Effect of the excess of bismuth on the morphology and properties of the BaBi$_2$Ta$_2$O$_9$ ceramics

A.Z. Simões$^a$, G.C.C. da Costa$^a$, M.A. Ramírez$^{a,b,*}$, J.A. Varela$^a$, E. Longo$^c$

$^a$Universidade Estadual Paulista, Instituto de Química de Araraquara, R. Prof. Francisco Degni, s/n, C. P.: 355, CEP: 14801-970, Araraquara, SP, Brasil

$^b$Universidade Estadual Paulista–Pós-graduação em Ciência e Tecnologia de Materiais, Av. Eng. Luiz Edmundo Coube, s/n, C.P.: 473, CEP: 17033-36, Bauru, SP, Brasil

$^c$Universidade Federal de São Carlos, Departamento de Química, Rod. Washington Luiz, Km 235 C. P.: 676, CEP: 13585-905, São Carlos, SP, Brasil

Received 27 August 2004; received in revised form 29 September 2004; accepted 3 November 2004

Available online 2 December 2004

Abstract

In this study, the effect of bismuth content on the crystal structure, morphology and electric properties of barium–bismuth–tantalate (BBT) ceramics was explored with the aid of X-ray diffraction (XRD), scanning electron microscopy (SEM), dielectric properties and ferroelectric hysteresis loops. BaBi$_2$Ta$_2$O$_9$ (BBT) ceramics have been successfully prepared by the solid-state reaction. The BBT phase was crystallized at 900°C for 2 h. The excess of bismuth controls the grain size, affecting the density of the material. Measurements of dielectric constant and dielectric losses confirm that the material is a ferroelectric with a Curie temperature around 77°C. The dielectric constant measured at room temperature was 400, with a dielectric loss of 0.03. Both the phase-transition behaviour and ferroelectric properties, such as spontaneous polarization ($P_s$), showed a dependence on Bi content.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Ceramics; Electrical properties; Fatigue; Sintering

1. Introduction

The layered structure perovskites have recently received considerable interest in view of their potential application as low-voltage, high-speed nonvolatile random access memories (NV-RAM; [1]). Despite the fact that conventional ferroelectric materials have great potential for high-density FeRAMs (typically 1 Mbit), their commercial utility has seen little success due to factors such as fatigue, imprint, retention and aging, which reduce their lifetime. BaBi$_2$Ta$_2$O$_9$ (BBT) is one material that seems to have excellent fatigue endurance; it has been demonstrated that there is practically no polarization fatigue up to about $10^{12}$ switching cycles [2].

These materials were first synthesized by Aurivillius [3–5] and were named Aurivillius compounds. The chemical formula of these compounds is expressed as $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_x\text{B}_{2}\text{O}_{3x+1})^{2-}$, where $x$ indicates the number of perovskite building blocks between two $(\text{Bi}_2\text{O}_2)^{2+}$ layers and $A$ and $B$ represent the different cations of low and high valences in the structure [6]. This group of compounds exhibits a perovskite-like structure in the way that the $B$ cations build BO$_6$ octahedrons with the oxygen ions, whereas the $A$ cations are located in the space between the BO$_6$ octahedrons. The BO$_6$ octahedrons compose continuous layers perpendicular to the $c$-axis direction but are interrupted by $(\text{Bi}_2\text{O}_2)^{2+}$ layers along the $c$-axis direction. The BO$_6$ octahedrons exhibit spontaneous polarization, thereby resulting in ferroelectric properties [7].

Mixed bismuth oxide layer compounds were first reported by Bengt Aurivillius in 1949, and the ferroelectric nature of the Aurivillius phase was investigated by Smolenskii and Agronovskaya [8] a decade later. In the 1990s, there has been a resurgence of interest in some of the bismuth oxide layered compounds for their interesting ferroelectric properties. Barium–bismuth–tantalate (BaBi$_2$-
Ta$_2$O$_9$, BBT) has been identified for potential applications in ferroelectric nonvolatile random access memories because of its excellent resistance to polarization fatigue [9]. In ferroelectric memory applications, improved performance is observed with BaBi$_2$Ta$_2$O$_9$ due to its specific domain structure, which is two dimensional. It does not induce high internal stress and makes it highly suitable for switching applications. Besides improvements of the fatigue characteristics, a longer polarization retention time, less tendency to imprint and lower leakage currents have also been observed [10].

