Songklanakarin J. Sci. Technol.
30 (6), 787-790, Nov. - Dec. 2008

Songklanakarin Journal of Science and Technology
http://rdo.psu.ac.th/sjst

Original Article

Submicron $Bi_4Ti_3O_{12}$ particles via molten salt synthesis with alkaline sulfate

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Received 28 September 2007; Accepted 12 October 2008

Abstract

Powder size is a major factor determining the characteristics of processing variables and end-products of ceramic materials. Conventionally, common particles sizes are employed in the micron range. It is now realized that better materials could be obtained through the use of submicron or nanoparticles, but they are available at much higher cost, leading to costly end-products.

The effects of molten salt synthesis (MSS) employing two different salt systems, alkaline chloride and sulfate, were investigated. Employing a mixture of NaCl-KCl, the obtained crystals could be as large as tens of microns. The shape of crystals was thin platelet. However, MSS using Na_2SO_4-K_2SO_4 yielded a very different result. The obtained particles were very small, in the submicron range. Moreover, the synthesizing temperature for $Bi_4Ti_3O_{12}$ was just 650°C, much lower than 850°C of MSS with NaCl-KCl. Therefore by employing MSS, it is possible to produce either $Bi_4Ti_3O_{12}$ crystals tens of microns in size using alkaline chloride system or very fine particles in the submicron range using an alkaline sulfate system.

Keywords: submicron particles, nanoparticles, molten salt synthesis, $Bi_4Ti_3O_{12}$

1. Introduction

Most ceramics processing employs starting and intermediate materials in powder form. Powder size is a major factor determining the characteristics of processing variables and end products. Common particle sizes are available in the micron range. Submicron or nanoparticles are also available but at much higher cost, contributing to costly end-products. However, the demand for submicron or nanoparticles for enhanced materials or products is increasing.

Nanoparticles are synthesized using two main techniques: gas phase synthesis and sol-gel processing (Siegel *et al.*, 1999). Gas phase synthesis includes combustion (Subramania *et al.*, 2006), flame spray pyrolysis (Tok *et al.*, 2006), plasma (Rao *et al.*, 1997) and laser ablation (Becker *et al.*, 1998). Sol-gel processing includes gelation (Daniele *et al.*, 2006), precipitation (Zhang *et al.*, 2006 and Mouzon *et al.*, 2007) and hydrothermal synthesis (Lester *et al.*, 2006). There are also some additional, specific techniques for synthesis of nanoparticles, such as: sonochemical processing, microemulsion processing, and high-energy ball milling. All of the aforementioned techniques (with the exception of high energy ball milling) exemplify the 'bottom-up' approach. High energy ball milling is the only technique which utilizes a 'top-down' approach. Starting materials in the micron size range are reduced to submicron or nanoparticles with high energy impact (Osamu *et al.*, 1991).

$Bi_4Ti_3O_{12}$ has a relatively low coercive field, a low dielectric constant, a high Curie temperature and a high breakdown strength (Shoji *et al.*, 1996). It can be employed in applications such as non-volatile memory, optical memory, piezoelectric and electro-optic devices (Joshi and Krupanidhi, 1992). The electrical properties of ceramics are greatly influenced by microstructure and compositional homogeneity. Both microstructure and compositional homogeneity are the results of the starting calcined powder. Smaller particles reduce the variation in composition when they are well dispersed. Submicron or nanoparticles have very large surface areas. The large surface area enhances the rate of reaction and reduces the reacting temperature. It is also the main driving force for densification during sintering, resulting in

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a lower sintering temperature and better densification with small grain size. Fine powders with submicron sizes are then preferred for lower processing cost and enhanced properties. Conventionally-prepared powders of $Bi_4Ti_3O_{12}$ from solid-state reactions often have high agglomeration and compositional inhomogeneity because of the high calcination temperature and repeated grinding (Kimura *et al.*, 1989).

Previous attempts at synthesizing $Bi_4Ti_3O_{12}$ nanoparticles include the hydrolysis of metal organic salts (Kimura *et al.*, 1989), the co-precipitation method (Jeffrey *et al.*, 1999), the sol-gel process (Gu *et al.*, 1998), and hydrothermal synthesis (Yang *et al.*, 2003). These chemical preparations use costly chemicals as raw materials. Although high energy mechanical milling has also been used to produce similar materials in the submicron range (Thanaboonsombut and Vaneesorn, 2007) using cheap metal-oxides, the energy cost is rather high and contaminants may be introduced.

