Molten Salt Synthesis and Structural Characterization of $BaTiO_3$ Nanocrystal Ceramics

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Abstract. A new synthesis route to obtain high-purity barium titanate powder, $BaTiO_3$, using the molten salt method by reacting the raw materials ($BaCO_3$ and TiO_2) in an atmosphere of molten NaCl and KCl, has been developed. The synthesized $BaTiO_3$ ceramic particles have been successfully carried out at the sintering temperature 950^{o}C for 4 hours. The Rietveld refinement of the XRD diffraction patterns was employed to characterize the structural information of the nanocrystalline $BaTiO_3$ ceramics. The lattice parameters (a=4.0043 Å, b=4.0308Å with space group P4mm) of tetragonal perovskite structure, as an indication of piezoelectric characteristics, have been successfully determined by the Rietveld refinement. While the crystallitte particle size and strains have been obtained for the values of 110.6 nm and 0.74 % respectively

1. Introduction

One of the ferroelectric materials is barium titanate ($BaTiO_3$) and has been a concern for several decades because of the attractive properties. Something interesting can be shown that it is chemically and mechanically very stable, and has also ferroelectric properties above room temperature. Therefore it can be easily prepared and applied in the form of a ceramic polycrystalline sample [1,2]. Material $BaTiO_3$ is also a strong candidate for the field induced piezoelectric transducers, due to their high polarization, high permittivity and large induced strain achievable [3]. Therefore to obtain good performance of materials, synthesis process which produces the perovskite crystal structure with a small particle size and uniform is needed.

The chemical formula of $BaTiO_3$, namely BT, is derived from an oxide of barium and titanium. It has five phases as a solid, listing from low temperature to high temperature: rhombohedral, orthorhombic, tetragonal, cubic and hexagonal crystal structure. Three of them show the piezoelectric effect, except cubic and hexagonal. At room temperature, BaTiO3 adopts a tetragonal perovskite type structure and high permittivity.It transforms to the cubic, paraelectric state at the Curie temperature,T_C, of approximates to 130 ^{0}C.

To improve the quality of materials (micro- and nano- $BaTiO_3$) has made various approaches to the process of synthesis which include a sol-gel [4], hydrothermal [5], high-temperature solid-state reaction [6,7], and the method of microwave synthesis method [8,9]. In order to synthesize nano-$BaTiO_3$, a low sintering temperature and a short isothermal holding (time) are both critical. In this study, we try to discuss the synthesis of the piezoelectric material with molten salt method which is

used to prepare $BaTiO_3$ fine powder. And so we will try to analyze the crystal structure of the synthesized product using the Rietveld refinement of X-ray diffraction (XRD) pattern in this study.
Common examples of the salt in the synthesis are molten salts of chloride and sulfate. In many experiments, the eutectic composition (0.5 NaCl - 0.5 KCl) of a mixture of salt is oftenly used and has a temperature lower than the temperature of liquid formation. While the melting point of NaCl and KCl are 801 °C and 770 °C, respectively, and for the eutectic composition is 650 °C [10,11]. At the heating temperature, the salt melts and the product particles form. The characteristics of the product powder are controlled by selecting the temperature and duration of the heating.

2. Experimental

Previously, the raw materials consisting of $BaCO_3$ (one mole) and TiO_2 (one mole) were mixed for $BaTiO_3$ and continued by grinding using a mortar for 4 hours. During grinding there were expected homogeneously mixed and particle size is getting smaller.The reaction mechanism in the molten salt method (MSS) is a little different from the solid-state reaction, due to the absence of the sample compaction, as long as the salt mixed in a reaction formation.

Carbonate and Oxides (as raw material, $BaCO_3$ and TiO_2) corresponding to a perovskite $BaTiO_3$ compound were mixed with salt of NaCl and KCl and then sintered at a temperature above the melting point (950 ^oC) of the salt. At this temperature, the oxides particles were rearranged and then diffused rapidly in a liquid state of the salt. With further sintering (during 4 hours), particles of the perovskite phase were formed through the nucleation and growth processes.

