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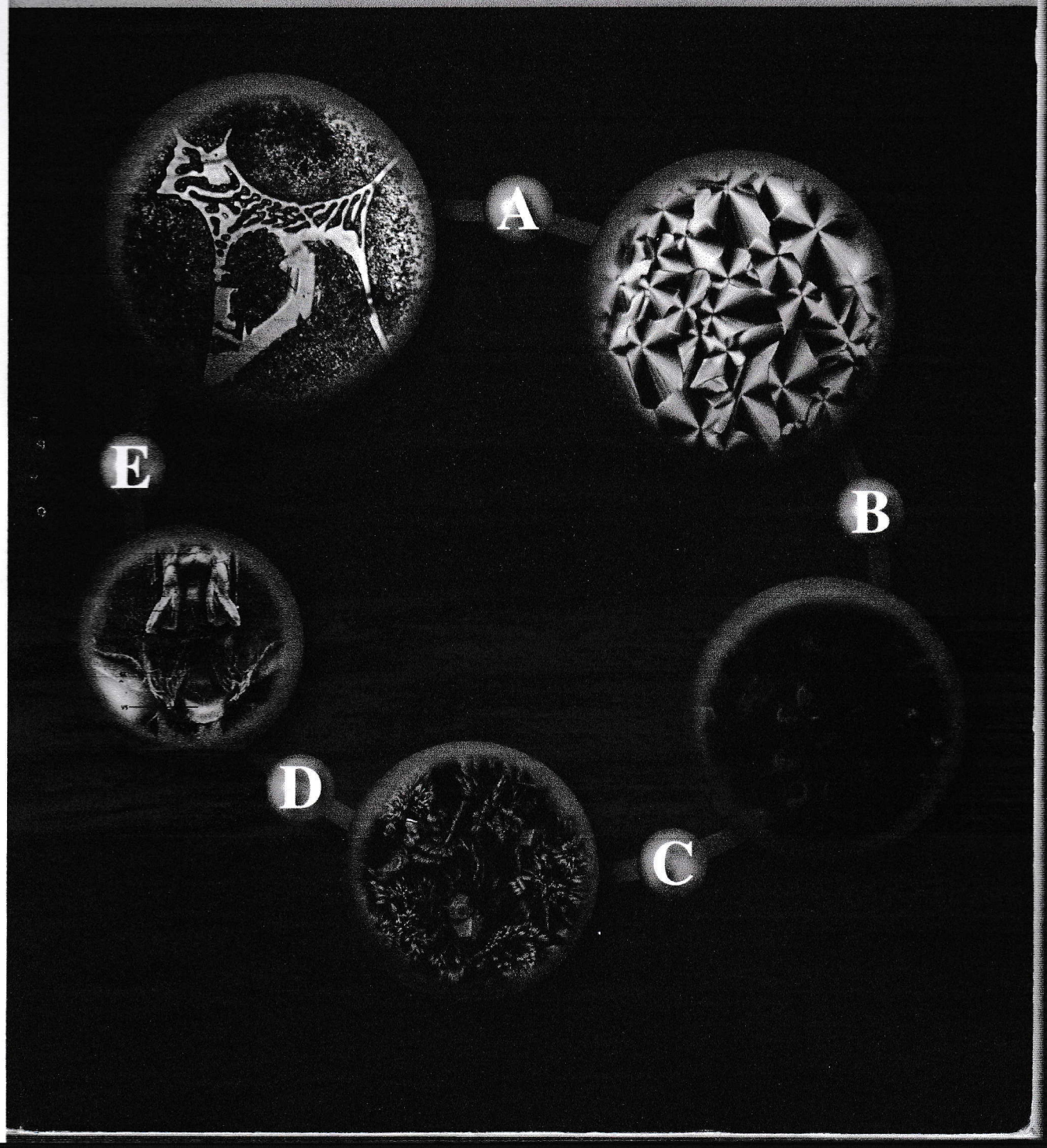

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LOW-TEMPERATURE COMBUSTION SYNTHESIS OF $Bi_4Ti_3O_{12}$ PLATE-LIKE STRUCTURE AND SOME OF ITS CHARACTERIZATION

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Bismuth titanate, $Bi_4Ti_3O_{12}$ was prepared at different hydrolysis temperatures and characterized with XRD, Rietveld analysis, TG-DTA, FESEM and TEM. The results indicated that the pure bismuth titanate was obtained after combustion at lower temperature of about 260 °C. Interestingly, no calcination step involved to obtain bismuth-structured layered. The effect of hydrolysis temperature at 40 °C, 50 °C, and 60 °C on phase formation, lattice parameter, crystallite size, thermal behavior as well as grain morphologies was investigated.

Keywords: $Bi_4Ti_3O_{12}$; Low-temperature combustion; Characterization

INTRODUCTION

Bismuth titanate, ($Bi_4Ti_3O_{12}$) has been used for ferroelectric random access memory (FRAM) devices due to its outstanding ferroelectricity [1]. This compound has been prepared using a wet chemical technique such as sol-gel, hydrothermal, precipitation and molten-salt synthesis [2]. Wet chemical technique is preferred because a single phase $Bi_4Ti_3O_{12}$ can be obtained at low temperature [3]. In early stage, $Bi_4Ti_3O_{12}$ has been prepared using conventional solid state which often results in high agglomeration and low sinterability of powders because of high calcination beyond 1000 °C and repeated grinding [4].

