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Structure, IR spectra and dielectric properties of Bi_2O_3–ZnO–SnO_2–Nb_2O_5 quarternary pyrochlore

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Abstract

A new series of pyrochlore compounds $(Bi_{1.5}Zn_{0.5})(Zn_{0.5-x/3}Sn_xNb_{1.5-2x/3})O_7$ $(0 \leqslant x \leqslant 1.5)$ have been prepared by the solid reaction technique. X-ray diffraction (XRD) and IR absorption spectra were used for analyzing the compositions. Single-phase specimens having cubic pyrochlore structure were obtained for various Sn content. Only one broad band ascribable to B–O stretching vibration was observed for each sample. The dielectric properties were systematically studied and the temperature dependence of the dielectric constant and dielectric loss was measured in the temperature range 150–200 °C. At room temperature (RT), the dielectric constant for Sn-doping Bi-based ceramics decreased and the temperature coefficient increased with increasing Sn^{4+} content. Rather low dielectric loss was obtained for series compositions. © 2002 Published by Elsevier Science Ltd and Techna S.r.l.

Keywords: Bi based pyrochlore; Cubic pyrochlore; Temperature coefficient

1. Introduction

Dielectric ceramics are widely used with advances in microelectronic technologies microwave communication, and high dielectric constant ceramics have received intensive attention in reducing the size of microelectronic circuits, where low dielectric loss and near-zero temperature coefficient of the dielectric constant are required for many applications.

Mixed metal oxides represented by the general formula are $A_2B_2O_7$ oxide pyrochlores with good chemical and thermal stability [1]. The crystal structure of most pyrochlores belongs to a cubic system whose lattice constant (a) is about 1.0 nm and there are eight formulas in a unit cell [2,3]. In the cubic oxide pyrochlore, the large A-ions have an eight fold coordination whereas the smaller B-ions have an octahedra type oxygen surrounding and a six-fold coordination by the nearest B neighbors. One can view the sublattice of the B-ions as a network of corner-linked tetrahedra or as an arrangement in which each B-ion is located within a trigonal antiprism of the other six B neighbors.

In recent years, many pyrochlore compounds with a more complicated composition $(A'A'')_2(B'B'')_2O_7$ have been synthesized [4,5]. Many researchers have focused on the application of high frequency dielectrics, such as the Ba–Nd–Ti and Bi–Zn–Nb systems. Bismuth based pyrochlore exhibit well known useful properties for multilayer capacitor [6]. The compositions studied so far contained Bi as A ion and Nb, Ti or Sb as B ion present per formula unit, as was the case with $Bi_{1.5}ZnNb_{1.5}O_7$, $Bi_{1.5}ZnSb_{1.5}O_7$ and $Bi_{1.5}Zn_{0.5}Nb_{0.5}Ti_{1.5}O_7$ [7–9].

In this paper, we report the synthesis, crystal structure and dielectric properties of a new pyrochlore system in Bi_2O_3–ZnO–Nb_2O_5–SnO_2 solid solution. Especially, the effect of Sn^{4+} ion substitution on the dielectric properties and crystal structure were systematically investigated.

2. Experimental procedure

Ceramic samples were prepared by solid state reaction. Raw materials (Bi_2O_3, ZnO, Nb_2O_5 and SnO_2) were weighed according to the composition $(Bi_{1.5}Zn_{0.5})(Zn_{0.5-x/3}Sn_xNb_{1.5-2x/3})O_7$, where $x = 0$, 0.25, 0.5, 1.0 and 1.5, respectively. The weighed batches

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were wet milled in an agate ball mill for a planetary type for 4 h. After drying, they were calcained at 800 °C for 2 h. The calcained powders were milled again, dried and pressed into disks. Finally, the samples were sintered from 1100 to 1200 °C for 2 h in air and furnace-cooled. The higher the Sn contents the higher the sintering temperature. X-ray diffraction (Rigaku, CuK_α radiation) was carried out for the sintered samples at room temperature and the lattice parameter was calculated precisely. The IR spectra in the range 400 to 4000 cm^{-1} were recorded on Nicolet-MAGNA 760 FTIR spectrometer in the transmission mode (KBr method). The dielectric properties ε and tanδ were studied at four constant frequencies (10^3, 10^4, 10^5 and 10^6 Hz) over a wide temperature range using a high precision LCR meter (HP 4284A) with a personal computer. The resistivity were calculated using a resistance data were obtained using a HP 4339A high-resistance meter at a measuring voltage of 100 V.