It is well known that the properties of materials depend on their synthesis processes. Besides the conventional method based on the solid-state reaction between Bi$_2$O$_3$, Ta$_2$O$_5$ and Ba$_2$Ta$_4$O$_{15}$ at high temperatures (about 1000 °C), other methods, such as sol–gel [11], polymeric gel [12], sputtering [13] or metal-organic chemical vapour deposition [14], have been studied to synthesize BaBi$_2$Ta$_2$O$_9$. The solid-state method has the disadvantage of high reaction temperatures, but it is simple to operate and uses the cheap and easily available oxides as starting materials. The chemical solution methods can provide products of fine and homogeneous particles with large specific surface areas, but the processes are generally complicated and the raw materials are very expensive. An excess amount of Bi in layered structure perovskites is known to affect the ferroelectric properties, as well as the crystallographic structure [15–17]. Lua and Wen [18] reported the influence of excess of bismuth on the ferroelectric characteristics of barium–bismuth–tantalate thin films. The authors observed that an excess amount of bismuth contents (10 mol%) in BaBi$_2$-Ta$_2$O$_9$ thin films substantially further improves their ferroelectric properties. However, adding bismuth species more than 10 mol% leads to the formation of Bi$_2$O$_3$, thereby inducing high leakage current. Therefore, a comprehensive study of the role of excess Bi on BBT ceramics is still lacking. The control of Bi composition during the crystallization process is found to be important in obtaining large remanent polarization values for SBT films [19]. To prevent the evaporation of Bi from bulk surface, excess Bi is usually required to achieve stoichiometry [20,21].

In view of this, our paper reports the role of Bi ions on the structural, morphological and electrical properties of BaBi$_2$Ta$_2$O$_9$ ceramics obtained by a mixed oxide procedure, with attempt to obtain dense ceramics with controlled microstructure.

2. Experimental procedure

BaCO$_3$ (Mallinckrodt), Bi$_2$O$_3$ (Baker Analyzed) and Ta$_2$O$_5$ (Alfa Aesar) were used as raw materials. An excess of bismuth varying from 0 to 30 mol% was added, aiming to obtain the desired stoichiometry and improve the electric properties. Appropriate quantities of BaCO$_3$, Bi$_2$O$_3$ and Ta$_2$O$_5$ were mixed and homogenized in an attritor (Szeguari Attritor 01HD) with zirconia balls at 400 rpm during 1 h in acetone medium. After drying and sieving, the powders were placed in a zirconium oxide crucible and calcinated in a conventional furnace at various temperatures ranging from 800 to 950 °C for 2 and 4 h. The resulting products were crashed in a mortar and prepared in fine powder form for X-ray diffraction (XRD) analysis. The XRD data were collected with a Rigaku 20-2000 diffractometer under the following experimental conditions: 40 kV, 30 mA, 20°≤2θ≤70°, Cu-K$_\alpha$ radiation monocrimatized by a graphite crystal, divergence slit=2 mm, reception slit=0.6 mm, step time=10 s.

To obtain sintered ceramics, the calcinated powders were pressed in cylinder form (5×8 mm), first by uniaxial pressure at 970 MPa and then by isostatic pressure (210 MPa). The obtained pellets were sintered in a box furnace with heating rate of 3 °C/min from room temperature up to the range of 800 to 1150 °C for 2 h with a constant heating rate of 5 °C/min. The sintering process was performed in a closed system containing 10 wt.% of BBT atmosphere powder to maintain the initial stoichiometry. The densities of the pellets were determined by the Archimedes method. A scanning electron microscope (SEM; Topcom SM-300) was used to analyze the microstructure, shape and grain size.

Fired-on silver paste was used as the electrode material for measurement of the dielectric properties of the sintered samples. The dielectric constant versus temperature [ε(T)] was measured in the range of room temperature up to 300 °C, with a heating rate of 1.5 °C/min and an impedance analyzer (model 4192A, Hewlett-Packard). Polarization versus electric field (P–E) curve) of the sintered samples was investigated at room temperature using a Radiant Technology RT6000 A in a virtual ground mode.

