Study of structure and dielectrc properties of non-stoichiometric Bi_2O_3-ZnO-Nb_2O_5 ceramics

Ding Shihua · Yao Xi · Yuan Li

Abstract Bi-based ceramics with pyrochlore structure exhibit interesting dielectric properties such as high dielectric constant and small dielectric loss at high frequency and low firing temperature. Structure and dielectric properties of non-stoichiometric ceramics $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ (with $x= -0.25\sim0.6$) were investigated. The compounds departured from stoichiomeric compositions lead to structural parameters change. The second phase appeared when $x \geq 0.4$. The lattice parameters of cubic pyrochlore $Bi_{1.5-x}ZnNb_{1.5}O_7$ and grain size decreased as x increased. The experimental results show that dielectric constant decrease with increasing of the x value. The dielectric relaxation and defect resulting from non-stoichiometric ceramics $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ were discussed.

Keywords Pyrochlore · Nonstoichiometry · Dielectric relaxation · Lattice parameter

1 Introduction

High dielectric constant and low dielectric loss ceramics have received intensive great attention in reducing the size of microelectronic circuits [1–3]. Bi_2O_3-ZnO-Nb_2O_5 (BZN) pyrochlore system has received special attention. High dielectric constant (~150), low dielectric loss (~10^{-4}) and low sintering temperature (~1000°C) make this system very appealing for low fire multilayer applications and electronic devices for microwave communication [4, 5].

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However this system appeared the low temperature relaxational character of the dielectric polarization [6]. The loss peak associated with the dielectric relaxation in this system could possibly increase the losses at microwave frequencies at room temperature. This becomes even more important if one acknowledges the low temperature relaxational character of the dielectric polarization in BZN cubic pyrochlore system. Golovshchikova et al. first studied this dielectric anomaly [7] and Cann, Randall, and Shrout later performed a detailed investigation on the dielectric properties of bismuth pyrochlores confirming the results for all the compounds studied [6]. Similar dielectric relaxations have been seen in dipolar and quadrupolar glasses such as $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) [8]. It is known that BZN cubic pyrochlore systems are not ferroelectric. It is not clear what is the origin of dielectric relaxation up to now. Chen Ang et al. [9] think that the dielectric relaxation is due to the hopping of cations in the more than one equivalent potential minima of A sites, and the reorientation of dipoles formed through interactions with the "seventh oxygen" and the Bi/Zn ions in the compound.

Stoichiometric cubic pyrochlores have the general formula $A_2B_2O_6O'$ that is closely related to fluorite and can be considered as an ordered defective fluorite [10]. It exhibits space group Fd3m with eight formula units within the cubic unit cell. Fixing its origin on the B site, the ions occupy four crystallographically nonequivalent positions: A at 16d, B at 16c, O at 48f and O' at 8b. The structure is composed of two different types of cation coordination polyhedra; the A-site positions are eight coordinate and are typically occupied by larger cations, while smaller sized cations favor the six-coordinate B-site positions. Zn ions occupy both A- and B-sites, Bi and Nb ions occupy A-sites and B-sites, respectively, in cubic pyrochlore $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$.

In this work, structure and dielectric properties of non-stoichiometric ceramics $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ($x=-0.25\sim0.6$) were investigated. The variation in the lattice parameter and dielectric relaxation was discussed.

2 Experimental procedure

$Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ is cubic pyrochlore structure when $x=-0.192\sim0.355$. In this work, $x=-0.25$, -0.15, -0.05, 0, 0.05, 0.10, 0.15, 0.20, 0.40, 0.50, 0.60. Samples were prepared by conventional solid-state methods. High-purity oxide powders (>99%) of Bi_2O_3, Nb_2O_5, and ZnO (Shanghai chemical agent Co.) were used as starting materials. Proportional amounts of starting materials of Bi_2O_3, Nb_2O_5 and ZnO, according to the composition of $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$, were mixed in distilled water for 24 h in a nylon jar using ZrO_2 media. Mixed powders were dried and calcined at 800°C for 2 h. Powders were remilled and dried before pressing into pellets with PVA solution (10% concentration) as a binder. Disks were sintered at about 1030°C for 2 h in air. The microstructure observation of the sintered ceramics was preformed by SEM (JOEL, 5510LV). The crystalline phase of sample was identified by XRD (BRUKER, D8). Lattice parameters were refined by a least square refinement procedures. The bulk density of sample was measured by the Archimedes method. Low-fire silver electrodes were used for dielectric measurements. Dielectric properties were measured using a HP 4284 LCR meter. The temperature dependence of the dielectric constant was measured at four different frequencies (1, 10, 100 K and 1 MHz) and temperature varying from −180 to 100°C by placing the discs in an automated measurement system consisting of a PC computer, a HP 4284A LCR meter and a temperature chamber.
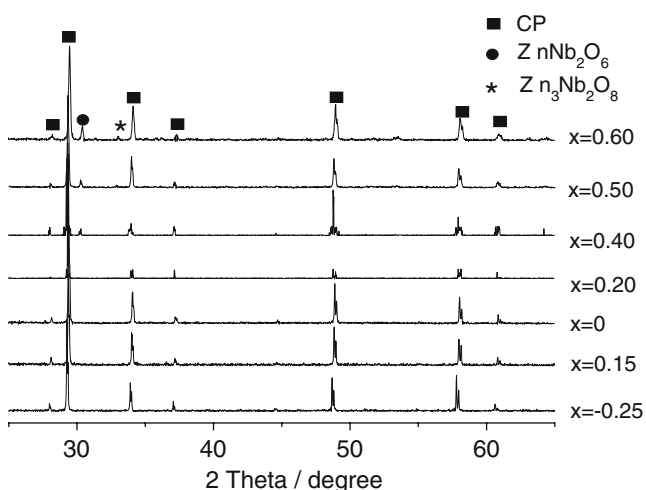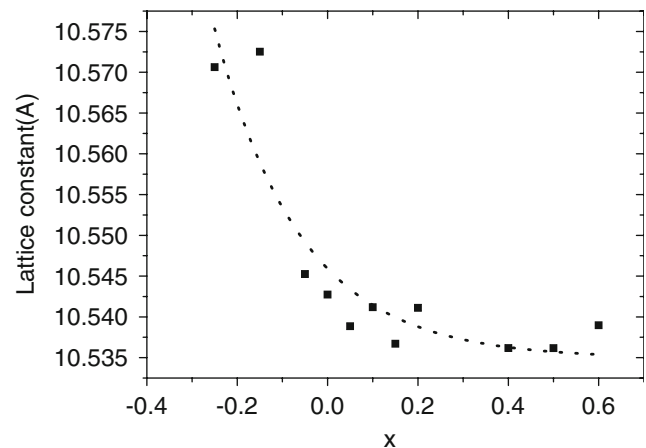