3. Results and discussions

3.1. XRD pattern

In those compound, the ionic radius of Zn^{2+}, Nb^{5+} and Sn^{4+} with eight-coordination number is 0.72, 0.64 and 0.69 Å, respectively [10]. The average ionic radius of the various amounts of Zn^{2+}, Nb^{5+} and Sn^{4+} at B-site in the lattice is shown in Table 1. Hence, the ratio of the ionic radius of the cation at A-site to that at B-site is about 1.50–1.53, this value is just in the region of the tolerance factor for the pyrochlore compounds proposed by Subramanian et al. [11]. The zinc ion is positive divalent, niobium ion is positive pentavalent and stannum ion is positive quadrivalent. It assumed that Sn^{4+} can co-substitute Zn^{2+} and Nb^{5+} at B-site. The mechanism of substitution can be presented: $3Sn^{4+} \rightarrow Zn^{2+} + 2Nb^{5+}$. Therefore, the criterion of the charge neutrality can also be satisfied.

The X-ray diffraction pattern for all the compounds shown in Fig. 1 was recorded using CuK_α radiation. All the reflections in the diffractogram are indexed with respect to the cubic pyrochlore phase of space group Fd3m with Zn^{2+}, Nb^{5+} and Sn^{4+} ions disordered at the B-site of pyrochlore unit cell. Fig. 2 shows the variation of the lattice constant (a) with the composition x. There is a almost linear relation between lattice constant and composition x. That is, lattice constant increased linearly with the increasing of Sn concentration, or average radius of B-site, as expected. In addition, cell parameters of the system were practically on the correlation line, indicating that Sn ions randomly occupy B site to form homogeneous solid solution phases.

Table 1
Structural parameter of the compositions

Composition x	Average radius of B-site (Å)	r_A/r_B	Lattice constant	ν(B–O)
0	0.6675	1.5281	10.5515	592.75
0.25	0.6692	1.5242	10.5595	606.67
0.5	0.6708	1.5206	10.5720	615.25
1.0	0.6742	1.5129	10.5827	628.85
1.5	0.6775	1.5055	10.5987	634.89

3.2. IR spectra

The infrared absorption spectroscopy can be used to characterize the compound. The IR spectra of the investigated compositions recorded in the range 400–1000 cm^{-1} are shown in Fig. 3 and the absorption bands are listed in Table 1. The IR absorption bands of solids in the range 100–1000 cm^{-1} are usually assigned to vibrations of ions in the crystal lattice [12]. The IR lattice vibration frequencies of some pyrochlore compounds with a formula $A_2B_2O_7$ have been studied. There are seven IR-active optic modes originating from vibration and bending metal-oxygen bonds in the infrared

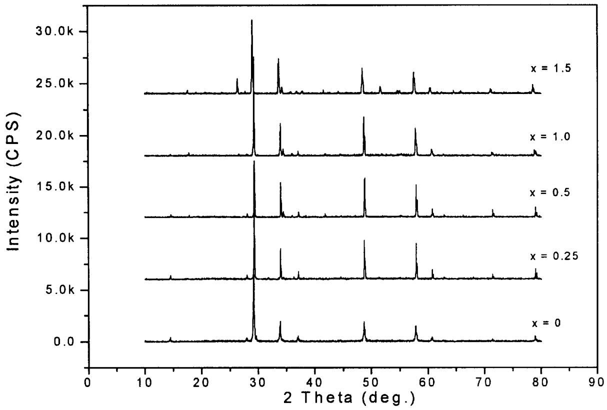

Fig. 1. The XRD pattern of $(Bi_{1.5}Zn_{0.5})(Zn_{0.5-x/3}Sn_xNb_{1.5-2x/3})O_7$ for $x = 0$, 0.25, 0.5, 1.0 and 1.5.

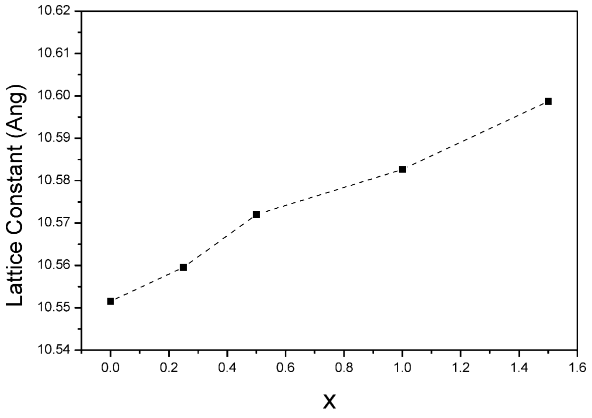

Fig. 2. The variation of lattice constant with x in composition $(Bi_{1.5}Zn_{0.5})(Zn_{0.5-x/3}Sn_xNb_{1.5-2x/3})O_7$.

