Niobium doped Bi$_4$Ti$_3$O$_{12}$ ceramics obtained by the polymeric precursor method

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Abstract

Pure and niobium doped bismuth titanate ceramics (Bi$_4$Ti$_{3-x}$Nb$_x$O$_{12}$ (BTN)), with $x$ ranging from 0 to 0.4 were prepared by the polymeric precursor method. X-ray diffraction showed no secondary phases. Increasing niobium content leads to more resistive ceramics. The shape and size of the grains are strongly influenced by the niobium added to the system. The dielectric constant is not influenced by the niobium addition while hysteresis loops are significantly narrowed.

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1. Introduction

Bismuth titanate (Bi$_4$Ti$_3$O$_{12}$) ceramics are potential candidates for ferroelectric device applications due to their high dielectric constant, high Curie temperature and high breakdown strength [1–3]. Bi$_4$Ti$_3$O$_{12}$ ceramics were conventionally prepared by solid-state reaction process, where a mixture containing Bi$_2$O$_3$ and TiO$_2$ was ball milled, calcinated and finally sintered at high temperature [4]. This conventional method requires a high calcination temperature, usually leading to inevitable particle coarsening and aggregation of the Bi$_4$Ti$_3$O$_{12}$ powder. The presence of hard particle agglomerates will also result in poor microstructure and properties of the Bi$_4$Ti$_3$O$_{12}$ ceramics. Many efforts have been made to avoid this problem by lowering the calcination temperature. The methods reported in the literature to prepare Bi$_4$Ti$_3$O$_{12}$ ceramics include co-precipitation [5–7], and sol–gel processing [8]. The sol–gel process utilizes expensive precursors and the drying process is critical operation. The co-precipitation process is limited to cation solutions with similar solubility constants. However, the polymeric precursor method, which employs complexing of cations in an organic media, makes use of low cost precursors resulting in a homogeneous ion distribution at a molecular level [9]. Because of the formation of a polyester resin during the synthesis, there is no segregation of cations during the thermal decomposition of organic matter.

The applications of Bi$_4$Ti$_3$O$_{12}$ ceramics have been limited because of its high electrical conductivity, which is maximum in the $a$–$b$ plane. It is difficult to polarize Bi$_4$Ti$_3$O$_{12}$ to obtain high piezoelectric activity. It is well known that donor dopants decrease the conductivity of Bi$_4$Ti$_3$O$_{12}$ which is a p-type semiconductor. There have been correlative investigations in the literature about a modified electrical conductivity of Bi$_4$Ti$_3$O$_{12}$ when Ti$^{4+}$ was substituted by Nb$^{5+}$ or W$^{6+}$ [8–12]. Obtaining high resistivity makes it possible to observe pronounced piezoelectric properties. In the present study, phase purity, microstructure, electrical conductivity, dielectric and ferroelectric properties of Nb(V)-doped Bi$_4$Ti$_3$O$_{12}$ prepared by polymeric precursor method have been investigated. To the best of our knowledge, this is the first time that the polymeric precursor method has been used for the preparation of niobium doped bismuth titanate.

2. Experimental procedure

The procedure of the Bi$_4$Ti$_{3-x}$Nb$_x$O$_{12}$ synthesis, based on the polymeric precursor method, starts from fact that certain organic $\alpha$-hydroxycarboxylic acids can form stable chelate complexes with several cations, including Bi, Ti and Nb. During heating of the mixture containing a polyhydroxyl alcohol and the metal...
chelates, these complexes transform into a polymer, with a completely homogeneous cation distribution. Titanium isopropoxide (Hulls AG, 97% purity), hydrated lanthanum carbonate (Aldrich, 99.9% purity), niobium(V) oxide (Alfa Aesar, 99.9985% purity) and bismuth nitrate (Aldrich, 99.99% purity) were used as raw materials. The precursor solutions of bismuth, titanium and niobium were prepared by adding the raw materials to ethylene glycol (Synth, 99% purity) and concentrate aqueous citric acid (Synth, 99% purity) under heating and stirring. The molar ratio of metal:citric acid:ethylene glycol was 1:4:16 in all precursor solutions. Appropriate quantities of solutions of Ti-, Bi- and Nb-precursors were mixed and homogenized by stirring at 90 °C for 3 h. In this work, an excess of 5 wt.% Bi was added to the ideal stoichiometric mixture aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Next, the temperature was increased to 130–140 °C, yielding a high viscous polyester resin. Most of the organic material was decomposed by thermal treatment at 400 °C for 3 h. The formed porous product was crushed and heated in a crucible alumina at 750 °C for 4 h to eliminate residues of organic material. The resulting material was milled in an attritor.

