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Dielectric relaxation and ferroelectric phase transition in $Sr_4BiRTi_4Nb_6O_{30}$ (R = Sm, Eu) ceramics

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ABSTRACT

$Sr_4BiRTi_4Nb_6O_{30}$ (R = Sm, Eu) ceramics with tetragonal tungsten bronze structure were prepared by the conventional solid state reaction method. The crystalline structure, microstructure, dielectric and ferroelectric properties of the ceramics were investigated. Structural analysis using the powder x-ray diffraction patterns revealed the formation of tetragonal tungsten bronze structure in space group *P4bm*. Columnar grains with a homogeneous distribution were formed in $Sr_4BiEuTi_4Nb_6O_{30}$ ceramics, while in $Sr_4BiSmTi_4Nb_6O_{30}$ ceramics the microstructure became inhomogeneous and some abnormal grains were also formed. The dielectric properties of the ceramics exhibited relaxor type phase transition which can be attributed to the random distribution of Bi and Sm/Eu ions at A1-sites and Ti and Nb ions at the B-sites of the TTB structure. The peak temperature shifted towards the higher temperatures and the magnitude of the dielectric constant decreased with increasing frequency. Moreover, the temperature of the dielectric maximum T_m increased as the radius of the R ion getting decreased. From the P-E hysteresis loops, remnant polarization of 0.83 μC/cm^2 and 0.6 μC/cm^2 were obtained for $Sr_4BiEuTi_4Nb_6O_{30}$ and $Sr_4BiSmTi_4Nb_6O_{30}$, respectively.

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1. Introduction

Relaxor ferroelectrics are characterized by high and broad maxima in the temperature dependence of the dielectric constant and dielectric loss along with their peaks shift towards higher temperature with increasing frequency [1]. In addition, the dielectric behavior of relaxor ferroelectrics is related to the dynamics and formation of polar clusters [2]. For the well-known classical ferroelectrics, the dielectric maximum temperature (T_m) corresponds to the ferroelectric-paraelectric (FE–PE) phase transition temperature (T_C) and it is frequency independent. However, for relaxor ferroelectrics the T_m shows a frequency dependent behavior. Relaxor ferroelectric materials have attracted much attention both in fundamental and applied researches, such as for the development of piezoelectric sensors and actuators, due to their excellent dielectric and electromechanical properties. However, most relaxors are lead-based, such as $PbMg_{1/3}Nb_{2/3}O_3$ and its derivative compounds, which present a disadvantage due to the volatility and toxicity of PbO [3]. Therefore, current research attracts attention towards lead free relaxor materials, such as tetragonal tungsten bronze (TTB) oxides, which are more environmentally friendly.

TTB oxides with a general formula of $(A_2)_4(A_1)_2(C)_4(B_1)_2(B_2)_8O_{30}$ received much attention owing to their dielectric, pyroelectric, piezoelectric and electro-optic properties [4–8]. TTB materials exhibit unique structural features with a complex array of distorted BO_6, which is the cause for the variable dielectric characteristics of TTBs, octahedral sharing corners and three different types of interstices A_1 (square), A_2 (pentagonal), and C (trigonal) with 12-, 15- and 9-fold coordination, respectively [9,10]. For the filled tungsten bronze structures, the smallest interstice C is empty and the general formula becomes $(A_2)_4(A_1)_2(B_1)_2(B_2)_8O_{30}$. According to the cationic occupation, TTB materials show several dielectric anomalies such as ferroelectric transition from commensurate *P4/mbm* to incommensurate *P4bm* and dielectric relaxation around or below the ferroelectric transition temperature [11]. Moreover, the dielectric relaxation behavior of TTB compounds can be attributed with the formation of dynamic polar clusters which are associated with the off-center Ti/Nb cationic displacements and the polar clusters grow in size with decreasing temperature [2,8].

The ferroelectric nature and the dielectric property of filled

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tungsten bronze structures, such as $M_4R_2Ti_4Nb_6O_{30}$ and $M_5RTi_3Nb_7O_{30}$ (where M = Ba, Sr, Ca; R = rare earth cations and Bi), are affected by the A-sites cationic occupation [11–16]. Consequently, the ferroelectric transition of the filled tungsten bronzes is controlled by the ionic radius of A_1 site cations. Meanwhile, a commensurate octahedral tilting arises when the average ionic radius of A_1 site cations decreases and thus normal ferroelectric transition occurs. Therefore, filled TTBs with smaller ionic radius difference (Δr) between A_1 and A_2 site cations have a tendency to be relaxor ferroelectrics, while larger Δr induces to be normal ferroelectrics [15]. In general, TTBs with larger Δr show normal ferroelectric peak followed by some low temperature dielectric relaxation but with decreasing Δr, the normal ferroelectric peak gradually changes to diffuse and relaxor type and finally the low temperature dielectric relaxation becomes stronger [17]. So, in order to tune the dielectric and ferroelectric properties in high temperature range, it is necessary to conduct further investigations by using different cationic substitutions. Recently, Zhu et al. [11,15,18] investigated the low temperature dielectric relaxation and ferroelectric phase transition in $Sr_4R_2Ti_4Nb_6O_{30}$ and $Sr_5RTi_3Nb_7O_{30}$ (for R = La, Sm, Eu) tungsten bronze structure compounds. However, to the best of our knowledge, no work has been reported on the dielectric relaxation and ferroelectric phase transition in $Sr_4BiRTi_4Nb_6O_{30}$ [SBRTN (R = Sm, Eu)] tungsten bronze compounds in the high temperature range.