This paper studies the phase and morphology of $Bi_4Ti_3O_{12}$ particles from molten salt synthesis (MSS). Two different salt systems, alkaline chloride and sulfate, were employed. Normally, the MSS technique is used to obtain a large number of small crystals for template grain growth techniques (Setasuwon and Kijamnajsuk, 2007). The sizes of useful crystals are in the range of tens of microns. It is found, later in this study, that MSS is also capable of producing very small particles.

2. Experimental procedures

Bi_2O_3 (Fluka, 98%) and TiO_2 (Fluka, 99%) were used as starting materials. They were mixed in proportion to yield $Bi_4Ti_3O_{12}$. Salt mixtures were added at 75 vol%. Two eutectic salt mixtures were employed; 1:1 mole of NaCl-KCl and 1:3 mole of Na_2SO_4-K_2SO_4. Their eutectic temperatures are 658°C and 441°C, respectively. Chemical grades are NaCl (AnalaR, 99.5%), KCl (Riedel-deHaën, 99.5%), Na_2SO_4 (AnalaR, 99%) and K_2SO_4, (AnalaR, 99%).

The mixture was then milled with zirconia balls and acetone in a plastic bottle. The mixture was dried and put in an alumina crucible. The lid was sealed with alumina cement. The synthesizing temperature were 650, 850 and 1050°C for 2 hr with heating and cooling rates of 180°C/hr. Salt was washed out with hot water several times. The size and shape of the synthesized particles were investigated with SEM (JEOL, JSM-6301F). X-ray diffraction analysis (Jeol JDX-3530) was performed for phase identification.

3. Results and Discussion

Phase analysis of MSS for $Bi_4Ti_3O_{12}$ in NaCl-KCl at 650, 850 and 1050°C was done with X-ray diffraction patterns (Figure 1). At 650°C, there existed $NaBi_3O_4Cl_2$ and $Bi_2Ti_2O_7$. This indicates that NaCl has entered into the reaction. Only at higher temperatures of 850 and 1050°C was the intended compound, $Bi_4Ti_3O_{12}$, produced. It is noticeable that although the peak positions are the same for 850 and

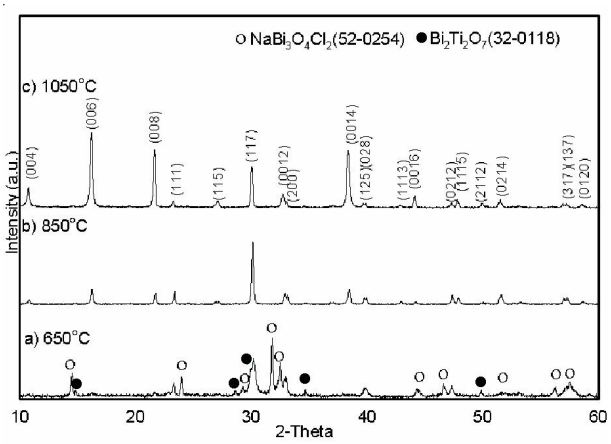

Figure 1. X-ray diffraction patterns of $Bi_4Ti_3O_{12}$ composition synthesized in NaCl-KCl at 650, 850 and 1050°C (indexed peaks are those of $Bi_4Ti_3O_{12}$).

1050°C, the relative intensities are different. This can be explained by examining the morphology of the synthesized particles.

At 650°C, two different kinds of particles were observed (Figure 2a); many small particles with some large ones. This observation is in agreement with the phase analysis above. The morphology of $Bi_4Ti_3O_{12}$ particles are thin platelet. The particle size is a few microns at 850°C (Figure 2b) and larger than 10 μm at 1050°C (Figure 2c). Although the treatment at the high temperature of 1050°C yielded much larger platelets, the size distribution is wide from a few to tens of microns. Of the X-ray diffraction pattern of 1050°C, the relative intensities of (00l) family increases substantially. In-packing arrangement of particles with very high aspect ratio, such as thin platelets, could result in a preferred orientation of particles or crystals (Setasuwon and Kijamnajsuk, 2007).