3. Results and discussion

The X-ray data for the powders calcinated from 800 to 950 °C for 2 and 4 h in a step of 50 °C and with different excess of bismuth are shown in Fig. 1(a) and (b), respectively. No significant influence of the annealing time on the crystallinity of material was observed, indicating that short periods are sufficient to obtain the full crystallization of the BBT phase. At 900 °C, the main peaks corresponding to the BBT phase were observed, indicating that the solid-state reaction has started, and its amount significantly increased with an increase in temperature (Fig. 1(a)). On the other hand, the secondary phases Ba$_3$Ta$_4$O$_{15}$ at 2θ=32°, Ta$_2$O$_5$ at 2θ=56° and Bi$_2$O$_3$ at 2θ=29° and 33° were present at lower temperatures. This indicates that the temperature to obtain the BBT phase by solid-state reaction is higher when compared with other preparation methods [12]. The peaks of the starting materials only dominate in the mixture annealed at 800 °C for 2 h, and their peak intensities decrease gradually with an increase in annealing temperature. The
presence of $\text{Ba}_3\text{Ta}_4\text{O}_{15}$ is accompanied with a corresponding decrease in the contents of the educts $\text{Bi}_2\text{O}_3$ and $\text{Ta}_2\text{O}_5$. Fig. 1(b) shows the influence of excess of bismuth on the phase formation of the BBT powders. As can be seen, the addition of 30 mol% in excess leads to strong modification in the crystal lattice of the BBT, resulting in a disappearance of some peaks related to the main phase. The formation of defects in the crystal structure of the system can be the reason for such behaviour. To understand all the phenomena involved on the role of excess of bismuth, a detailed analysis of the structure factor by using Rietveld method should be performed. However, as a consequence, one can say that the excess of bismuth lower than 20 mol% is the suitable condition to obtain the BBT phase.

To evaluate the influence of temperature and the excess of bismuth on the densification process of the BBT phase, pellets obtained from the homogenized raw powders were pressed and sintered in the range of 800–1150 °C for 2 h in a step of 50 °C. Fig. 2 shows the dependence of the sintered temperature and excess of bismuth as a function of the ceramics density. It can be noted that independently of the excess of bismuth added on the system, the density increases up to a sintered temperature of 1000 °C. However, it drops markedly at higher temperatures due the volatilization of bismuth oxide. Compared with the theorical density reported in the literature, the maximum density obtained in our samples were observed for the system containing 15 mol% in excess of bismuth (95.2% of theorical density; [22]). For samples with excess of bismuth > 20 mol%, the
density decreased, indicating that the system reached the limit of solubility of excess of bismuth in the matrix.

To evaluate the influence of excess on bismuth on the shape and size of the grains, SEM analyses were performed. Considering that, for temperatures higher than 1000 °C, bismuth volatilization occurs, it was necessary to investigate the behaviour at lower temperatures. The microstructures of the pellets sintered at 1000 °C for 2 h were examined by SEM and are illustrated in Fig. 3. The excess of bismuth was found to change the microstructure drastically. Relatively small grain sizes (0.1–0.2 μm) were observed for the samples with lower excess of bismuth. For samples with 30 mol% in excess of bismuth (Fig. 3c), an abnormal grain growth was observed (1.5–2.5 μm), whereas ceramics with 20 mol% of bismuth exhibited a large number of BaBi2Ta2O9 faceted grains with a plate-like morphology (Fig. 3b).