Fig. 1. X-ray data for Bi$_4$Ti$_3$$_{1-x}$Nb$_x$O$_{12}$ powders calcinated at 750 °C for 4 h and different niobium content: (a) $x=0$; (b) 0.02; (c) $x=0.04$.

Fig. 2. Infrared data for Bi$_4$Ti$_3$$_{1-x}$Nb$_x$O$_{12}$ powder with $x=0.02$ after calcination at 750 °C for 2 h.

Fig. 3. SEM micrographs for Bi$_4$Ti$_3$$_{1-x}$Nb$_x$O$_{12}$ ceramics sintered at 1000 °C for 4 h as a function of niobium content: (a) $x=0$; (b) $x=0.02$ and (c) $x=0.04$. 

Fig. 4. Spectral transmittance for Bi$_4$Ti$_3$$_{1-x}$Nb$_x$O$_{12}$ as a function of niobium content.
with zirconia balls in acetone medium for 40 min using a procedure according to the literature [13].

Pure Bi$_4$Ti$_3$O$_{12}$ and niobium modified bismuth titanate, Bi$_4$Ti$_{3-x}$Nb$_x$O$_{12}$, ceramics with $x$ equal to 0, 0.02 and 0.04 were prepared as described above. Powders were first analyzed by X-ray diffraction (XRD) for phase determination. The powders were isostatically pressed (210 MPa) into pellets. The pellets were sintered inside a box furnace (heating and cooling rate of 10 °C/min) at 1000 °C for 4 h using a closed system containing 3 wt.% of Bi$_4$Ti$_3$O$_{12}$ relative to the pellets’ mass, to generate a bismuth oxide rich atmosphere. The density of the pellets was determined by the water displacement method (Archimedes). A scanning electron microscope (SEM) was used to analyze the morphology and shape of the grains (Topcom SM-300).

Gold electrodes for electrical measurements were deposited to the polished surface of sintered discs by evaporation through a sputtering system. A high resistance meter (KEITHLEY 6517A) was used to measure electrical conductivity in a direct current circuit. The relative dielectric constant, $\varepsilon_r$, in dependence of frequency was measured using an impedance analyzer (model 4192 A, Hewlett-Packard). Ferroelectric properties were measured on a Radiant Technology RT6600A tester equipped with a micrometer probe station in a virtual ground mode.

3. Results and discussion

The influence of niobium addition on the crystallinity of BIT powders calcined at 750 °C for 4 h were observed by XRD analyses (Fig. 1). Among the three different investigated compositions (Bi$_4$Ti$_{3-x}$Nb$_x$O$_{12}$, where $x=0; 0.02$ and $0.04$), all diffraction data showed the existence of a single orthorhombic phase, without any detectable secondary phase.

![Graph](image1.png)

**Fig. 4.** Conductivity as a function of niobium content for bismuth titanate ceramics sintered at 1000 °C for 4 h.

![Graph](image2.png)

**Fig. 5.** Dielectric constant as a function of frequency and niobium content for BIT ceramics sintered at 1000 °C for 4 h.

![Graph](image3.png)

**Fig. 6.** Hysteresis loops for Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ ceramics sintered at 1000 °C for 4 h as a function of niobium content: (a) $x=0$; (b) $x=0.02$ and (c) $x=0.04$. 

![Graph](image4.png)

**Fig. 4.** Conductivity as a function of niobium content for bismuth titanate ceramics sintered at 1000 °C for 4 h.
Finally, niobium at low concentrations does not change the crystal structure of the undoped system.

