Physica B 407 (2012) 4752–4759

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Study of $(Bi_2O_3)(Ba_xMo_{1-x}O_3)$ polycrystalline ceramic as relaxor ferroelectric

Paramjeet Singh [a], Ashish Agarwal [a], Sujata Sanghi [a,*], Navneet Singh [a], Satish Khasa [b]

[a] Department of Applied Physics, Guru Jambheshwar University of Science and Technology, Hisar-125001, Haryana, India
[b] Department of Physics, Deenbandhu Chhotu Ram University of Science and Technology, Murthal, Sonipat-131093, Haryana, India

ARTICLE INFO

Article history:
Received 27 April 2012
Received in revised form
22 August 2012
Accepted 26 August 2012
Available online 31 August 2012

Keywords:
Bismuth layered ceramics
Solid-state reaction method
Dielectric properties
Electric modulus

ABSTRACT

Solid solutions of bismuth layered $(Bi_2O_3)(Ba_xMo_{1-x}O_3)$ ($0.2 \le x \le 0.8$, x is in step of 0.2) ceramics were prepared by conventional solid-state reaction of the constitutive oxides at optimized temperatures with a view to study its electrical properties. Powder X-ray diffraction has been employed for physical characterization and an average grain size of ~16 to 22 nm was obtained. XRD study reveals the single phase structure of the samples. Dielectric properties such as dielectric constant (ε'), dielectric loss ($\tan\delta$) and ac electrical conductivity (σ_{ac}) of the prepared ceramics sintered at various temperatures in the frequency range 10^1–10^7 Hz have been studied. A strong dispersion observed in the dielectric properties shows the relaxor type behavior of the ceramic. The presence of maxima in the dielectric permittivity spectra indicates the ferroelectric behavior of the samples. Impedance plots (Cole–Cole plots) at different frequencies and temperatures were used to analyze the electric behavior. The value of grain resistance increases with the increase in Ba ion concentration. The conductivity mechanism shows a frequency dependence, which can be ascribed to the space charge mainly due to the oxygen vacancies. The relaxation observed for the M'' (ω) or Z'' (ω) curves is correlated to both localized and long range conduction. A single 'master curve' for the normalized plots of all the modulus isotherms observed for a given composition indicates that the conductivity relaxation is temperature independent.

1. Introduction

Bismuth layer-structured ferroelectric (BLSF) ceramics are having tremendous importance because they are not only lead-free piezoelectrics but also offer high transition temperatures (T_c) thereby, making them important and attractive in today's environment [1,2]. These materials exhibit low temperature coefficients of dielectric properties which make them suitable as pressure sensors and trapped energy filters. In addition to this, good ferroelectric, ferromagnetic and piezoelectric properties, low aging rate and strong anisotropic electromechanical coupling factor make them suitable as nonvolatile ferroelectric random access memory (FRAM) devices [3,4]. Some of the Fe containing compounds of this family show simultaneous ferroelectric and ferromagnetic properties, and hence exhibit magnetoelecric (ME) effect under the influence of external magnetic/electric field [5]. The general formula for oxides of the Aurivillius family is given as $Bi_2A_{n-1}B_nO_{3n+3}$ or $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ which consists of regular intergrowth of $A_{n-1}B_nO_{3n+1}$ perovskite-like slabs and Bi_2O_2 sheets, where A is mono-, di-, or trivalent elements (Na, K, Ca, Sr, Ba, Bi, or Pb) allowing dodecahedral coordination and B is tri-pentavalent transition elements (Fe, Ti, Nb, Ta, Mo or W) allowing octahedral coordination and n is number of perovskite-like slabs which varies from 1 to 6 [4,5]. The double-sided Bi_2O_2 sheets are composed of square pyramidal BiO_4 groups sharing their basal edge. Generally, the crystal structure, microstructure and physical properties of materials are influenced by the composition fluctuation and experimental conditions. In addition to the broad structural range of these materials, extensive research has been carried out in the form of acceptor and donor dopants to further affect the dielectric and piezoelectric properties [6,7]. Modifications on the B-site offer improved electrical resistivity and microstructural effects. Detailed structural studies by Villegas et al. [8] have shown that the major contribution to the ferroelectric polarization of bismuth layered perovskites is due to the displacement of A-site cations along the 'a' axis of the perovskite unit accompanied by octahedral rotations around 'a' and 'c' axes. Due to relatively high T_c of these materials they are difficult to polarize, and also restricted by their inherent low number of polarization directions, associated with their low symmetry [9]. A lot of research work has been carried out on BLSF ceramics since the beginning of 1960s. Smolenskii had reported a considerable diffuseness of the phase transformation in Ba-based ferroelectrics with Bi-layered structure in $BaBi_2Ta_2O_9$ (BBTO) and $BaBi_2Nb_2O_9$ (BBNO) ceramics [10]. It was observed that these materials have excellent stability against

