DOI: 10.21776/ub.jpacr.2021.010.01.570 *J. Pure App. Chem. Res.*, **2021**, 10 (1), 64-71
01 May 2021

The Effect of Synthesis Temperature on the Plate-Like Particle of $Bi_4Ti_3O_{12}$ Obtained by Molten NaCl Salt Method

Sheley Dea Marella,[1] Nur Aini,[1] Arie Hardian,[2] Veinardi Suendo,[3,4] Anton Prasetyo[1*]

[1]Department of Chemistry, Faculty of Science and Technology, Universitas Islam Negeri Maulana Malik Ibrahim Malang, Jl. Gajayana 50, Malang, Indonesia, 65144.
[2]Department of Chemistry, Universitas Jenderal Ahmad Yani, Cimahi, Indonesia
[3]Division of Inorganic and Physical Chemistry, Faculty Mathematics and Natural Sciences, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia
[4]Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia

[*]Corresponding email: anton@kim.uin-malang.ac.id

Received 23 September 2020; Accepted 01 May 2021

ABSTRACT

Three-layer Aurivillius compound bismuth titanate ($Bi_4Ti_3O_{12}$) is well known for having interesting properties such as ferroelectric and photocatalyst. Many researchers reported that the unique plate-like shaped particle affecting ferroelectric and photocatalyst properties. The molten salt synthesis is the common simple method to obtain that unique morphology. In this research, $Bi_4Ti_3O_{12}$ was synthesized using single molten salt NaCl at various temperatures, which is 800, 850, 900, and 950 °C. X-Ray Diffraction data showed that all obtained $Bi_4Ti_3O_{12}$ have a B2*cb* space group with no impurities detected. The Raman spectra shows the characteristic vibration modes of $Bi_4Ti_3O_{12}$ at 62, 117, 228, 269, 332, 364, 536, 851 cm^{-1}. The plate-like shaped particle was confirmed by SEM analysis. Based on SEM images, the size of the particle increases as the synthesis temperature increased, which is due to the thermal effect on grain growth.

Keywords: Bismuth titanate, synthesis temperature, molten salt synthesis, plate-like shaped particle

INTRODUCTION

Aurivillius-structure compound has got more attention due to interesting properties such as ferroelectric, photocatalytic, and luminescence properties [1-3]. Aurivillius structure compound consists of two-layered structure: (a) pseudo perovskite structure layer, and (b) bismuth oxide layers with the general formula $(Bi_2O_2)^{2+}$ $(A_{m-1}B_mO_{3m+1})^{2-}$. *A* is bigger cations with a low charge such as Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, and Bi^{3+}, whereas *B* is smaller cations with a high charge such as Fe^{3+}, Ti^{4+}, Ta^{5+}, dan W^{6+}, and *m* represent the number of perovskite layer [4,5]. $Bi_4Ti_3O_{12}$ (BIT) is one of three-layered Aurivillius compound family member that is potentially applied as ferroelectric materials, and recently, many researchers reported the possibility of being applied as photocatalysts [6-8].

Plate-like morphology in the grain particles of the Aurivillius compounds was reported to affect their ferroelectricity properties [9]. As photocatalyst materials, the particle morphology of Aurivillius compounds also influences their photocatalytic properties [10-12]. It is well known that a smaller particle size has higher photocatalytic activity. In addition, many researchers also reported that the particle morphology also correlated to the photocatalytic

The journal homepage www.jpacr.ub.ac.id
p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

activity [13]. Lin et al. (2012) successfully synthesized BIT with microsphere morphology using a hydrothermal method, and reported that photocatalytic activity of BIT is higher than that of TiO_2-N [14]. Meanwhile, Zhao et al. (2013) also reported that plate-like particle of BIT has higher photocatalytic properties than TiO_2 [12]. It is suspected that the morphology of particles is strongly affecting its photocatalytic activity.