Fig. 2 Lattice parameter of $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ceramics as a function of x

3 Results and discussions

Figure 1 shows the XRD patterns of $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ceramics with various x. it indicates that only crystallized cubic pyrochlore structures exist in samples when x is less than 0.4. In this case, non-stoichiometric $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ceramics ($x<0.4$) have the same phase structure as $Bi_{1.5}ZnNb_{1.5}O_7$. But some $ZnNb_2O_6$ and $Zn_3Nb_2O_8$ appeared in samples when $x\geq0.4$. In $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$, Bi in A-sites deficient stoichiometry existed with increasing x. The presence of these phases suggests the excess Nb_2O_5 and ZnO could form Nb-Zn-O compounds. Figure 2 shows lattice parameter of $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ as a function of x. When $x<0.4$, a slightly decrease in lattice parameter was observed with increasing x. The decrease of the lattice parameter is attributed to the deficiency of Bi ion in A-sites that has a large ionic radius. As a result, the presence of
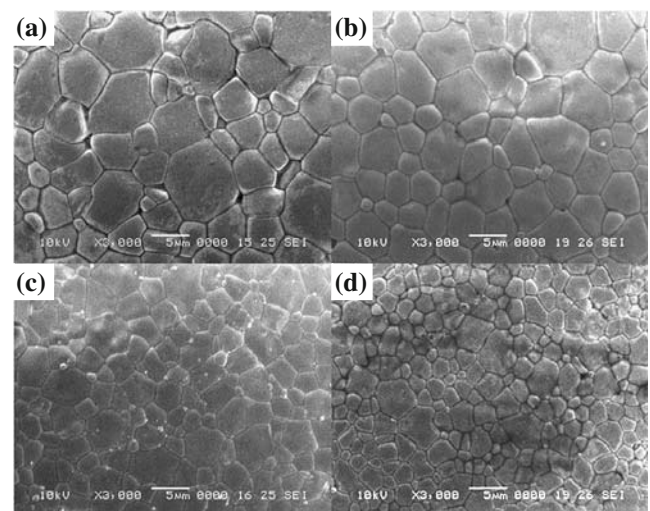

Fig. 1 XRD patterns for $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ceramics (CP Cubic Pyrochlore)

Fig. 3 SEM micrographs of $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ceramics. (a) $x=-0.25$, (b) $x=-0.15$, (c) $x=0$, (d) $x=0.20$

A-site vacancies resulting from the deficiency of Bi ion in A-sites could make the shrinkage of lattice.

Figure 3 shows SEM micrographs of the natural surface of samples. The grain size of samples decreased with increasing x. As we know, Bi_2O_3 is a low melting-point oxide that can enhance sintering processing. When x increases, the deficiency of Bi in A-sites would restrain the growth of grain.

Figure 4 presents the room temperature dielectric properties for $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ at 1MHz. The dielectric constants range from 100 to 170, and dielectric losses are low ($\sim10^{-4}$). The dielectric constant decreases with increasing x. According to the Clausius-Mosotti relation, the dielectric constant of oxide compounds can be calculated as follows [11].

$$\varepsilon_r = \frac{3V_m + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D}$$

α_D is the sum of polarizabilities of constituent ions in $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ and V_m is the molar volume. The dielectric constant is mainly determined by α_D. Thus the decrease in dielectric constant can be ascribed to a decrease in the α_D that results from the deficiency of the Bi^{3+} with a big polarizabilty in $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$. As to $x\geq0.4$, the decrease in dielectric constant due to the existence of other phases $ZnNb_2O_6$ and $Zn_3Nb_2O_8$ that have a lower dielectric constant (~30).