Phase analysis of MSS for $Bi_4Ti_3O_{12}$ in Na_2SO_4-K_2SO_4 was done with X-ray diffraction patterns at 650, 850 and 1050°C (Figure 3). At all temperatures the intended compound, $Bi_4Ti_3O_{12}$, was produced in sulfate salt. Sulfate salt did not enter into the reaction as chloride salt did at the low temperature of 650°C. Therefore, compared with NaCl-KCl, Na_2SO_4-K_2SO_4 can be used to synthesis $Bi_4Ti_3O_{12}$ at lower temperature.

At 650°C, the relative intensities are slightly different. The peak splitting characteristics (approximately 33, 40 and 57 degrees of 2-Theta) of 850°C and 1050°C do not appear in the pattern of 650°C. These split peaks are indicators of the orthorhombic phase (Yang *et al.*, 2003), which is the stable phase at low temperature. $Bi_4Ti_3O_{12}$ undergoes a phase-transition of orthorhombic-tetragonal phase at the Curie point of 675°C (Billegas *et al.*, 1996). The X-ray diffraction pattern for 650°C, without peak splitting, is similar to that of the tetragonal phase, spontaneously obtained from hydrothermal synthesis of $Bi_4Ti_3O_{12}$ nanoparticles (Yang *et al.*, 2003). The hydrothermal synthesized $Bi_4Ti_3O_{12}$ nano-

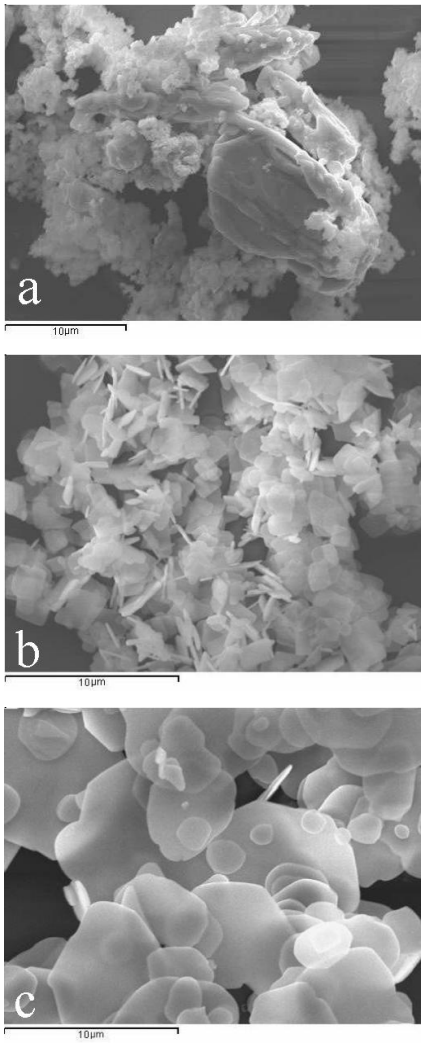

Figure 2. SEM micrographs of $Bi_4Ti_3O_{12}$ composition synthesized in NaCl-KCl at a) 650 b) 850 and c) 1050°C.

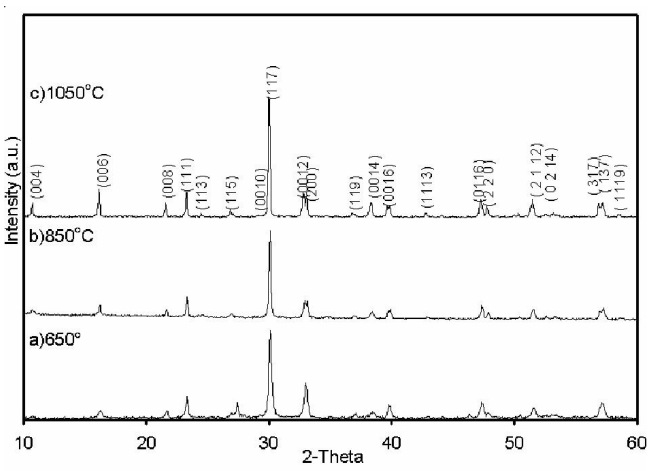

Figure 3. X-ray diffraction patterns of $Bi_4Ti_3O_{12}$ composition synthesized in Na_2SO_4-K_2SO_4 at 650, 850 and 1050°C (indexed peaks are those of $Bi_4Ti_3O_{12}$).