Schematic diagram of the molten salt method [7] is shown in figure 1. At the beginning a reaction batch was contained the reactants (raw materials) and salts. After the sintering process the existing salt was removed by washing with hot water repeatedly and then dried again. The chloride ions were detected by an $AgNO_3$ solution even after ten times of washing.

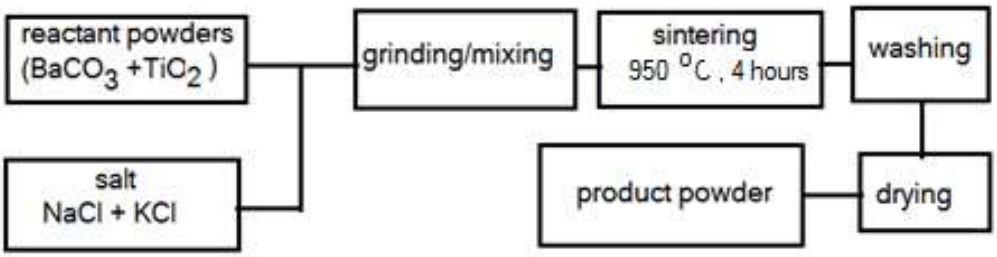

Figure 1. Preparation procedure in molten salt synthesis.

3. Result and Discussion

Regarding our experts in the preparation of ceramic powder, it was clear that the molten salt method that was used to obtain homogenous and ultrafine powder, whereas the conventional one (solid state reaction) needs high temperature of approximately (1000°C - 1400°C). Solid state reaction in this method was considered as an indirect method because the reaction was carried out in a molten salt directly between Ba^{+2}, Ti^{+4} and O^{-2} (diffuse) to obtain $BaTiO_3$ precursor. The synthesis products and materials used are clear by X-Ray Diffraction (XRD) as shown in Figure 2.

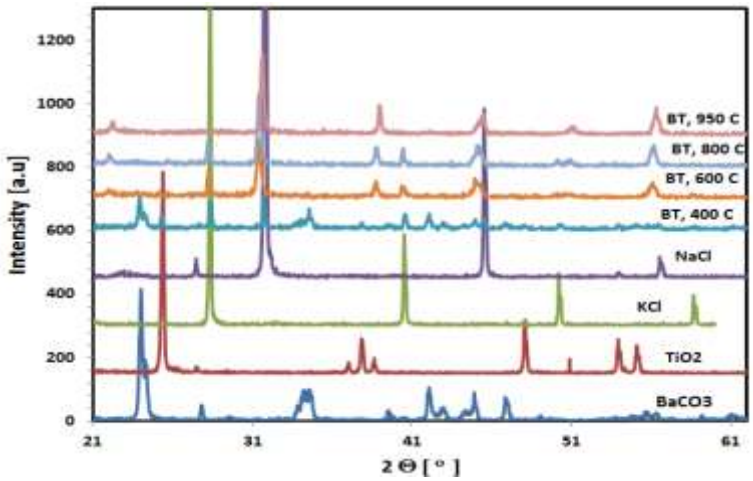

Figure 2. XRD pattern for the raw materials ($BaCO_3$ & TiO_2), the Salt (NaCl and KCl) and the sample prepared at the sintering temperature of 400, 600, 800, and 950 ^oC, respectively.

For the sample at sintering temperatureof 400, 600, 800 and 950 ° C (as the powder product), as shown at figure 2, the XRD patterns do not indicate the existence of raw material peaks of $BaCO_3$ and TiO_2 . However, samples at 400, 600 and 800 ^oC, that have not been washed with hot water, indicates the presence of NaCl and KCl peaks. And on the sample at 950 ^oC that has been washed does not show the peaks of the salt material. This means that the salt solution did not react with the sample. The resulting powder products show a distinct diffraction pattern to form new compounds. It explains that the synthesis process using molten salt method has been successfully carried out.

In the x-ray diffraction pattern for the sample at sintering temperature of 950 ^oC, we employed the Rietveld program to identify the crystal structure of the $BaTiO_3$ ceramic powder. The program also required and refined an approximate structural model for the actual structure. Firstly, we performed the Rietveld refinement based on the tetragonal perovskite crystal systems with space group of P4mm. The initial refinement was done by the zero-point shift, background and the unit-cell parameters.

