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$, molten salt synthesis method, molar ratio $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{NaCl}$, the plate-like particle

I. INTRODUCTION

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) is a three layered aurivillius compound. Aurivillius compound composed of bismuth layer $(\text{Bi}_2\text{O}_2)_2^+$ and perovskite layer $(\text{Am-1BmO}_{3m+1})_2$, which m indicate amount of perovskite layers (Rosyidah, et.al., 2008, Moon, et.al., 2002). Cation A is large cation such as Na^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Bi^{3+} , whereas cation B is highly charged cation such as Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} , or Mo^{6+} (Aurivillius, 1949). Aurivillius compound is noted to have ferroelectric properties at high temperature (675°C) and potentially as Ferroelectric Random Access Memory (FRAM) as well as sensor and actuator (Jardiel, et.al., 2008).

Recently, BIT have been widely synthesized in plate-like forms, due to particles with plate-like forms affect the physical properties such as ferroelectric, piezoelectric and dielectric (Saito, et.al., 2006). Moreover particle shape also affect the photocatalytic activity. Wang, et.al. (2011) dan Zhao, et.al. (2014) mention that particle shape such as whisker and plate-like can affect the photocatalytic activity. Therefore many studies do various ways to get typical morphology particle. One of method that widely used is molten salt method.

Molten salt method is one of method to form ceramic powder that involves molten salt as a medium to arrange oxide complex from precursor (oxide and carbonate). This method is modification of powder metallurgical method, while molten salt as solvent for controlling powder characteristics such as shape and size (Kimura, et.al., 2006). The profit of molten salt method is easy to do, provident, and effective to obtaining pure crystal (Zhou, et.al., 2007). He, et.al. (2014) reported that change of the mole ratio salt/BIT affect the growth rate of plate-like shape. The increase mole ratio of salt ($\text{NaCl}:\text{KCl}$):BIT from 4:1, 8:1, 16:1, 32:1, 40:1 and 50:1, the average width of BIT partiles are 1,8; 1,4; 1,0; 0,8 and 0,5 μm . The increase mole ratio from 4 to 16 causes a decrease the average of particle thickness (from 150 nm to 75-90 nm), whereas the increase mole ratio from 32:1 to 60:1 cause the particle thickness to 55 nm.

Salt that widely used in molten salt synthesis method is NaCl . Zhou, et.al., (2007) reported that synthesize aurivillius compound BaC_2O_4 using NaCl obtain 93,3% of purities, whereas synthesis non-salt only obtain on 69% of purities. Compare with other salt, NaCl has many advantages such as inexpensive and obtain high purity BIT. So in this research will be synthesize the BIT compound with mole ratio

NaCl/BIT and expected to know the best mole ratio of NaCl/BIT to obtain plate-like particle using molten salt method. Structure evolution of formed compound will be studied using X-rsy diffraction pattern, whereas morphology particle confirmed using Scanning Electron Microscopy (SEM) data.

II. EXPERIMENTAL

Precursor consisting 2 moles of Bi₂O₃ and 3 moles of TiO₂ weighed in stoichiometry (to obtain Bi₄Ti₃O₁₂ 4 grams). Grinded Bi₂O₃ and TiO₂ on mortar agate for 1 hour with added acetone to homogenize the compound. Calcined the compound at 700 oC for 24 hours aim to increase the melting point. Mixed the compound with NaCl with various mole ratio BIT:NaCl = 1:4, 1:6, 1: 8 and 1: 10. Grinded the compound on mortar agate for 1 hour and added acetone. Mixture is grinded on mortar agate for 1 hour and added asetone. Put down the compound in alumina crucible and calcined at 900oC for 6 hours (Marella, 2017 and He, et.al., 2014). Washed the compound for several times used warm aquades to remove NaCl. Identified salt content with added AgNO₃ solution.

III. RESULT AND DISCUSSION

The XRD technique is used to determine the phase of the sample. The diffraction pattern of the BIT sample is showed in Figure 4.1. The XRD pattern shows that the synthesized BIT peaks are similar to the BIT standard based on ICSD 159929. This shows that the components formed have a single phase and no impurities. The mole ratio of salt influences of the intensity and peak position. The crystallinity of BIT compounds increases with the increasing ratio of mole. The peak position corresponds to the size of the crystal. The typical peak of the BIT compound is at $2\theta = 30$. If the peak is enlarged it will look clamped like Figure 1.