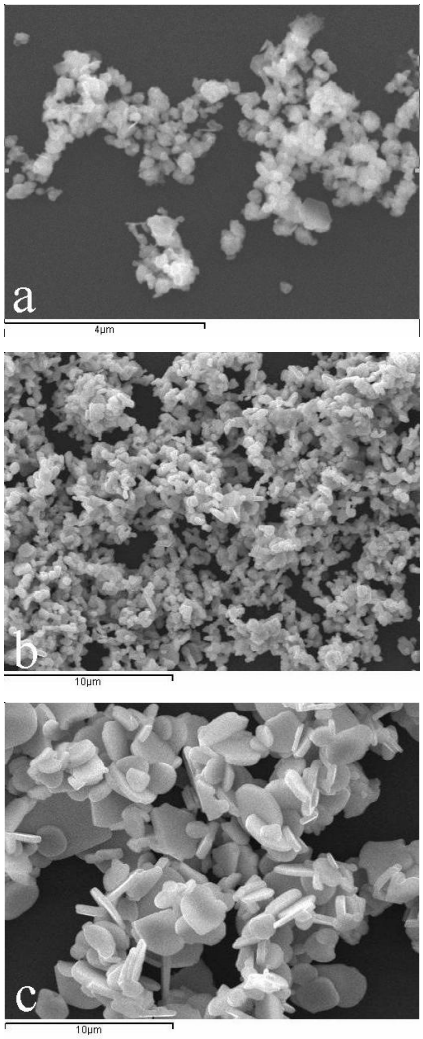

Figure 4. SEM micrographs of $Bi_4Ti_3O_{12}$ composition synthesized in Na_2SO_4-K_2SO_4 at a) 650 b) 850 and c) 1050°C.

particles were tabular, and the sizes were about 200 nm. The structural anomaly was also observed in $Bi_4Ti_3O_{12}$ nanoparticles prepared by chemical co-precipitation (Du *et al.*, 2002) and sol-gel (Osamu *et al.*, 1991).

SEM micrographs of $Bi_4Ti_3O_{12}$ particles synthesized in Na_2SO_4-K_2SO_4 at 650, 850 and 1050°C are shown in Figure 4. At 1050°C, the particle morphology is platelet, similar to those obtained with NaCl-KCl. However, the platelet particles from Na_2SO_4-K_2SO_4 are smaller, although thicker than those from NaCl-KCl. At 850°C, the particle size reduced to around one micron or less. The smaller and thicker particles should be the result of higher surface energy between the particles and sulfate salt, compared to that between the particles and chloride salt. Submicron particles were obtained at the lower temperature of 650°C, comparable to those obtained by hydrothermal synthesis (Yang *et al.*, 2003). The powder processed at 650°C corresponds very well with the structural anomaly found with other $Bi_4Ti_3O_{12}$ nanoparticles, discussed earlier.

4. Conclusions

$Bi_4Ti_3O_{12}$ crystals could be as large as tens of microns when employing a mixture of NaCl-KCl. These crystals possess a thin platelet geometry However, a much different result was obtained with Na2SO4-K2SO4. In this case, submicron particles were obtained. In addition, the temperature (650°C) required to synthesize $Bi_4Ti_3O_{12}$ was much lower than that required to synthesize $Bi_4Ti_3O_{12}$ from NaCl-KCl (850°C). Therefore, by employing MSS, it is possible to produce large $Bi_4Ti_3O_{12}$ crystals tens of microns in size using an alkaline chloride system or very fine particles in the submicron range using an alkaline sulfate system.

MSS is equivalent to a 'top-down' approach but requiring much less energy. The MSS approach is also low cost in terms of starting materials compared to gas-phase synthesis and sol-gel processing. A novel method to produce submicron oxide powder of $Bi_4Ti_3O_{12}$ ferroelectric material is thus realized.

Acknowledgements

The authors would like to thank the MTEC X-ray technical staff for their support, and The Editorial Board, Songklanakarin Journal of Science and Technology for their excellent revision on English

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