Several studies have emerged as the leading techniques to form $Bi_4Ti_3O_{12}$ have been reported. Han and Ko [5] produced nanocrystalline $Bi_4Ti_3O_{12}$ powder using an intense mechanical activation of a mixture of α-Bi_2O_3 and TiO_2 after a milling time of 9 hours. Gu et al. [6] reported that $Bi_4Ti_3O_{12}$ nanoplates were synthesized by polyethylene glycol-assisted hydrothermal method at 200 °C. However, there are some limitations in both processes such as the difficulty to understand the phase evolution and mechanical activation condition and the complexity of hydrothermal process in terms of experimental set up.

Therefore, in this work we use the combustion method to produce $Bi_4Ti_3O_{12}$. The current approach offers great advantages such as simple experimental set up, capability to produce high purity powder with excellent homogeneity, eliminate calcination step and relatively low formation temperature of a single phase [7-9]. However, comprehensive investigation on the processing parameter needs to be conducted in order to understand the relation between processing parameter with properties of the $Bi_4Ti_3O_{12}$. In this paper, the effect of hydrolysis temperature on the formation of $Bi_4Ti_3O_{12}$ is reported.

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METHODS AND MATERIALS

Bismuth nitrate penthahydrate, citric acid and titanium (IV) isopropoxide were used as starting materials. Initially, bismuth nitrate penthahydrate was added into a conical flask that contained distilled water. The conical flask was then placed in a water bath and the temperature was controlled at 40 °C under constant stirring. Simultaneously, citric acid was dissolved in distilled water and stirred at room temperature. After that, citric aqueous were added to bismuth aqueous and constantly stirred to form bismuth mixture. Separately, titanium (IV) isopropoxide was dissolved in 2-Methaoxyethanol (Sigma-Aldrich, ≥99 %) to form aqueous solution of Ti^{4+} ion. Then, the aqueous of Ti^{4+} ion was slowly added into bismuth mixture. The obtained mixture (which also known as precursor solution) was adjusted to pH 7 by using NH_4OH (29 % solution). The precursor solution with milky color was hydrolyzed at 40 °C, 50 °C, and 60 °C and stirred for 24 h to obtain more homogeneous solution. After that, the temperature was raised to 80 °C to form a dried powder mixture, subsequently, gently crushed using an agate mortar pestle. The crushed powder was placed back on a hot plate to complete the combustion process. The combustion temperature was then recorded by thermocouple.

The dried powders (before combustion) were analyzed using a thermogravimetry-differential thermal analysis (TG-DTA). On the other hand, the as-combusted powders were characterized by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM). The lattice parameter and crystallite size of the as-combusted powders were calculated using High-Score Pluss software and Scherrer's formula, respectively.

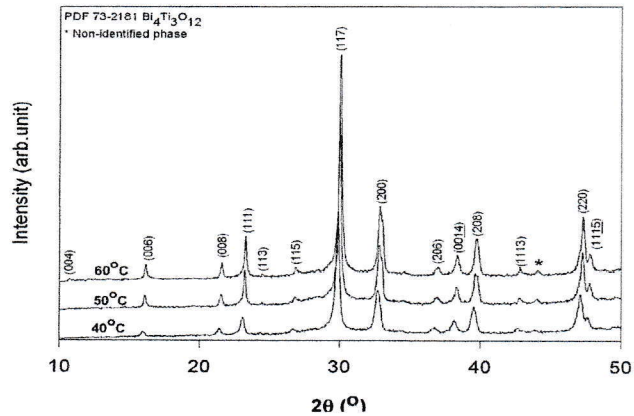

Fig. 1. XRD profile for the as-combusted powders prepared at different hydrolysis temperature.

RESULTS AND DISCUSSIONS

XRD analysis

The XRD profile for the as-combusted powders prepared at different hydrolysis temperature is shown in Fig. 1. The result show that all the diffraction peaks are corresponding to $Bi_4Ti_3O_{12}$ phase and matched well with PDF # 73-2181. The absence of any other peak confirming a single phase of $Bi_4Ti_3O_{12}$ was successfully obtained at low-temperature combustion synthesis. Besides that, it was also noticed that the hydrolysis temperature had significant influence on diffraction peak characteristic. It was noted that the broadness of the peak reduced with increasing of hydrolysis temperature, indicating high crystallinity degree. Based on Rietveld analysis, the variation of lattice parameter was clearly affected by hydrolysis temperature. We also found that a- and b-parameters were not always close; therefore it confirmed that $Bi_4Ti_3O_{12}$ compounds matched well with pseudo- orthorhombic structure. With the increase of this parameter, the volume of orthorhombic structure of $Bi_4Ti_3O_{12}$ also slightly increased and the result obtained at 60 °C was considered very close to the standard file. As mentioned in the experimental section, the crystallite size at the peak position (117) was calculated using Scherrer's equation [10] and the result is shown in Table 1. The result showed that the crystallite size was strongly dependent on the hydrolysis temperature. This was attributed by the increase of grain size.