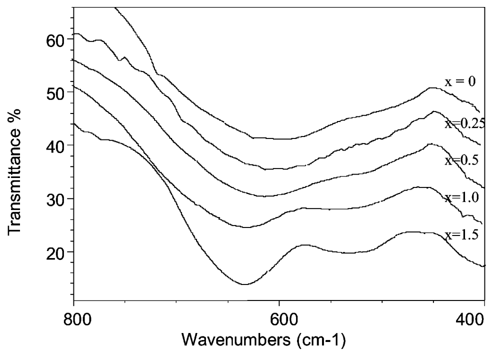

Fig. 3. IR spectra of compositions for various x values.

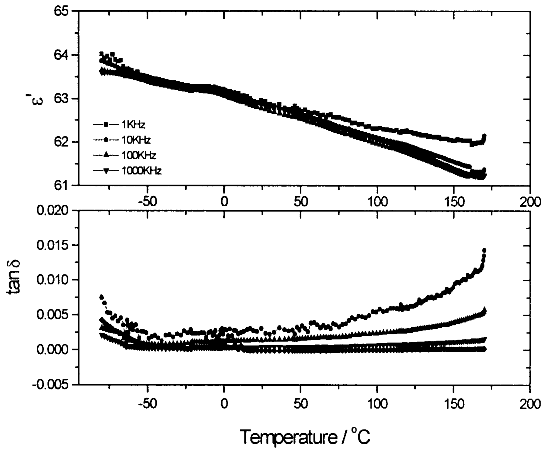

Fig. 4. The variation with temperature of dielectric constant and dielectric loss at various frequencies for $x = 1.5$.

spectra of the pyrochlore oxides [13]. The band (ν_1) at about 600 cm^{-1} is from the B–O stretching vibration in the BO_6 octahedron and the band (ν_2) at about 500 cm^{-1} is from the A–O′ stretching vibration. In our IR spectra experiments, the spectra only in the region 400–4000 cm^{-1} are recorded. Only one broad bands ascribable to B–O stretching vibration was observed for each sample. The frequency of the band maximum, ν(B–O), progressively increased with increase of Sn concentration. The ν(B–O) value increased almost linear with increasing the lattice constant a, or average radius of B-site (r_B), indicating that the B–O bond strength enhanced with an increase in a or r_B. The volume increase associated with the replacement of smaller ion (Nb^{5+}) by larger ion (Sn^{4+}) at the B-site has appreciable influence the bonding character of B–O bonds.

A linear relationship between the frequency of the Sn–O vibration and the A ion radius with constant B ion radius in pyrochlores has been described by Teraoka [14]. However, the dependence of the B–O vibration frequency on the B ion of Bi-based pyrochlore has not been studied. In the present study we notice a regularly shift of ν(B–O) to high frequency with increasing Sn content. This can be explained by an increase in force constant when the atomic number increases. Further more, there is another trend of the dependence of the B–O vibrational frequency on the size of the B ion. The larger the B ion radius (with the same A ion) the higher the observed B–O vibrational frequency, indicating that the force constant has increased. The same results are observed for In-doped $Bi_2Sn_2O_7$ [15].

3.3. Dielectric properties

The values of the dielectric loss (tanδ), as well as of dielectric constant (ε'), depend on the variation of external factors such as temperature and frequency. The dependences of tanδ and ε' on these two factors are shown in Fig. 4. It can be noticed that tanδ remains rather small value around broad temperature range at higher frequencies than lower frequencies. Dielectric constant decreases linearly at higher frequencies (10^5 and 10^6 Hz), whereas at lower frequencies (10^3 and 10^4 Hz), decreases very little with temperature. The general trends of ε' and tanδ appreciably increase when temperature above 100 °C. In general the temperature dependence of ε' and tanδ may be due to polarization effect. The space-charge polarization is governed by the number of space-charge carriers. With the rise in temperature the number of carriers increases, resulting in an enhanced build-up of space-charge polarization and hence an increase in the dielectric properties [16]. The dielectric anomalous behavior at high temperature will be dealt with further.