The data of electric characterizations present the average measurement values of three samples. The dielectric constant of the ceramics as a function of temperature and the amount of excess of bismuth are given in Fig. 4. Here, the dielectric constant was measured at a frequency of 100 kHz. The dielectric constant increases until 1050 °C for BBT pellets with an excess of bismuth <20 mol%, except for the sample with an excess of bismuth of 15 mol%. After that, a strong decay is observed, indicating a degradation of the BBT phase, which results from the volatilization of Bi2O3 and possible formation of BaTa2O6. Since the Bi-content dependence of XRD and dielectric constant in BBT ceramics was not reported before, it is difficult to compare these parameters in this study with the literature. However, the systematic variation of dielectric constant and the XRD analysis of phases revealed the limit of the Bi content, which
could be incorporated into the lattice of BBT ceramics. The maximum Bi content that the BBT structure can tolerate is approximately 10 mol%. Although the samples having an excess of bismuth of 10% present a small amount of bismuth oxide besides the main BBT phase, its dielectric constant reaches the maximum value compared with all investigated systems. A higher dielectric constant value in the sample free of excess of bismuth obtained from the solid state reaction with the literature data can be observed [1]. This difference can be attributed to different grain size, density and sintered temperature to obtain the ceramics.

At room temperature, the dielectric constant for the BBT sample with 10% of bismuth excess and sintered at 1000 °C for 2 h has a value of 400 and a dissipation factor of 0.03 (Fig. 5). The highest dielectric constant obtained at 1000 °C is also due to the better densification and crystallization process observed for the BaBi$_2$Ta$_2$O$_9$ pellets. The smaller solid solution limit in this study arose from the greater grain size found in this work, which cannot tolerate more grain boundary phases. No strong relation between dielectric constant and temperature was verified, indicating that the material possesses a relaxor behaviour. The increase in dielectric loss with temperature can be the reason for the observed finite conductivity arising from some space charge layer and can also be attributed to the parasitic series resistance in the circuit. Our dielectric measurements are in good agreement with the data reported in the literature [8].

Fig. 6 shows the ferroelectric hysteresis loops for BBT ceramics sintered at 1000 °C for 2 h with different excess of bismuth. It can be clearly seen that regularly shaped hysteresis loops were observed for BBT pellets free of excess of bismuth and with 10 mol%, indicating that the

![Graph](image)
polarization process can be easily accomplished. The polarization switching in films with rounded grains is usually more difficult. The domain walls in plate-like grains are easier to be switched under external field. On the other hand, for BBT pellets with excess of bismuth equal to 30 mol%, the pinning the domain walls occurs and makes the polarization process difficult to accomplish. The lack of reversal polarization was caused by the high electrical losses, which are related to a number of structural defects. The domains with different orientation, grain boundaries, oxygen vacancies and accumulation of stoichiometry defects during crystal growth could cause the higher losses. The small remanent polarization for the sample free of excess of bismuth results from a relatively poor crystallinity caused by bismuth oxide volatization from the ceramic surface. For the sample with 30 mol% in excess of bismuth, a change in the crystal structure according to the X-ray data was observed and also lead to a small remanent polarization. For the sample with 10 mol% in excess of bismuth, the limit of solubility is not overcome, and it compensates the loss of Bi induced by the evaporation of Bi through the surface of ceramics, improving the value of remanent polarization. It should also be noted that the hysteresis loop of all ceramics shows a significant shift along the electric field axis towards the positive side, which is defined as imprint. The voltage shifts may lead to a failure of the capacitor due to the apparent loss of polarization in one of the remanent states. Consequently, an increase in the coercive voltage in one direction occurs. The main cause of this behaviour is the presence of charge species, oxygen vacancies and dipoles complexes formed in the ceramic [23].

4. Conclusions

In this study, the role of excess Bi ions on the structural, morphological and electrical properties of BBT was studied with the aid of XRD, SEM, dielectric properties and P–E curve. Dense BaBi₂Ta₂O₉ ceramics were obtained by the mixed oxide procedure at sintering temperatures of 1000 and 1050 °C for 2 h. From the SEM analyses, it was noted that the increase in Bi excess favored the grain growth in the ceramic. The excess of bismuth strongly influence on the dielectric properties of the BBT ceramics. Independently of the sintering temperature, the excess of bismuth of 10 mol% led to a high dielectric constant and low dielectric losses of about 400 and 0.03, respectively. No strong dependence of dielectric constant with temperature was noticed for the BBT pellet sintered at 1000 and 1050 °C for 2 h, indicating a relaxor behaviour. The P–E curve indicated that an excess of bismuth of 10 mol% is desirable to switch the domains and increase the ferroelectric properties of BBT ceramics.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq and CAPES.

References