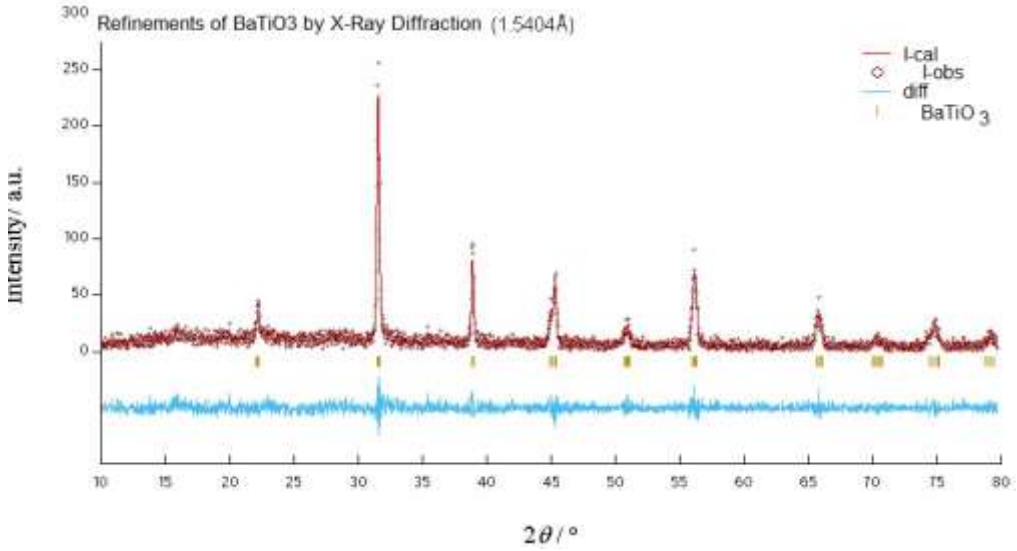

Figure 3. The structural refinement patterns of $BaTiO_3$ using X-ray powder diffraction.

The final results of this refinement were obtained the weighted R-factors of 33.63% (Rwp) and the goodness of fit indicator of 1.104 ($S=R_{wp}/R_e$). Figure 3 exhibits the Rietveld refinement (I_{cal}), experimental pattern (I_{obs}), differences (diff =I_{obs}- I_{cal}) and the peaks of diffraction planes.

Table 1. Structural parameters for $BaTiO_3$ obtained from the structural refinement using X-ray powder diffraction data at room temperature.

Symmetry and lattice parameter	Sites	Atomic coordinates		
Space group = P4mm		x	y	z
a = b = 4.0043(9) Å	Ba	0.5	0.5	0.5
c = 4.0308(12) Å	Ti	0	0	0
c/a = 1.0066	O(1)	0	0	0.475(69)
	O(2)	0.549(27)	0	0

So it could conclude that this approach may be suitable to determine the structural parameters for the nanocrystalline $BaTiO_3$ ceramics, such as lattice parameters, atomic coordinates, and isotropic thermal parameters (U_{iso}). Lattice parameters for the crystal system of perovskite tetragonal show that the value of a = 4.0043 Å and c = 4.0308 Å and has close to each other with the difference 0.66%.

The $BaTiO_3$ synthesis using different method (hydrothermal) by Song Wei Lu [12] has obtained cubic perovskite phase. It is possible to obtain a different phase, due to differences in lattice parameter for cubic (c/a = 1), while tetragonal (c/a~ 1) could close to cubic and also depends on the synthesis parameters performed. Cubic crystal system does not have piezoelectric properties. Diffraction pattern for standard cubic phase of $BaTiO_3$ [13], JCPDS No. 31-174, has a peak at diffraction angles (2□□ of about 31.5 and 45^o, representing the plane of (110) and (200), respectively. Figure 4 shows the experimental $BaTiO_3$ peaks indicates the overlap of the two peaks (blue dot) and also in other words the refinemenet results can also show spliting (red line and dot) into two peaks. While in this experiment we can exhibite the presence of $BaTiO_3$ tetragonal phase, because there is the existence of two overlapping peaks at between 31 to 32^o for planes of (101) and (110) and 44 to 47 ^{o} for planes of (002) and (200), as shown in figure 4. In same way, the analysis of the peaks of the x-ray diffraction patterns to clarify the tetragonal phase was also done by some researchers [14,15].

