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Effect of hot pressing on processing and properties of BBN ceramics

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Abstract

BBN ($BaBi_2Nb_2O_9$) is very interesting and promising lead free material with relaxor properties in capacitors, sensors and actuators.

Results of investigations of fine-grained, weakly porous, BBN-type ceramics using hot-pressing method are presented. Based on a thermal deformation curve (i.e. a shrinkage curve) of a sample the method for optimisation of the hot-pressing sintering conditions has been proposed. Some advantages of hot-pressing method over the classical ceramic method used for BBN ceramics fabrication is shown. It has been found that the deficiency in bismuth causes a change of the space group of the perovskite phase crystalline structure of BBN and unit cell parameters. The influence of bismuth deficiency on dielectric properties materials and relaxor features is presented. The measurements of pyroelectric and thermally stimulated depolarization currents (TSDC) were carried out in order to better display unusual behaviour of dielectric characteristics.

Keywords: C. Dielectric properties; Relaxor ferroelectrics; Ceramics

1. Introduction

In recent years there has been increasing interest for the ferroelectric relaxors, mainly due to their widely technical applications, for example in multilayer capatitors, sensors and actuators. The most widespread representatives of these materials are $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and $Pb_{1-0.x}La_{0.x}Zr_{0.65}Ti_{0.35}$ (PLZT x/65/35 for $x > 5$) ceramics containing lead-oxide, but considering environmental interactions they are toxic. It is the main reason for exploration the lead free alternatives materials with relaxors properties. The very promising group of this ceramics seems to be Bi-layered perovskites, belonging to the Aurivillius family. The chemical formula of these compounds is expressed as $(Bi_2O_2)^{2+}(A_{x-1}B_xO_{3x+1})^{2-}$, where x indicates the number of perovskite building blocks between two $(Bi_2O_2)^{2+}$ layers and A and B represent the different cations of low and high valences [1]. The layered structure characterized by higher value of c-parameter in comparison with a and b in orthorhombic cell and consequently lead to high anisotropy of crystallographic structure. Such effect is directly connected with high anisotropy of electrical properties. The most known representatives of this family, which are currently investigated from point of view nonvolatile ferroelectric memories, are $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN) [2,3].

The BBN ($BaBi_2Nb_2O_9$) seems also to be very interesting and promising materials. These materials were widely described by Kholkin et al. [4] and Miranda et al. [5] and also in our previous article [6]. Materials samples were prepared using conventional mixed-oxide processing technique. It is commonly assumed that for relaxor behaviour the chemical disorder caused by Ba ions is responsible. They are entering not only in the perovskites blocks but also $(Bi_2O_2)^{2+}$ layers. It is resulting in inhomogeneous distribution of Ba ions and local charge imbalance in the layered structure [7]. Ismunadar et al. [8] showed, on the basis of XRD measurements that in BBN ceramics 15–20% of Ba^{2+} ions were located in the $(Bi_2O_2)^{2+}$layers.

A crucial question in the technology of ceramic ferroelectric materials is assuring the consistence in the stoichiometry between the obtained ceramics and the chemical composition described by a chemical formula. In case of ferroelectrics ceramics containing bismuth it is of great importance. The sintering temperature of these ceramics is higher than the bismuth sublimation temperature (860 °C). This is the main reason that the real ceramics of that type exhibit a disturbance in the stoichiometry. This disturbance is connected with the

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creation of Bi vacancies in the BBN crystalline structure. It influences strongly the electrical properties (is leading to additional contributions to the intergrain impedance) and the structure parameters of elementary cell.

The experiments, described in this paper, were carried out in order to study the effect of the hot-pressing process on the relaxor behaviour of BBN ceramics. Based on a thermal deformation curve (i.e. a shrinkage curve) of a sample the method for optimisation of the hot-pressing sintering conditions was used in preparation of BBN ceramics. Optimal temperature of sintering (T_s) at a given pressure (p_s) and time of thermal processing (t_s) correspond with the point on the shrinkage curve, which shows the end of consolidation process of the sample. During the sintering under pressure there is an increase powder liquidity what leads to close defects and cracks and simultaneously a homogeneous microstructure with a density close to the theoretical one is obtained.

Some advantages of hot-pressing method over the classical ceramic method were used for ferroelectric oxides fabrication especially for materials containing elusive elements (La, Pb, $ZrTiO_3$) because this way of ceramics consolidation allow to decrease the sintering temperature of 100–200 °C [9].

In case of PLZT and PMN ceramics, the mentioned method significantly improved the quality of investigated ceramics [10].