Fig. 2 shows the IR spectrum of the ceramic powder for the $x=0.02$ composition. The main band characteristic of the oxygen–metal bond was observed in the region 450–640 cm$^{-1}$. Due to the absence of a C=O vibration around 1450 cm$^{-1}$, it follows that the powders are free of carbonates. This result is satisfactory from a technological point of view since the electrical properties are dependent on the quality of the raw powders used to sinter the ceramic. There was, however, a vibration band noted that is associated to the deformation of O–H bonds near 1680 cm$^{-1}$. This is attributed to water adsorbed at the powder surface when the sample was in contact with the environment.

SEM images do not reveal a clear trend on the shape and size of the grains after niobium addition (Fig. 3). No precipitates were evident in the grain boundary indicating the formation of a continuous solid solution. A typical plate-like morphology was noted for pure and 0.02 niobium doped bismuth titanate. On the other hand, for the 0.04 composition a rounded morphology was observed indicating a change in the kinetics of the grain growth.

The niobium dependence of electrical conductivity measured in a direct current circuit containing bismuth titanate ceramics was studied at a temperature of 300 °C (Fig. 4).

At lower temperatures, the conductivity was too small to be measured accurately. The conductivity of niobium doped BIT was obviously lower than that of the undoped one, which is in agreement with the fact that donor dopants decrease the conductivity of a p-type semiconductors. Actually, the conductivity was dramatically decreased with a very small content of Nb$^{5+}$ doping ($x=0.02$). In Bi$_5$Ti$_3$O$_{12}$, hole compensation of bismuth vacancies ($F^\prime^+_{\text{Bi}}+3h^+$) promotes p-type electronic conductivity. When Nb$^{5+}$ substitutes Ti$^{4+}$, a positive charge center at Nb site and an electron will be created under charge neutrality restriction, which can be described as Nb$^{5+}+e^-$. These electrons neutralize the influence of the holes. According to the electronic conductivity relationship $\sigma = nq\mu$, where $n$ is the number of the carriers, $q$ the charge and $\mu$ the mobility, it becomes clear that the number of the hole carriers, $n$, was decreased, since Nb does not induce structural changes to the crystal lattice that can justify a change in the charge carrier mobility. The conductivity decreases with donor doping to a minimum value that is reached when the concentration of the electrons is equal to the hole concentration.

The dielectric constant measurements were carried out at room temperature as a function of frequency in the range of 10 Hz–10$^7$ Hz. As shown in Fig. 5, the dielectric constant shows slight dispersion with frequency indicating that our ceramics possess low defect concentrations. The low dispersion of the dielectric constant and the absence of any relaxation peak indicated that both, interfacial polarization of the Maxwell Wagner type and a polarization produced by the electrode barrier can be neglected. In this way, Nb$^{5+}$ can be considered as a kind of soft additive in Bi$_5$Ti$_3$O$_{12}$ ceramics. It softens piezoelectric ceramics, i.e. increases dielectric constant and decreases electrical conductivity.

Fig. 6 shows the ferroelectric hysteresis loops for pure and niobium doped Bi$_5$Ti$_3$O$_{12}$ ceramics. The loops never showed saturation, instead, the ceramics behave as lossy linear dielectric materials. The narrowing of the curve when increasing the niobium concentration indicates a decrease in the system conductivity, i.e. the leakage current as dielectric loss mechanism can be discarded. These results were similar to the investigations of other authors [14,15], where Nb$^{5+}$ substituting for Ti$^{4+}$ in BiTN ceramics efficiently decreased the concentration of oxygen vacancies, which weakened the influence of domain pinning on the polarization. Furthermore, as it can be seen from the SEM images, the niobium content influences the shape and size of the grains irregularly. This is also reflected in the losses determined from the hysteresis loops, which do not show a regular trend despite the obvious fact that Nb addition reduces the losses.

4. Conclusions

In summary, it was shown for the first time the successful preparation of niobium doped bismuth titanate ceramics by the polymeric precursor method. Our results support that a single phase system free of carbonate phase was obtained. The addition of niobium causes a change in the grains morphology. The conductivity of the system is strongly influenced by niobium addition. The dielectric constant was almost not influenced by the niobium content. An increase in niobium concentration leads to the narrowing of hysteresis loops due to the decrease in the conductivity.

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