Molten salt synthesis (MSS) method is a simple method to synthesize particle with typical morphology such as whisker, microsphere, and plate-like. MSS method uses molten salt as a reaction medium of the precursors. Other advantage of MSS method is it only requires a lower temperature of synthesis. There are many factors that affecting the MSS method, i.e. (a) synthesis temperature, (b) flux salt type, and (c) oxide to salt ratio [15]. In previous reports, many researchers used the salt mixtures, such as NaCl-KCl and Na_2SO_4-K_2SO_4, to synthesize BIT. Zhang and Guo (2012) synthesized BIT by the MSS method, and used NaCl-KCl mixture at different calcination temperature. They reported that the agglomeration was observed on the BIT plate-like particles, and resulting in larger particles at higher calcination temperature [16]. Meanwhile, Zhao et al. (2014) reported that the BIT plate-like particles were obtained from the MSS method with Na_2SO_4-K_2SO_4 salt mixture. They also reported that larger plate-like particles were obtained at higher calcination temperature [17].

NaCl is one of the salt that widely used in the MSS method with many advantages such as abundant in nature, inexpensive, and non-toxic. Our group had synthesized the BIT using molten NaCl only in various synthesis time, and successfully produced BIT plate-like particles, in which the longer synthesis time the larger particles size produced [18]. This result indicates that NaCl has a great opportunity to be widely used in the BIT synthesis. Therefore, the study to optimize the synthesis parameters are necessary. In this paper, effect of synthesis temperature on BIT particles synthesized using single molten NaCl is studied.

EXPERIMENT

Chemicals and instrumentations

Bismuth oxide (Bi_2O_3) (Sigma-Aldrich), titanium (IV) oxide (TiO_2) (Sigma-Aldrich), and sodium chloride (NaCl) (Merck) were analytical grade, and used without further purification.

X-ray diffraction (XRD) characterization was performed by Panalytical Xpert-pro diffractometer using Cu-Kα radiation from 2θ (°) of 10–90 at room temperature. The result was compared by the Inorganic Crystal Structure Database (ICSD) number 1559929, and refined using Rietica software with the Le-Bail method [19]. The Raman spectra were measured using Bruker-Senterra spectrometer at spectral range 30-1560 cm^{-1} with resolution of ~3-5 cm^{-1}. The excitation source of Raman spectrometer is 532 nm (green laser). The particles morphology was captured using Scanning Electron Microscopy (SEM) JEOL-JSM-6510L with magnification between 2000-10000×.

Reaction Procedure

The target mass of all samples are 3 g. Consequently, the precursor requirement is: 2.3859 g of Bi_2O_3, and 0.6136 g of TiO_2 (mol ratio 2:3). All of precursors were grinded in an agate mortar for an hour, and added acetone (nonstoichiometric calculation) to get a more homogeneous mixture. The mixture was placed onto the alumina crucible, and then heated at 700 °C for 6 hours. NaCl (2,3598 g) was added into the mixture with a molar ratio to the $Bi_4Ti_3O_{12}$ of 1:15.8, then the mixture was grinded once again for an hour in the addition of 1 mL acetone, and calcined at various temperatures of 800, 850, 900, and 950 °C for 4 hours.

The journal homepage www.jpacr.ub.ac.id
p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

The samples were then cooled down to 500 °C with cooling rate of 2 °C/min, and continuously cooled down to room temperature without further control on the cooling rate. The removal of salt content in the sample was carried by washing the mixture several times by hot deionized water.

RESULT AND DISCUSSION

Figure 1 shows the XRD pattern of the synthesized $Bi_4Ti_3O_{12}$, which obtained from the molten salt synthesis using NaCl at various calcination temperatures of 800, 850, 900, and 950 °C. XRD data shows that the pure $Bi_4Ti_3O_{12}$ was obtained with no impurities. All peaks in the XRD pattern of the samples can be indexed to the International Crystallography Standard Data (ICSD) No. 35-0795 (BIT database with space group *B*2*cb*). The XRD data of BIT obtained at the highest calcination temperature (950 °C) indicates that this sample has less crystallinity than that of other samples. This due to the growth of crystal at higher temperature is quicker which resulting in irregular atoms packing. Therefore, samples that synthesized at higher temperature tend to have low crystallinity.