* Corresponding author. Tel.: +91 1662 263384; fax: +91 1662 276240.
E-mail address: sutkash@yahoo.com (S. Sanghi).

0921-4526/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2012.08.037

repetitive switching, useful piezoelectric properties and can be used in nonvolatile ferroelectric memories [11]. Detailed literature survey on structure, microstructure and dielectric properties of the titled compound shows that these said properties have not been reported so far. Therefore, this paper mainly reports the structural and dielectric properties of $(Bi_2O_3)(Ba_xMo_{1-x}O_3)$ (BBMO) ceramics.

2. Experimental details

Stoichiometric mixtures of $(Bi_2O_3)(Ba_xMo_{1-x}O_3)$ i.e. BBMO samples ($0.2 \le x \le 0.8$, x is in step of 0.2) were prepared using solid state reaction method. Bi_2O_3, $BaCO_3$ and MoO_3 were used as the starting materials for the preparation of the bulk samples. Appropriate amount of the powders was mixed and grinded for two hours. The powdered mixture was then sintered at different temperatures starting from 600 °C up to 800 °C for 4 h. in a programmable furnace with an increasing rate of temperature at 2 °C per minute. In first step the samples were sintered at 600 °C, then cooled at room temperature, grinded and then again sintered at 700 °C, then again cooled and grinded and finally sintered at 800 °C and then cooled. The sintered powder was pressed at 15 MPa to form pellets of approx. 13 mm in diameter. PVA (polyvinyl alcohol) is used as binder (3% by weight). The pellets were then sintered at 500 °C for 1 h to remove the binder and then painted with silver for electrical contact.

The X-ray diffraction patterns of the powdered samples were recorded using Miniflex-II X-ray diffractometer (Rigaku) using CuK_α radiations of wavelength 1.5404 Å in the range $10^0 \le 2\theta \le 90^0$ at a scanning rate of 2°/minute. The dielectric and impedance measurements were carried out using impedance analyzer on pellets with different thickness. The complex impedance measurements were conducted at different temperatures (25 °C to 500 °C) as a function of frequency in the range 1 Hz–10 MHz by applying a small ac signal of ~30 mV magnitude.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the X-ray diffraction patterns of all the prepared BBMO samples sintered at 700 °C. The samples were found to be well crystallized in the single phase. There were no detectable secondary phases for sample $x=0.8$, indicating the complete solid solution of the BBMO composition. The diffraction patterns of the compounds are in good agreement with those reported earlier [10,11]. The position and intensity of intense peaks suggest the formation of perovskite structure. It is observed that the peaks in the pattern for $x=0.8$ ceramic belongs to monoclinic system with centrosymmetric space group 12/m (ICDD# 896097). For $x=0.2$ and 0.4 ceramics the strongest peak (2 0 0) at angle 28.82° matches the main phase of tetragonal structure with body centered structure with space group 14/mmm (ICDD# 891723). Some variations in the peak intensities of certain peaks have been observed which can be attributed to the variation in lattice distortions in the samples. In addition, it is found that a small shift of diffraction peaks is observed towards higher diffraction angles as the Ba content increases, which could be ascribed due to the larger ionic radius of Ba^{2+} (1.60 Å) ion than that of Mo (0.59 Å) ion. The intensities of the major peaks increase with increase in the value of 'x' and sharp peaks are observed for the sample with $x=0.8$, which shows the formation of single crystalline phase. The coherently scattered crystallite size (D) of the samples was estimated from the broadening of reflection peaks

