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Effect of sintering temperature and micro structural analysis on sol-gel derived silver bismuth titanate ceramics

S. Supriya*

Department of Physics Faculty of Engineering & Technology, SRM University, Bharathi Salai, Ramapuram, Chennai 600 089, Tamilnadu, India

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ABSTRACT

The silver bismuth titanate – $Ag_{0.5}Bi_{0.5}TiO_3$ (ABT) ceramics with various grain sizes were synthesized by stearic acid gel method. The density measurement was calculated based on pycnometer method. The relative density of ABT pellet was calculated as 64.91%. The microstructure analysis establishes the relationship between the sintering temperature and grain size. Moreover, the micrographs show the pores and oriented particles of nano meter to micrometer size. The effect of sintering temperature on grain growth behavior of sol-gel derived porous silver bismuth titanate sample was discussed in detail.

1. Introduction

Ceramics with bismuth and barium titanate (BTO) compositions are considered as alternatives to lead zirconate titanate Pb(Zr, Ti)O_3 (PZT) for the applications such as sensors, actuators and infrared detectors, etc. [1]. Historically, BTO ceramics are widely used polycrystalline materials for industrial applications. This ceramics have been proved to exhibit advanced microstructure property which is incomparable with PZT ceramics. The dependence of grain size behaviour on sintering temperature has been investigated rarely. Therefore, the syntheses of lead free titanium based ceramics are important for the development of the miniature devices and microelectronics industries [2]. The Sb_2O_3 compounds and ZnO whiskers with PZT composites show improved micro structural properties due to heat treatment [3]. The niobium with monolithic PZT reveals the enhancement in grain growth and electrical properties [4]. The grain size with effect of temperature and dopant materials in polycrystalline ceramic compounds have been analysed in many investigations [5–24].

Sol-gel reaction method is one of the best methods to synthesis titanate based compounds at low sintering temperature with single phase. However, this technique is well proven among other synthesis methods to get high quality polycrystalline ceramic powders. Grains size and shape of the ceramics is the important factor which influence piezoelectric, ferroelectric and dielectric properties. The fine grain size with piezoelectric property produces higher mechanical strength and improved dielectric properties. Many recent experimental studies proved that, the shape of the grains can be changed into rounded by increasing the sintering temperature and addition of doping materials. For example in the NbC–Co system, the grain shape was changed with effect of calcinations temperature. The effect of Ti dopant on grain size behaviour in $Nb_{1-x}Ti_xC$–Co system was analysed. The Ti doping changes the grain shape from round-edge cube to well faceted cube [25].

In sol-gel synthesis method, the step size increase in sintering temperature is required for adequate improvement in grain size which yields better mechanical properties. Based on the observation of grain size effect, many mechanisms have been proposed, like role of grain boundary layer, grain shape, etc. However, most of the research publications [26] about the grain size effect and its intrinsic mechanisms were focused on thermal and optical properties, which are considered potential for the electrical storage purpose. The high mechanical strength and improved dielectric strength can be achieved from fine grains. It is worth to study the grain size effect of ABT ceramics for the applications in energy storage devices [27–29].

Recently, the ceramics with layered porous nanostructures with various pore sizes and shapes became important in the area of bio chemistry. Many studies showed the improved stability in layered porous inorganic nanomaterials [30]. The oriented plate like morphology (templates) can be produced by sintering process. The term “mesocrystal” is defined as, well-aligned and oriented poly crystal with nano meter to micrometer size [31]. It is

* Correspondence to: Department of Physics Faculty of Engineering & Technology, SRM University, Bharathi Salai, Ramapuram, Chennai 600 089, Tamilnadu, India.
E-mail address: sciencepriya@gmail.com (S. Supriya).

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technologically important for domain and texture engineering in the piezoelectric applications. The present work investigates the effect of temperature on grain size, plate like mesocrystal, porous morphology and nano size particles in a silver bismuth titanate system. The microstructure has been analysed with scanning electron microscope (SEM). The porosity and grain growth behaviour of the ABT compound was discussed in detail.

2. Experimental procedure

The polycrystalline silver bismuth titanate -$Ag_{0.5}Bi_{0.5}TiO_3$ (ABT) ceramic powder was synthesized by stearic acid – sol-gel reaction method [32]. The high purity chemicals of bismuth (III) nitrate – Bi $(NO_3)_3$ (99%), silver nitrate – $AgNO_3$ (99.5%), sodium acetate – CH_3COONa (99%), and tetrabutyl titanate – $Ti(OC_4H_9)$ (99.8%) were selected as starting raw materials. Initially, 100 ml of stearic acid – $C_{17}H_{35}COOH$ (99%) was melted at 80 °C. The stoichiometric ratio of chemicals was added in stearic acid and continuously stirred using magnetic stirrer for 3 h. The temperature of the solution was increased upto 100 °C. The resulted ABT compound was in the form of semi solid gel and it was cooled down to room temperature. The molten ABT compound was subjected to step wise heat treatment (100 °C) about 700–1000 °C for 8 h and cooled to room temperature. To calculate density, the sintered powder was grounded well in agate mortar for 3 h and pressed into cylindrical pellets of 10 mm in diameter, 1–2 mm thickness using hydraulic press at a pressure of 8×10^3 kg m^{-2}. The pellets were sintered at 1000 °C for 3 h in air atmosphere. The microstructure of heat treated powder sample was investigated by scanning electron microscope (Jeol JSM-5610LV).