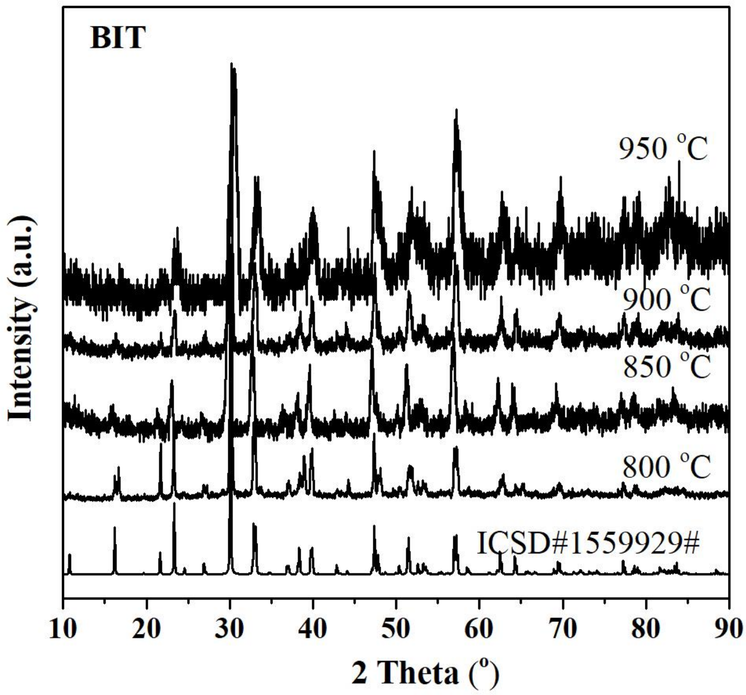

Figure 1. Powder X-Ray Diffraction Pattern of BIT Synthesized by Molten NaCl Salt at Various Temperatures: 800, 850, 900, and 950 °C.

XRD database of BIT (ICSD No. 27-0595) with space group B2*cb* was refined using The Le-Bail method. An XRD pattern intensities may overlaps due to the symmetry, or near-equivalence d-values for nonequivalent reflections. Pattern decomposition using Le Bail method adjust the intensity of the reflections, instead of structural paramenters to calculate diffraction pattern [20]. Figure 2 shows the fitting results of X-ray diffraction refinement data of all of the samples. The refinement results are shown in Table 1, in which the obtained cell parameters of all samples (*a*, *b*, and *c*) are relatively identical. The R_p value for sample 950 °C is higher than the others. It corresponds to (a) the noise of XRD data of the 950 °C sample,

The journal homepage www.jpacr.ub.ac.id
p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

which is high, and (b) The degree of crystallinity of the sample synthesized at 950 °C, which is less than the others.

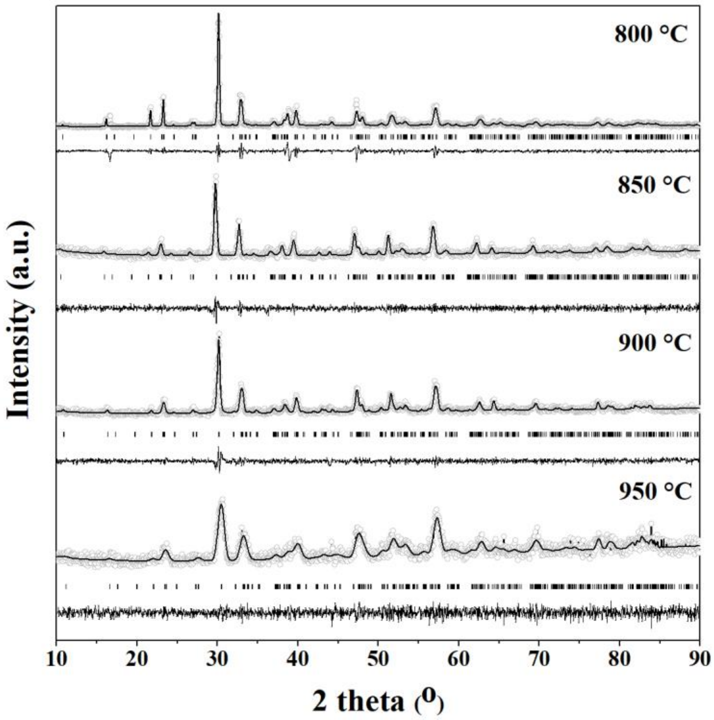

Figure 2. Plot of Le Bail of X-Ray Diffraction Pattern of BIT Synthesized by Molten salt method using NaCl at Various Temperatures of 800, 850, 900, and 950 °C.