The temperature dependence of dielectric constant (ε) and dielectric loss (tanδ) at 1 MHz are shown in Fig. 5 with respect to x in composition $(Bi_{1.5}Zn_{0.5})(Zn_{0.5-x/3}Sn_xNb_{1.5-2x/3})O_7$. The tendency of the dielectric behavior vs temperature are similar while the pertinency of temperature decrease with higher Sn contents. The dielectric constant decrease with the increase of the Sn^{4+} ions substitution, and show the minimum value of 65 at the $x = 1.5$ composition, Sn-rich region. Sn incorporation in BZN pyrochlore could increase temperature coefficient of dielectric constant. Through Sn-doping, the excellent dielectric properties with low temperature coefficient could be achieved.

The composition dependence of the dielectric parameters (ε' and α_c) is shown in Fig. 6. It can be seen that the dielectric behavior varies strongly with the amount of the Sn doping, with an increase of Sn concentration in $(Bi_{1.5}Zn_{0.5})(Zn_{0.5-x/3}Sn_xNb_{1.5-2x/3})O_7$ pyrochlore, ε' decreases while tanδ remains the rather low level. Dielectric loss (tanδ) is not varied with composition of materials, but dielectric constant (ε'), temperature coefficient of dielectric constant (α_c), is varied with compositions. It can be seen from the figure that with increasing Sn concentration, ε decrease from 150 to near 70 and α_c increase from −520 ppm/°C to −120 ppm/°C regularly.

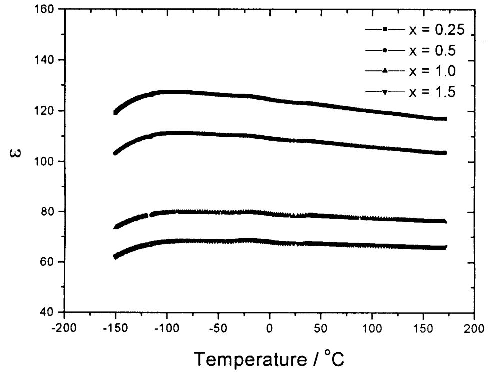

Fig. 5. Temperature dependence of dielectric constant for various x values.

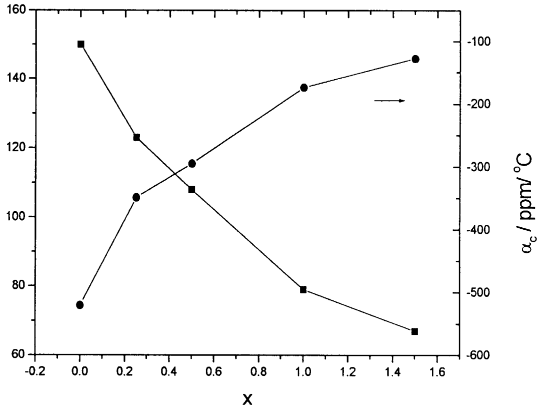

Fig. 6. The variation of the dielectric constant and temperature coefficient of dielectric constant with x values in composition $(Bi_{1.5}Zn_{0.5})(Zn_{0.5-x/3}Sn_xNb_{1.5-2x/3})O_7$.

4. Conclusion

A new series of the pyrochlore compounds $(Bi_{1.5}Zn_{0.5})(Zn_{0.5-x/3}Sn_xNb_{1.5-2x/3})O_7$ $(0 \leqslant x \leqslant 1.5)$ has been synthesized by solid state reaction processing. Dielectric ceramics with SnO_2 doped compositions in the system of Bi_2O_3–ZnO–Nb_2O_5 were investigated in order to obtain dielectrics with low temperature coefficient of permittivity. The incorporation of Sn^{4+} into the bismuth zinc niobate ceramics induced the increase of lattice constant while remaining cubic pyrochlore phase. The B–O bond strength evaluated from the stretching IR band decreased almost linearly with increasing cubic cell parameter or Sn concentration.

SnO_2 play an important role in modifying the permittivity and temperature coefficient of bismuth based ceramics. For the series composition involved, permittivity decreased from 150 to 67 and temperature coefficient increased from −520 ppm/°C to −120 ppm/°C with increasing Sn content. Low dielectric loss level was remained for various x due to single-phasic pyrochlore structure.

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