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STRUCTURAL REFINEMENT OF SAMARIUM BISMUTH TITANATE USING RIETVELD METHOD

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ABSTRACT

The crystal structure of Bismuth titanate (BT) and Samarium Bismuth titanate (SBT) was analyzed using Rietveld method. Through the analysis, we found that the orthorhombic structure of BT was gradually changed to be a tetragonal structure which belongs to the SBT. A great influence was clearly seen on the crystal structure as a result of Samarium content added to the system. Other parameters such as lattice parameter, volume unit and crystallite size were also changed due to such addition.

Keywords: Bismuth titanate, Samarium, Structural

INTRODUCTION

Bismuth titanate, ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) or generally called BT is a ferroelectric material which has a perovskite structure ^[1]. BT also is the promising candidate for potential use in the application of ferroelectric random access memory (FRAM) owing to its large remnant polarization, good fatigue properties on metal electrodes and excellent dielectric properties. However, BT compound exhibits relatively high leakage current, domain pinning and small remanent polarization, which makes it difficult to use BT for real device applications ^[2]. In previous studies revealed that trivalent cations of lanthanide (e.g. La^{3+} , Nd^{3+} , Sm^{3+} , Pr^{3+}) have attracted much attention due to their ferroelectric properties were in the reasonable ranges for memory application ^[3]. Among these, Sm^{3+} (0.117 nm) ions were used to substitute Bi^{3+} (0.108 nm) ions in BT due to larger of their ionic size difference ^[4]. It is known that the degree of enhancement of remanent polarization in BT is governed by the difference between ionic sizes of Bi^{3+} and the Sm^{3+} ions. Thus, the larger the ionic size difference, the larger the polarization will be. In the present study, we adopted the Rietveld method to

investigate the crystal structure of samarium substituted bismuth titanate (SBT). It is necessary to study this method on such parameter of SBT as it has not been performed yet. Due to this reason, therefore we have reported this work throughly in this paper.

EXPERIMENTAL PROCEDURE

The sample was prepared by a modified combustion synthesis using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ as the starting materials. The powder mixture was calcined at 800°C for 3 h and then, the powder was ground by agate mortar to obtain fine powder. The process was consistently repeated for other samples. These samples were afterward sent to X-ray diffraction (XRD) (Bruker D8 Advanced) and analyzed by Rietveld method. The parameters setting for XRD were as follows: $\text{Cu } \alpha$ ($\lambda_{\text{K}\alpha 1} = 1.5405 \text{ \AA}$ and $\lambda_{\text{K}\alpha 2} = 1.5443 \text{ \AA}$, 2θ range between 10° and 90° , step size of 0.034° (2θ), fixed divergence slit = 0.2° , receiving slit = 0.2mm . The crystallite size was calculated using Scherrer's formula [5].

RESULT AND DISCUSSION

The Rietveld method of the sample was initiated with the starting model based on the orthorhombic data with space group B2cb. This space group shows an excellent fit to our diffraction data. The profile refinement was started with scale and background parameters followed by the unit cell parameters. The typical observed and calculated diffraction patterns for BT and SBT are shown in Figure 1. The refined unit cell parameters, crystal density and refinement index are given in Table 1.

In Fig. 1, it shows that BT and 0.2SBT are an orthorhombic structure and 1.0SBT is a tetragonal structure. The transition from orthorhombic to tetragonal is significantly influenced by increasing the Sm content. It is indicated by 'a' and 'b' parameters become closer as seen in Table 1. Among these parameters, 'a' parameter is observed to extremely reduce for about 1%. It is also found that the crystallite size for respective samples was found to be decreased with increasing the Sm content in bismuth titanate compound as listed in Table 2. Averagely, BT sample has larger crystallite size (69.1nm) as compared with SBT samples. It reveals that the crystallite size can be tailored by significant amount of Sm content.