Table 1. The Refinement result of XRD sample data using Le-Bail Method

Parameter	Sample			
	800 °C	**850 °C**	**900 °C**	**950 °C**
a (Å)	5.421(1)	5.433(2)	5.439(2)	5.436(2)
b (Å)	5.418(1)	5.420(2)	5.424(1)	5.429(1)
c (Å)	32.698(7)	32.69(1)	32.71(1)	32.76(1)
R_p	12.23	13.91	12.89	15.02
R_{wp}	15.85	16.64	16.74	20.00
GoF	0.4049	0.04249	0.05770	0.02195

Figure 3 shows the Raman spectra of all BIT samples. The vibrational modes of the Aurivillius compound can be divided into two group: (a) vibrational modes at less than 200 cm^{-1} related to external modes of BO_6, and, (b) vibrational modes at higher than 200 cm^{-1}, which are related to internal modes of BO_6. Aurivillius structure has vibrational fingerprint mode at 60 cm^{-1}, representing the displacements of the Bi_2O_2 planes relative to perovskite-like blocks. The Raman spectra of BIT samples obtained are appropriate to previous works by other researchers. List of vibration modes, and the BIT sample's peak position are tabulated in Table 2. This Raman spectra is identical to the Raman spectra of BIT in other works, which indicated that BIT has synthesized with no impurities, and suitable for XRD data [21-25]

The journal homepage www.jpacr.ub.ac.id
p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

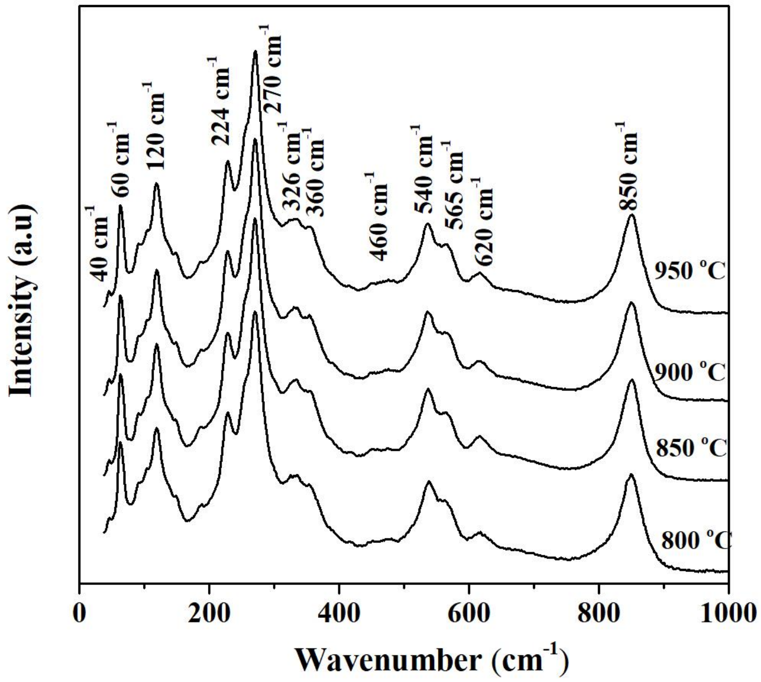

Figure 3. The Raman spectra of BIT Synthesized by Molten salt method using NaCl at Various Temperatures of 800, 850, 900, and 950 °C.

Table 2. List of vibration modes of BIT samples [21-25]

Peak Position (cm^{-1})	Assignment
40	*A*/Bi-site cation displacement
60	Rigid layer (*RL*) mode
120	Translational mode of Bi or Ti
224, 270	TiO_6 bending
326, 360	The bending-stretching vibration TiO_6
460	Ti-O torsional mode
540, 565, 620	TiO_6 stretching mode
850	TiO_6 symmetric stretching

The journal homepage www.jpacr.ub.ac.id
p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