2. Experimental procedure

Stoichiometric amounts of $BaCO_3$, Bi_2O_3, Nb_2O_5 were weighted and mixed. The sintering process was carried out by two-step sintering. In the first step the conventional sintering at 950 °C for 2 h was carried out. Then the materials were crushed, milled and sieved. The hot-pressing technological unit was used in the second step. Pressure was constant and equal to $p_s = 20$ MPa, time of sintering was $t_s = 2$ and 6 h and sintering temperature was $T_s = 1060$ °C.

The Archimedes displacement method with distilled water was employed for the evaluation of the samples density. XRD measurements were carried out on all ceramics samples, at room temperature, using a Huber diffractometer (Seemann–Bohlin geometry) with a monochromatic Cu Kα_1 radiation (30 kV, 30 mA). XRD patterns were made from 22° to 100° in 2θ with 0.02° steps and a 2 s counting time. The angle scale of received diffraction diagrams was scaled to 2θ (Bragg–Brentano geometry) by Au standard (JCPDS number 12-0403). The cut and polished 0.6 mm thick samples, coated with silver electrodes, were used for the measurements of the real (ε') and imaginary (ε'') parts of dielectric permittivity versus temperature. The measurements were carried out during heating by using an impedance analyzer HP4192A. The samples were heated at 723 K prior to measurement allowing the recombination and relaxation of part of the frozen defects, formed during the sintering.

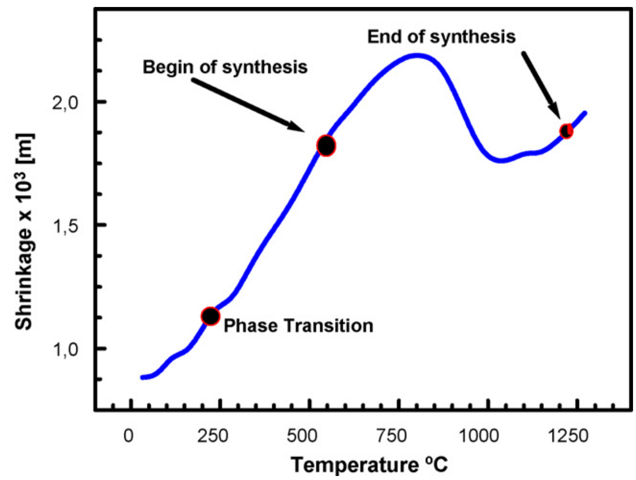

Fig. 1. Characteristic points on the shrinkage curve indicating the state of ceramics synthesis.

3. Results and discussion

For fabrication of fine-grained, low porous, high density BBN-type ceramics the hot pressing was used. The method for optimisation of the hot-pressing sintering conditions based on a thermal deformation curve (i.e. a shrinkage curve) of a sample has been proposed. Optimal temperature of sintering (T_s) at a given pressure (p_s) and time of thermal processing (t_s) correspond with the point on the shrinkage curve, which shows the end of consolidation process of the sample (Fig. 1).

The characteristic points on the shrinkage curve indicates the temperature $T_s = 1060$ °C as optimal sintering temperature, in which the shrinkage of the sample finishes (Fig. 2a). Additional increasing in temperature ($T_s = 1075$ °C) leads to abnormal grain growth and to an increase of porosity.

The best chemical constitution and improvement of structure and microstructure (decrease in porosity, increase in density, decrease in grain size) is achieved at temperature $T_s = 1060$ °C (Fig. 2b).

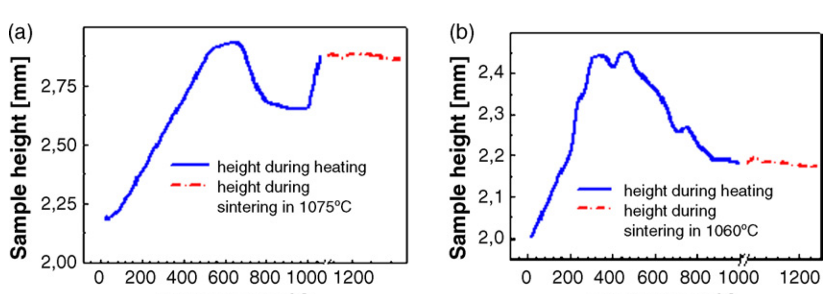

Fig. 2. Shrinkage curves of BBN ceramics in sintering temperature $T_s = 1075$ °C (a) and $T_s = 1060$ °C (b).