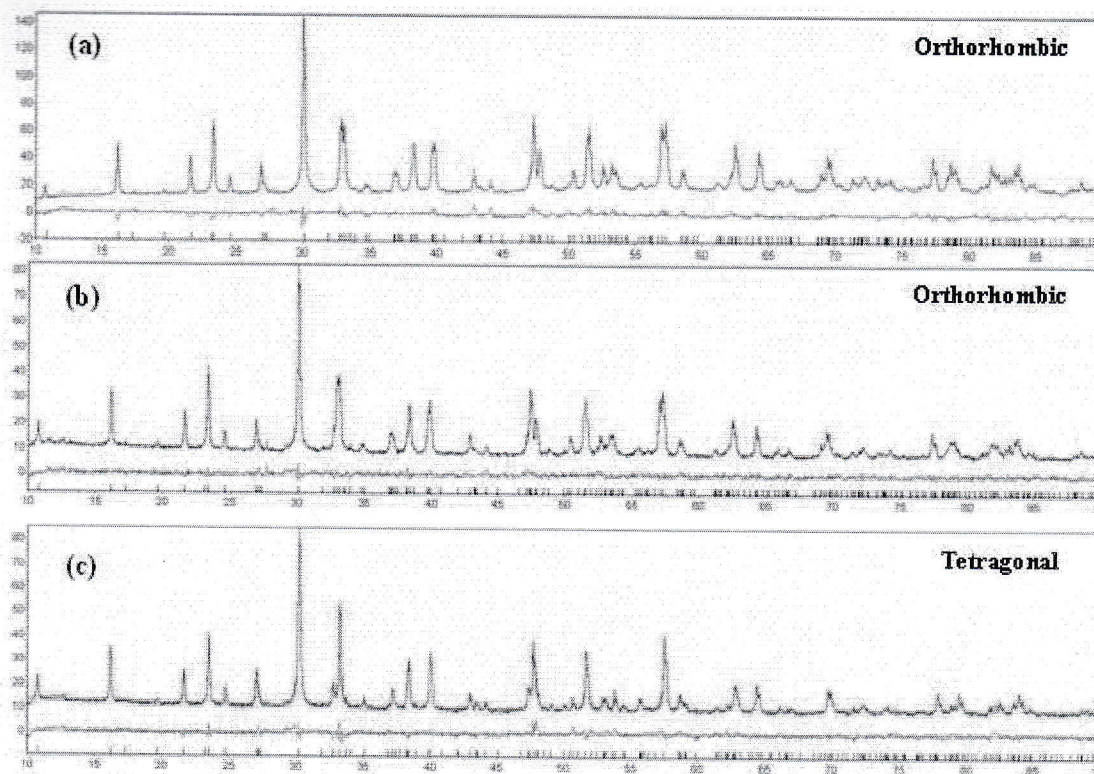


Fig. 1: The structural refinement patterns of (a) BT, (b) 0.2SBT and (c) 1.0SBT. Experimental and calculated diffraction pattern is given at the top. The difference profile is shown at the bottom. The Bragg positions are indicated by the vertical marker below the observed patterns.

In order to make a judgment whether a crystal structural model is adequate or not, the structural refinement adopts numerical criteria, e.g. R_{wp} , R_{exp} , R_p and R_{bragg} . Among several criteria of fit that are commonly used, the most meaningful indices are R_{wp} because it shows in the numerator for quantity minimized. From numerical and graphical criteria point of view for the model, considering the final converged R-factors goodness-of-fit indicator for the model obtained from the structural refinement using X-ray, it can be concluded that the orthorhombic system is more suitable for BT and 0.2SBT and the tetragonal for 1.0SBT.

Table 1: Typical crystallographic and refinement of BT and SBT

Sample	BT	0.2SBT	1.0SBT
Space group	B2cb	B2cb	B2cb
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Lattice parameter			
a, Å	5.4431	5.4327	5.3887
b, Å	5.4074	5.4047	5.3886
c, Å	32.8126	32.8249	32.7920
V, Å ³	965.79	963.79	952.21
Density, gcm ⁻³	7.8354	7.8490	7.9477
R _{wp} %	10.65	11.39	12.40
R _{exp}	4.12	8.13	7.32

Table 2: Crystallite size calculated by Scherrer's formula

Sample	BT	0.2SBT	1.0SBT
Peak position			
(006)	74.3	72.3	43.8
(008)	74.2	67.4	51.8
(111)	69.3	65.9	43.1
(117)	58.8	54.8	38.4
Average			
Crystallite size, nm	69.1	65.1	44.3

CONCLUSION

Through the structural refinement, we found that the crystal structure was greatly influenced with significant amount of Sm content in bismuth titanate compound. It was confirmed through the analysis which was discussed in this paper.

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REFERENCE

- [1]Z. Lazarević, B. D. Stojanović, J. A. Varela, "An Approach to Analyzing Synthesis, Structure and Properties of Bismuth Titanate Ceramics," *Sci. Sintering*, 37 (2005) 199-216.
- [2]S. S. Kim, W.J. Kim, Ferroelectric properties of randomly oriented $\text{Bi}_{1-x}\text{Pr}_x\text{Ti}_3\text{O}_{12}$ thin films fabricated by a sol-gel method, *Thin Solid Films*, 484 (2005) 303 – 309.
- [3]Y.C. Chen, C.P. Hsiung, C.Y. Chen, J.Y. Gan, Y.M. Sun, C.P. Lin, Crystallinity and electrical properties of neodymium-substituted bismuth titanate thin films, *Thin Solid Films*, 513 (2006) 331–337.
- [4]X. Hu, A. Garg, Z. H. Barber, Structural and electrical properties of samarium-substituted bismuth titanate ferroelectric thin films on $\text{Pt/TiO}_x/\text{SiO}_2/\text{Si}$ substrates, *Thin Solid Films*, 484 (2005) 188 – 195.
- [5]A. W. Burton, K. Ong, T. Rea, I. Y. Chan, On the estimation of average crystallite size of zeolites from the Scherrer equation: A critical evaluation of its application to zeolites with one-dimensional pore systems, *Microporous and Mesoporous Materials* 117 (2009) 75–90.