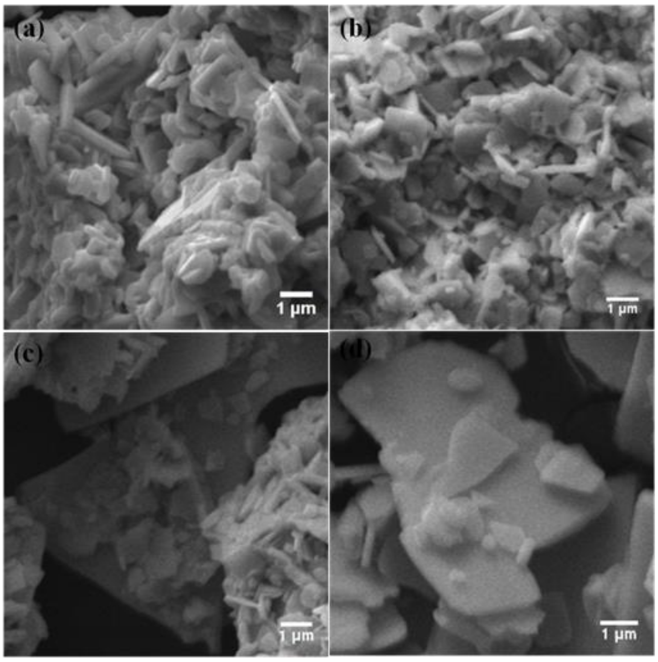

Figure 4. SEM Image of BIT Synthesized by Molten salt method using NaCl at Various Temperature of (a) 800, (b) 850, (c) 900, and (d) 950 °C.

The typical morphology of all BIT samples is shown in Figure 4. The shape of the BIT sample is plate-like. It can be seen that the BIT particles in the samples at 800 and 850 °C are smaller, and become larger at the higher temperature. This phenomenon relates to crystal, growth mechanism in MSS. There are two main stages in growth particle i.e. (a) nucleation, and crystal growth, and (b) particle growth. The particle size was influenced by the step of nucleation, and crystal growth rate [26-27]. In this case, the nucleation rate is faster at lower temperatures (800 and 850 °C). As a results, the reactions at 800 and 850 °C produces a lot of smaller particle size due to the fast formation of crystal nuclei or seeds. Meanwhile, the crystal growth rate is faster at higher temperatures (900 and 950 °C); therefore, the size of particles obtained at 900 and 950 °C is significantly larger. In addition, at higher temperatures, the atomic diffusion rate becomes higher that results in the enlargement of the BIT plate-like particle size [17].

The second stage of particle growth is mainly occurred in cooling down process. The controlled cooling down treatment to 500 °C give the appropriate energy to the sample to absorb the other particles, and arrange their morphology in order, and resulting bigger particle size [28]. In previous study, single salt NaCl had shown to limiting the accelerating effect on crystal formation [29]. On the other hand, the high temperature of calcination increase the rate of the BIT particle nucleus. Both two effect resulting anisotropic growth of the particle, and consequently the morphology of the grain changes to plate like particle.

CONCLUSION

The effect of temperature on the molten salt synthesis of BIT using single salt, NaCl was studied. The single-phase BIT with plate-like particle shape was obtained. At lower temperature (800-850 °C), crystal nucleation was faster, and resulted in smaller particle size; while at higher temperature (900-950 °C), crystal growth, and diffusion rate were faster, and

The journal homepage www.jpacr.ub.ac.id
p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

resulted in bigger particle size. However, the appearance of molten NaCl in reaction medium tend to limit the acceleration of crystal formation, and compete with the calcination effect at the same time, therefore, induced the anisotropic growth, and resulted in plate like morphology.

ACKNOWLEDGMENT
This work was financially supported by Bantuan Penguatan Program Studi (P3S) 2017 dan Bantuan Publikasi Ilmiah 2018 Faculty of Science and Technology, Universitas Islam Negeri Maulana Malik Ibrahim Malang.