Table 1. Lattice parameter and crystallite size of the as-combusted powder at different hydrolysis temperature calculated from XRD data

Lattice parameters	40°C	50°C	60°C
a/ Å	5.4150(1)	5.4140(1)	5.420(2)
b/ Å	5.4400(1)	5.4440(1)	5.447(2)
c/ Å	32.7730(6)	32.7840(6)	32.775(8)
V/ 10^6 pm^3	965.3804	966.2748	967.5442
Space group (No.)	F m m m (69)	F m m m (69)	F m m m (69)
R (expected)/ %	4.62321	4.32741	4.92416
R (profile)/ %	10.45851	11.86494	11.96359
R (weighted profile)/ %	12.3173	14.20051	14.25008
Density (calculated)/ g/cm^3	8.06	8.0525	8.0419
Crystallite size (nm)	20.1	26.4	26.5

TG-DTA analysis

The thermal behavior of the dried powder with different hydrolysis temperatures is shown in Fig. 2. As seen the decomposition process can be divided into two distinct stages in the TG plot (Fig. 2(a)). This trend was shown by three different hydrolysis

temperatures. The first weight loss took place at temperature range at temperature range of 50 – 181 °C. This causes to the vaporization of the residual water, organic solvent such as 2-methaoxyethanol, isopropoxide and hydroxyl groups. It was correlated with the small endothermic peak at 121 °C and 151 °C (not shown here). The second weight loss accompanied by a sharp exothermic peak took place at different temperatures i.e. 242 °C, 244 °C and 246 °C for 40 °C, 50 °C and 60 °C, respectively. Large exothermic peak was due to vigorous oxidation-reduction reaction or combustion between decomposed citric acid and nitrate ions which then led to crystallization of bismuth titanate.

This finding confirmed that the combustion reaction dependent on the hydrolysis temperatures of the precursor solution. It was worth to note that no further weight changes and heat effects were observed in the TG-DTA curve up to 500 °C, indicating the temperature of below 260 °C represents a sufficient temperature for the formation of a crystalline $Bi_4Ti_3O_{12}$ from the combustion reaction.

Microstructure analysis

The FESEM (Fig. 3(a)) microstructures of the combusted powders hydrolyzed at 60 °C are shown in Fig. 3. The images for 40 °C and 50 °C were not shown as the change in terms of size and shape were not so obvious. The $Bi_4Ti_3O_{12}$ powder was mostly composed of plate-like grains and the approximate diameter of grains was about 200 nm. Since the size was quite fine, the particles formed with high agglomeration as clearly observed by TEM (Fig. 3(b)).

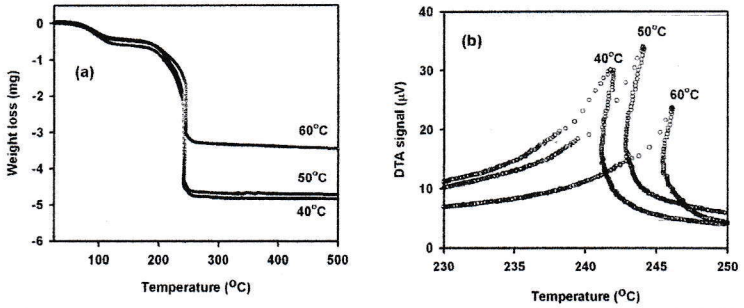

Fig. 2. Thermal behavior of as-combusted powders with different hydrolysis temperature: (a) TG and (b) DTA.

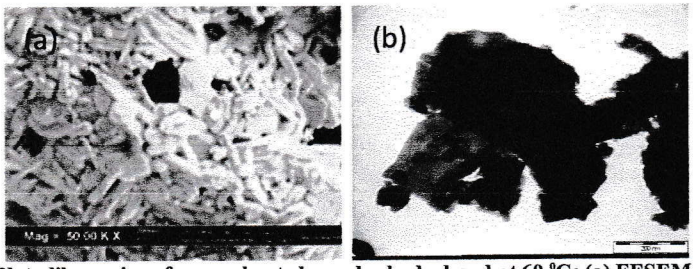

Fig. 3. Plate-like grains of as-combusted powder hydrolyzed at 60 °C: (a) FESEM and (b) TEM.

CONCLUSION

$Bi_4Ti_3O_{12}$ powder was successfully obtained by a combustion synthesis at very low temperature. It was confirmed by XRD and TG-DTA. Study on hydrolysis temperature showed the variation of structure lattice parameter that was confirmed by Rietveld analysis. Different exothermic temperatures were also recorded in DTA, indicating the hydrolysis temperature was essential parameter to produce $Bi_4Ti_3O_{12}$ powder. Nano-platey structure of $Bi_4Ti_3O_{12}$ was clearly observed by FESEM and TEM.

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