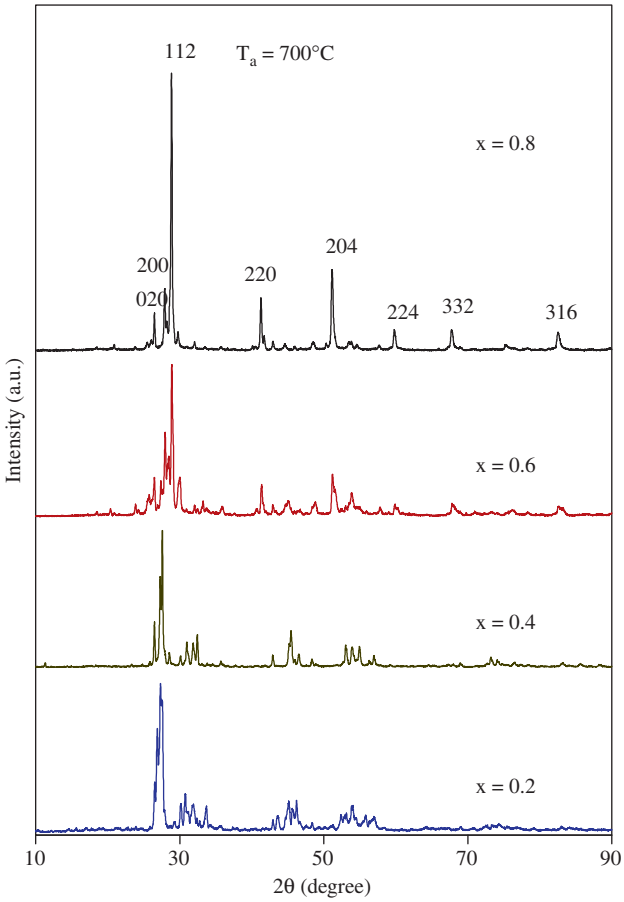

Fig. 1. X-ray diffraction patterns of $(Bi_2O_3)(Ba_xMo_{1-x}O_3)$ samples (T_a=700 °C).

Table 1
Average grain size (D), transition temperature (T_c), activation energies (E_a), grain resistance (R_g), relaxation times for tan δ ($\tau_{\tan\delta}$), complex impedance ($\tau_{Z''}$) and complex modulus ($\tau_{M''}$) of $(Bi_2O_3)(Ba_xMo_{1-x}O_3)$ samples for T_a=700°C.

x	D (nm)	T_c (°C)	E_a (ev)		R_g (MΩ)	$\tau_{\tan\delta}$ ($\times 10^{-3}$) (s)	τ_Z ($\times 10^{-4}$) (s)	τ_M ($\times 10^{-5}$) (s)
			low T (°C)	high T (°C)				
0.2	16	420	0.13	0.65	0.16	1.66	2.61	2.92
0.4	18	400	0.35	0.67	3.16	3.19	2.33	2.78
0.6	20	390	0.61	0.82	6.46	6.13	0.14	0.77
0.8	22	380	0.82	1.06	16.83	12.31	0.09	0.42

(widely scattered in 2θ) using Scherrer's equation,

$$D = \frac{0.89\lambda}{\beta_{1/2}\cos\theta} \quad (1)$$

where λ (1.5404 Å) is X-ray wavelength and $\beta_{1/2}$ is the peak width of reflections at half-maximum intensity. The average crystallite size was found to be ~16 to 22 nm (ignoring strain and other effects) and is given in Table 1 for all the samples.

3.2. Dielectric properties

The dielectric properties were measured in terms of dielectric constant and loss factor ($\tan\delta$). Fig. 2 illustrates the variations of the real part of dielectric permittivity (ε') as a function of