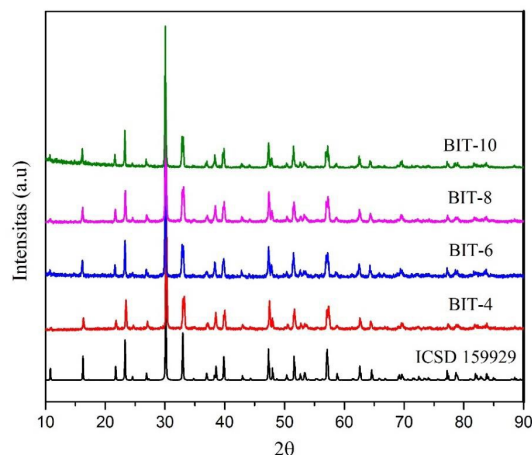
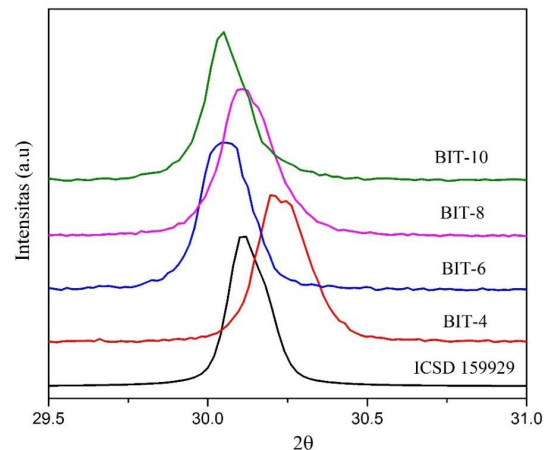


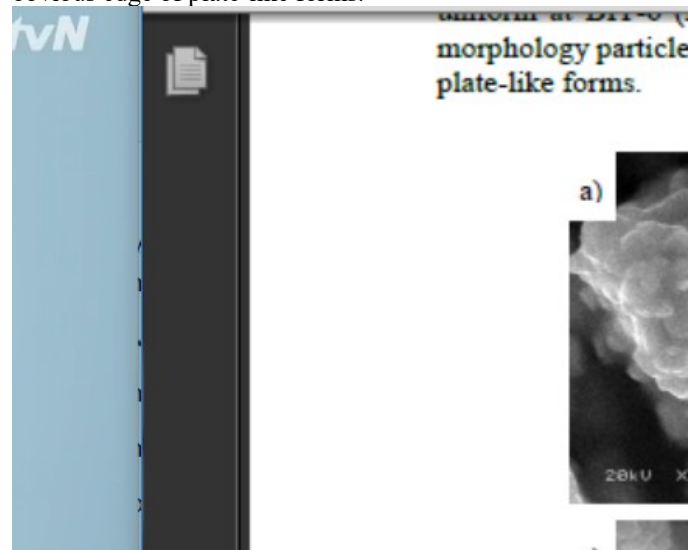
Figure 1. XRD pattern of the BIT-4, BIT-6, BIT-8 and BIT-10



Gambar 2. Magnification of the diffractogram at an angle $2\theta = 29,5o-30,1o$

Figure 2. shows that the increase in the mole ratio causes the peak to shift to the left. This shows the difference in the size of the crystals formed by the influence of the salt mole ratio. The larger particle size causes the peak to shift to the left, because the distance between the crystal fields is farther away.

Morphology particle of BIT synthesis showed in Figure 4.5 and characterization using SEM describe that morphology particle has plate-like forms at ratio BIT-4, BIT-6, BIT-8, or BIT-10. Morphology particle describe that size of plate-like BIT increases with increasing moles ratio of salt. BIT-4 plate-like shaped small and random (Figure 4.5a), then particle size start to appear uniform at BIT-6 (Figure 4.5b) and at BIT-8 the size is increasing (Figure 4.5c). The best morphology particle of BIT showed at BIT-10 (Figure 4.5d) with the perfect and obvious edge of plate-like forms.



Gambar 3. SEM images of the morfologi plate-like a) BIT-4, b) BIT-6, c) BIT-8 dan d) BIT-10

Increased mole ratio causes increasing the particle size of plate-like BIT due to increasing the solubility of precursor and causes the particles size get smaller. In high saturation condition and stimulate the edge nucleation process, that is crystal thickness growth. If many dissolved particles have undergone particle nucleation, the level of saturation decreases. As a result the thickness of crystal doesn't change, but the growth of epitaxiation (surface) occurs. Appropriate with report from Zhao, et.al., (2014) that the average of particle size affected by diffusion coefficient, solubility, and particle surface.

IV. CONCLUSIONS

Bi₄Ti₃O₁₂ (BIT) compound has been synthesized from Bi₂O₃ and TiO₂ (anatase) precursors using molten salt method. The increase in the mole ratio of BIT-4, BIT-6, BIT-8 and BIT-10 does not affect the phase of the compound formed, this is indicated by the peak suitability of the ICSD standard of BIT 159929 in X-ray diffraction technique data. In addition, the morphology of the particles displayed by scanning electron microscopy (SEM) data shows that the particle size increases as the mole ratio increases.

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