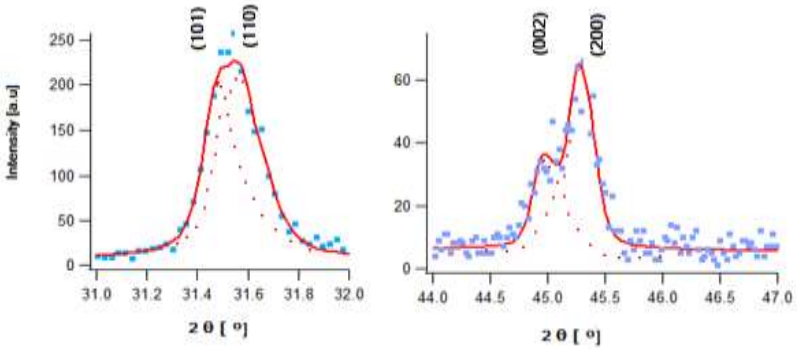

Figure 4. Peak broadening of BT nanocrystals (blue dot) and peak split of the tetragonal phase (red line-refinement out put and blue dot- experimeal data)

Polycrystalline aggregation formation during the synthesis process can also cause crystal defects. Deviations from perfect crystallinity can lead to broadening the diffraction peaks. Crystallite size and lattice strain are two main characteristics can be processed from the peak width analysis [16]. The size and strain can affect the peak broadening. By using **Williamson-Hall** analytical methods can estimate size-induced and strain as a function broadenings peak width and peak position 2θ [17,18]. The strain induced in powders due to crystal imperfection and distortion was calculated using the formula $\varepsilon = \beta/4\tan\theta$, where □ (full width at the half maximum, FWHM) was taken from the refinement results and

θ is the diffracted angle. With this approach, the Williamson_Hall plots can be drawn below in Fig. 5, and the examined formula [19,20] is given asfollows:

$$\beta \cos \theta = k\lambda/d + 4\,\varepsilon\{\sin \theta\} \quad (1)$$

where *d* is the crystallite particle size, (ε) elastic strain and k is Scherrer constant (somewhat arbitrary value that fall sin the range 0.87-1.0. We usually assume k = 1).

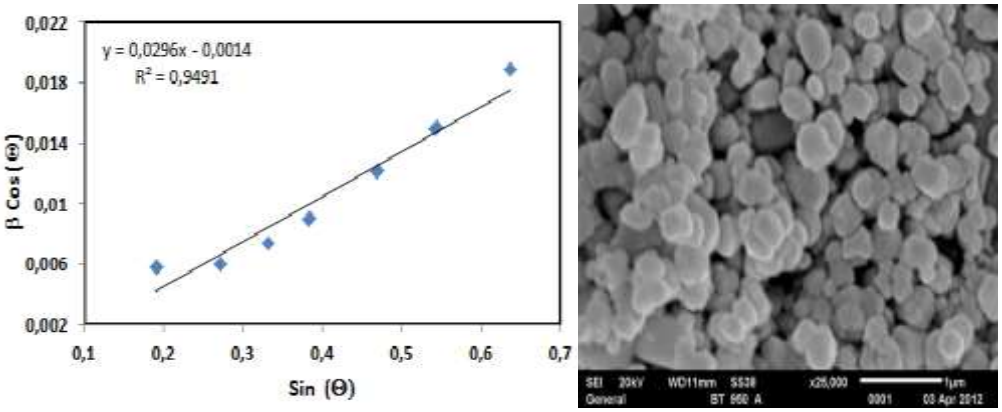

Figure 5. Williamson-Hall plot for molten salt method and the SEM (Scanning Electron Microscope) micrograph of a BT ceramic after sintering at 950°C/4hr

Crystallite particle size and strain can be calculated from the slope and y-intercept of the fitted line and obtained for d= 110,2 nm and ε=0,74 % respectively. The microstructure of a $BaTiO_3$ or a grain size sample can be shown in Fig 5. measured by SEM method. Analysis on SEM micrograph was done by measuring the grain size at horizontal with range of 116.7 to 500 nm. The crystallite size which was calculated by using the Wiliamson- Hall method and compared with the results estimated from SEM micrographs are able to show close to the same value range.