REFERENCES

[1] De Araujo, C.P., Cuchiaro, J.D., McMillan, L.D., Scott, M.C., and Scott, J.F., *Nature*, **1995**, 374(6523), 627-629.
[2] Liu, X., Xu, L., Huang, Y., Qin, C., Qin, L., and Seo, H.J., *Ceram. Int.*, **2017**, 43(15), 12372–12380.
[3] Yu, L., Hao, J., Xu, Z., Li, W., Chu, R., Li, G., *Ceram. Int.*, **2016**, 42(13), 14849–14854.
[4] Aurivillius, B., *Ark. Kemi Band I*, **1949**, 54, 463–480.
[5] Aurivillius, B., *Ark. Kemi Band I* **1949**, 58 499–512.
[6] Khomchenko, V.A., Kakazei, G.N., Pogorelov, Y.G., Araujo, J.P., Bushinsky, M.V., Kiselev, D.A., Kholkin, A.L., and Paixao, J.A., *Mater. Lett.*, **2010**, 64(9), 1066–1068.
[7] Osada, M., Tada, M., Kakihana, M., Noguchi, Y., and Miyayama, M., *Mater. Sci. Eng., B.*, **2005**, 120(1-3), 95–99.
[8] Withers R.L., Thompson J.G., and Rae A.D., *J. Solid State Chem.*, **1991**, 94(2), 404–417.
[9] Nunes L.M., Antonelli, E., Bernardi, M.I.B., Oladeinde, T.O., Caceres, J.A.S., and M'Peko, J.C., *Mater. Res. Bull.*, **2011**, 46(1), 136-139.
[10] Chen, Z., Jiang, X., Zhu, C, and Shi, C., *Appl. Catal. B.*, **2016**, 199, 241–251.
[11] Zhao, X., Yang, H., Li, S., Cui, Z., and Zhang, C., *Mater. Res. Bull.*, **2018**, 107, 180-188.
[12] Zhao, W., Jia, Z., Lei, E., Wang, L., Li, Z., and Dai, Y., *J. Phys. Chem. Solids.*, **2013**, 74(11), 1604–1607.
[13] Arney, D., Porter, B., Greve, B., and Maggard, P.A., *J. Photochem. Photobiol. A.*, **2008**, 199(2-3), 230–235.
[14] Lin, X., Lv, P., Guan, Q., Li, H., Zhai, H., and Liu, C., *Appl. Surf. Sci.*, **2012**, 258(18), 7146–7153.
[15] Akdogan, E.K., Brennad, R.E., Allahverdi, M, and Safari, A., **2006**, *J Electroceram*. 16(2), 159–165.
[16] Zhang, C.S., and Guo, C.J., *Adv. Mater. Res.*, **2011**, 239–2422, 2170–2173.
[17] Zhao, Z., Li, X., Ji, H., Deng, M., *Integr. Ferroelectr.*, **2014**, 154, 154–158.
[18] Januari, T., Aini, N., Barorroh, H., dan Prasetyo, A., *IOP Conf. Ser.: Earth Environ. Sci.* **2020**, 456, 012013.
[19] Hunter, B.A., and Howard, C.J., A computer program for Rietveld analysis of X-ray and neutron powder diffraction patterns, Lucas Heights Research Laboratories, NSW, Australia, **2000**,1–27.
[20] Ladd, M.F.C., and Palmer, R.A., *Structure Determination by X-ray Crystallography.*, **1977**, New York, Plenum Press.
[21] Dobal, P.S., and Katiyar, R.S., *J. Raman Spectrosc.*, **2002**, 33(6), 405–423.

The journal homepage www.jpacr.ub.ac.id
p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

[22] Prasetyo, A., Mihailova, B., Suendo, V., Nugroho, A.A., and Ismunandar., *J. Appl. Phys.* **2015**, 117.
[23] Prasetyo, A., Mihailova, B., Suendo, V., Nugroho, A.A., Zulhadjri, Ismunandar, *IOP Conf. Ser: Mater. Sci. Eng.*, **2017**, 196(1), 012041.
[24] Du, Y.L., Zhang, M.S., Chen, Q., and Yin, Z., *Appl. Phys. A. Mater.*, **2003**, 76(7), 1099-1103.
[25] Ranieri, M.G.A., Aguiar, E.C., Cilense, M., Simões, A.Z., and Varela, J.A., *Cer. Int.*, **2013**., 39(7), 7291-7296.
[26] Mullin, J.W., *Crystallization*, Butterworth-Heinemann, **2001**, London, UK.
[27] Meir, R., Vradman, L., Zana, J., and Herskowitz, M., *Mater. Chem. Phys.*, **2019**, 231, 181-187.
[27] Jiang, D., Zhou, Z., Liang, R., and Dong, X., *J. Eur. Cer. Soc,* **2021**, 41-2, 1244-1250.
[28] Liu, C., Liu, X., Hou, Z., Jia, Q., Cheng, B., and Zhang, S., *Mat*, **2020**., 13-70.

The journal homepage www.jpacr.ub.ac.id
p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733