In the present work, the dielectric relaxation and ferroelectric transition properties of $Sr_4BiRTi_4Nb_6O_{30}$ (R = Sm, Eu) tetragonal tungsten bronze ceramics were investigated over a broad temperature range. The effects of the A-sites cationic radius difference on the dielectric relaxations and ferroelectric transitions were evaluated and discussed in detail as well. Moreover, the features of the ferroelectric transition and the origin of the dielectric relaxation below the ferroelectric transition temperature are discussed intensively.

2. Experimental procedures

All the dense SBRTN ceramics were prepared by a conventional solid-state reaction and ceramic processing technique. The starting carbonates and oxides of $SrCO_3$(99%), Bi_2O_3(99%), Sm_2O_3(99.9%), Eu_2O_3(99.99%), TiO_2(99%) and Nb_2O_5(99.99%) were mixed in stoichiometric amounts using an agate mortar and pestle for 8 h. The mixed powders were calcined at 1100 °C for 3 h in an alumina crucible. The calcined mixtures were reground for 2 h and pelletized under a pressure of 30 MPa into disks of a 12 mm in diameter and a 1 mm thickness. Finally, the pellets were sintered at a temperature of 1300 °C for 3 h and the temperature was slowly cooled to 1100 °C at a rate of 2 °C/min and finally cooled with the furnace to room temperature.

Phase analysis was carried out by powder x-ray diffraction (XRD, Philips X'Pert pro, PANalytical Company, Almelo, Holland) with Cu $K\alpha$ radiation (λ = 1.5414 Å) at room temperature. The XRD data were collected in the range of $2\theta = 20°–75°$ with a step size of 0.02°. The surfaces of the ceramics samples were platinum coated by sputtering technique to check the surface morphologies of the pellets. The morphologies of the ceramic samples were characterized using field emission scanning electron microscopy (FESEM, FEI SIRION 200) at room temperature. For more detailed structural and micro-structural investigation, transmission electron microscopy study was implemented. The samples for TEM measurements were prepared by focused ion beam (to make the samples thinner) equipped with SEM machine and accordingly the nanostructure is characterized by TEM. The dielectric properties were measured using Precision Impedance Analyzer (WAYNE KERR 6500B, Wayne Kerr Electronics; Wayne Kerr Company, Bognor Regis, West Sussex, UK). The leakage current density and ferroelectric polarization were measured by a standard ferroelectric tester (Precision Premier II, Radiant Technology, USA).

3. Results and discussion

As shown in Fig. 1, the tungsten bronze structure with space group *P4bm* was determined by x-ray diffraction patterns for both $Sr_4BiSmTi_4Nb_6O_{30}$ (SBSTN) and $Sr_4BiEuTi_4Nb_6O_{30}$ (SBETN) ceramics. Assessment of the peak intensities clearly demonstrates that the ceramics are TTB structures with very small secondary phases which are in agreement with $Sr_5BiTi_3Nb_7O_{30}$ ceramics (JCPDS card file No. 00-038-1250).

The scanning electron micrographs of SBSTN ceramic samples are presented in Fig. 2. It can be seen that columnar grains are homogeneously distributed over the entire sample for SBETN ceramics [Fig. 2(b)] with an average length and diameter of 10 μm and 1.75 μm, respectively. However, for SBSTN ceramics [Fig. 2(a)] normal grains with an average length and diameter of 8 μm and 1.6 μm, respectively and some anisometric grains with an average width of 4 μm have been formed. Abnormal grain growth and crack formation are common in tetragonal tungsten bronze structure materials when they are sintered with a very high temperature [19]. Therefore, the formation of abnormal grain growth indicates the existence of a liquid phase sintering. Homogeneously columnar grain distribution is very helpful to get large dielectric constant of a material by blocking the conduction current as compared to the heterogeneously columnar grain distribution. Due to this reason, as shown in Fig. 4, the maximum dielectric constant is larger in SBETN than that of SBSTN ceramics.

Room temperature ferroelectric domain structure of SBSTN compound is shown in Fig. 3. Selected area electron diffraction (SAED) patterns were conducted from a number of different areas. Obvious ferroelectric domain structures (needle like nanodomains) are observed for SBSTN ceramics. The diameter of these nanodomains ranges from 0.2 nm to 3 nm. Moreover, the orientation, shape and size of these domains are not uniform which is an indication of the domain boundaries. However, it is not easy to see clearly the grain-to-grain domain variation across the sample. Hence, it is necessary to conduct further study to analyze the domain structure. According to the selected area electron diffraction patterns, the features of the ferroelectric domains are spike-like structure which are parallelly oriented with the polar axis, indicating ferroelectric 180° domains [10].

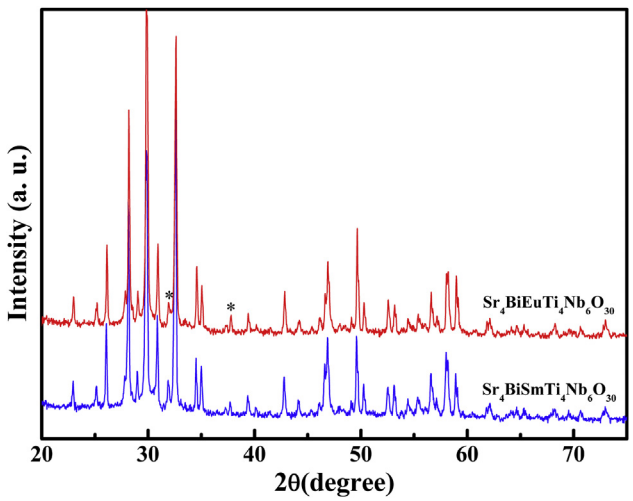

Fig. 1. The XRD patterns of $Sr_4BiRTi_4Nb_6O_{30}$ (R = Sm and Eu) ceramics.

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