4. Conclusion.

Tetragonal phase of $BaTiO_3$ was achieved through molten salt method at the sintering temperature 950 ^oC within 2 hours in a solution of NaCl + KCl at mole ratio of 1: 1.

The presence of tetragonal perovskite system has been confirmed by the calculated lattice parameter using Rietveld refinement program and analyzed by the presence of overlapping peaks as its characteristic. Crystallite particle size of 110.2 nm can be estimated through the hall wiliamson- plot and close to as shown in micrograph SEM measurement, while the crystal strain of 0.74 % was obtained.

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Reference

[1] Jona, Shirane G 1993 *Ferroelectric crystals*, Dover Publications INC. New York.
[2] Burcu Ertuğ 2013 *American Journal of Engineering Research (AJER)* Volume-02 Issue-**08** pp-01-07.
[3] Sonia, Patel R K, Kumar P, Prakash C, Agrawal D K 2012 *Ceramics International* **38** p.1585-1589.
[4] Sharma N, Gaur A, Gaur U 2014 *Ceramics International* **40 10** p.16441-16448.

[5] Cao Y, Zhu K, Wu Q, Gu Q, Qiu J 2014 *Materials Research Bulletin* **57 9** p.162-169.
[6] Kambale K R, Kulkarnin A R, Venkataramani N 2014 *Ceramics International* **40 1** p. 667-673.
[7] Syahfandi Ahda 2011(August) *Journal of Materials Science Indonesia* Vol. Materials for Sensor Special Edition page : 33 – 36.
[8] Fang C Y, Wang C, Polotai A V, Agrawal D K, Lanagan M T 2008 *Materials Letters* **62 17-18** p. 2551-2553.
[9] Souza A E, Silva R A, Santosa G T A, Moreira M L, Volanti D P, Teixeira S R, Longo E 2010 *Chemical Physics Letters* **488 1-3** p.54-56.
[10] Toshio Kimura 2011 *Molten Salt Synthesis of Ceramic Powders, Advances in Ceramics - Synthesis and Characterization*, Processing and Specific Applications, edited by Prof. Costas Sikalidis In Tech. (2011) p-75-100 ISBN 978-953-307-505-1.
[11] Syahfandi Ahda, Mardiyanto and Alimin Mahyudin 2013 *Journal of Materials Science Indonesia* Vol. **14** No. **4** p.284 – 289.
[12] Song W L, Burtrand I L, Wang Z L, William D S 2000 *Journal of Crystal Growth* **219** p.269-276.
[13] Vijayalaksmi R, Rajendran V 2010, *Digest Journal of Nanomaterials and Biostructures*, Vol. **5**, No 2, p. 511 – 517.
[14] Wu M, Xu R, Feng S H, Li L, Chen D and Luo Y J 1996*J. Mater. Sci*. **31** p.6201.
[15] Mehrnoosh Atashfaraz, Mojtaba Shariaty-Niassar, and Tadafumi Adschiri 2008 *Proceedings of the World Congress on Engineering and Computer Science 2008 (WCECS 2008*) October 22 - 24 San Francisco USA.
[16] Prabhu Y T, Rao K V, Kumar V S S and Kumari B S 2014 *World Journal of Nano Science and Engineering* **4** p.21-28.
[17] Suranarayana and Norton C M G 1998 *X-Ray Diffraction*: *A Practical Approach*. Springer, New York.
[18] Yendrapati Taraka Prabhu, Kalagadda Venkateswara Rao, Vemula Sesha Sai Kumar, Bandla Siva Kumari 2014 *World Journal of Nano Science and Engineering* 4 p.21-28.
[19] Mote VD, Purushotham Y and Dole BN 2012 *Journal of Theoretical and Applied Physics* **6**:6.
[20] Chrunika M J, Kosowicza S, Perkowskia P, Mrukiewicza M, Morawiaka P and Zasadab D 2013 *Acta Physica Polonica* A, Vol. **124.**