3. Results and discussion

3.1. Density measurement

The Fig. 1 represents the ABT pellets before (a) and after (b) heat treatment. The relative density (ρ_r) of heat treated pellet can be measured by Eq. no (1).

$$\rho_r = \frac{\rho_m}{\rho_t} \times 100 \quad (1)$$

ρ_t and ρ_m are the theoretical density and the measured density respectively. The theoretical density of silver bismuth titanate was calculated as 6.125 g/cm^3. To find out measured density [33,34], the ABT pellet was initially heated in an oven at a temperature of 100 °C for 30 min. The mass of the dried pellet (m_D) was measured by high precision balance. The pellet was heated in distilled water for 5 min to remove air bubbles which is trapped inside the tiny holes of the pellet. The pellet was allowed to reach the room temperature, and dried with tissue paper. It is dipped again in the distilled water. The increase in volume was calculated. The measured volume is denoted as ΔV. According to pycnometer method, the measured density (ρ_m) can be calculated from Eq. no (2),

$$\rho_m = \frac{m_D}{\Delta V} \quad (2)$$

From Eq. no. (1), the relative density (ρ_r) of ABT pellet was calculated as 64.91%.

3.2. Grain growth control and grain size measurements—microstructural analysis

The silver bismuth titanate powders heat treated at a temperature range of 700–1000 °C was examined in scanning electron microscope. Fig. 2. illustrates the grain size behaviour of polycrystalline ABT powders.

Grain growth and collapse depends on increasing and decreasing the sintering temperature. The radius of the grain is written as R_G. Also, R_c is critical radius of the grain which varies with sintering time. The relationship between grain radius and critical radius can be obtained as, $R_G > R_c$, $R_G < R_c$, the grain growth and collapse depends factors like sintering time and sintering atmosphere. The relationship between the appearance and absence of porosity in the grain growth under thermal conditions is expressed by the following grain growth kinetics Eq. no (3)

$$R^2_{MG}(t) - R^2_{MG}(0) = K(T)\, t \quad (3)$$

Where, K is the rate constant, $R^2_{MG}(0)$ and $R^2_{MG}(t)$ are the average grain radii of ABT samples before and after sintering time t, at a temperature T, respectively [35]. The scanning microscope image result suggests that the size of the grain is directly proportional to sintering temperature.

The grain size from critical radius (after sintering) was measured by linear intercept method. The schematic representation of linear intercept method and the magnified image of pore which appeared due to heat treatment in ABT samples are shown in Fig. 3. After heat treatment many pores has been observed from nanometer to micrometer size. It is expected that the porous ABT compound may also play a significant role in improvement of stability. To calculate grain size, at first the two straight line in the middle point and four straight lines connected with two diagonal lines were drawn in the obtained micrograph. The total number of grains was calculated and the total width and length of the four straight lines was measured using the scale. The thermal, electrical

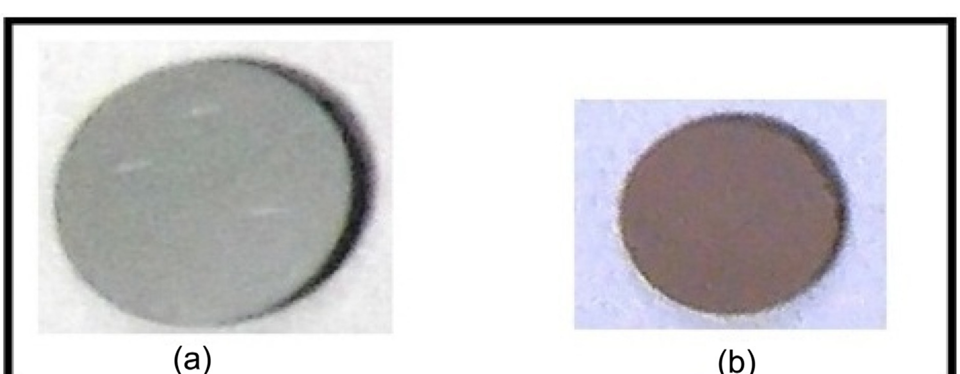

Fig. 1. ABT pellets of before and after heat treatment.