The real and imaginary parts of the complex dielectric constant as a function of temperature for $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ($x=-0.25$, the same behavior was found in other composition) are given in Fig. 5. The frequency dispersive decrease in the real part of the dielectric and a correlated peak in the imaginary part are found at low temperature for $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$. The corresponding dielectric dispersive is similar to that found in relaxor ferroelectrics. But the detail of the dipolar origin of the relaxation in Bi_2O_3-ZnO-

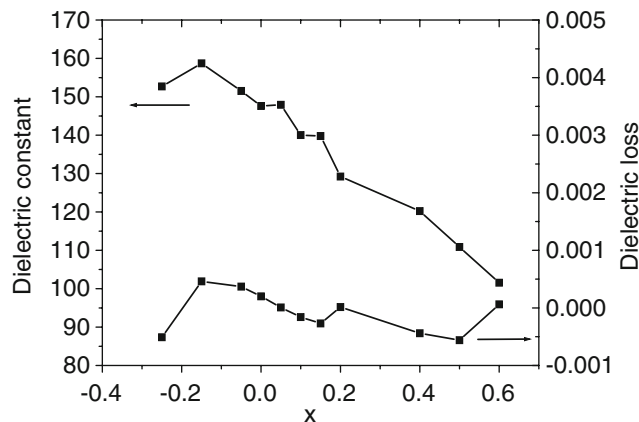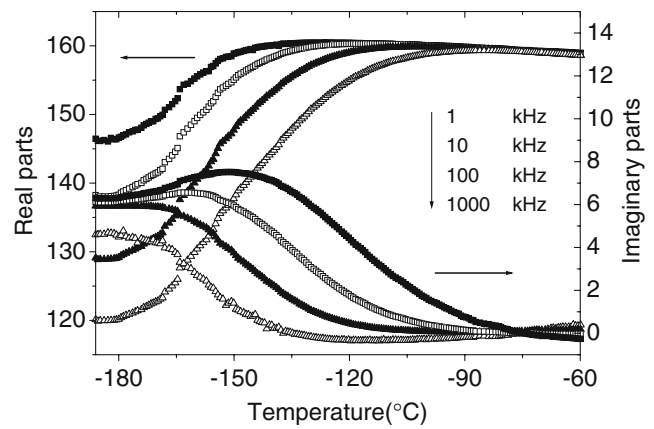**Fig. 5** Real and imaginary parts of the dielectric permittivities for $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ceramics ($x=-0.25$) measured at 1, 10, 100, 1,000 kHz

Nb_2O_5 pyrochlores is not clear. However there are a number of possibilities. Cooperative hopping of the loosely bound "seventh" oxygen ion in the pyrochlore structure has been proposed as the origin of ferroelectricity in $Cd_2Nb_2O_7$, and it is possible that this mechanism may be involved in the behavior of the cubic pyrochlores $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$. In addition, vacancies in the pyrochlore structure are believed to have a significant role as found in the perovskite role [12–14].

The dielectric constant as a function of temperature for cubic pyrochlore $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ is showed in Fig. 6. The maximum in the dielectric constant at 1 MHz is shifted to lower temperature with the increase of x. This phenomenon may be related with the change of environment in A-sites. Levin et al. [15] think that both A-cations and O' anions from their ideal high symmetry positions (16d-A, 8b-O') in cubic pyrochlore have significant local deviations from the ideal pyrochlore arrangement, and suggested substantial displacive disorder in the A_2O' network. Thus

Fig. 4 Dielectric constant as a function of x at room temperature (at 1 MHz)
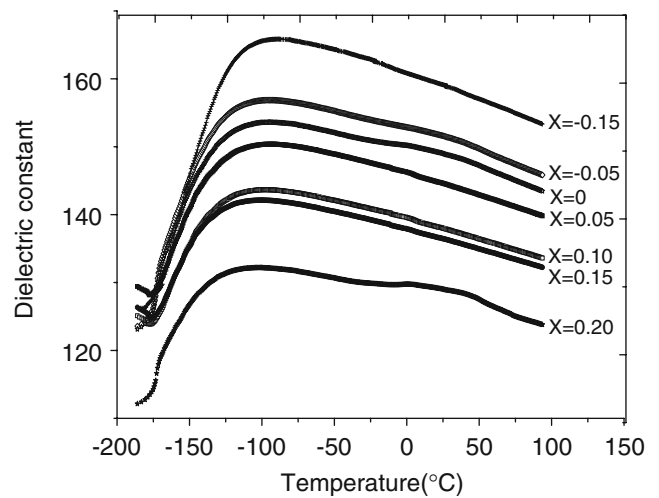

Fig. 6 Dielectric constant as a function of temperature (at 1 MHz)

coupling between the displacements of the O′ atoms, the occupancy of the A-sites (Bi, Zn, or vacancy), and the directions of the A-cation displacements is expected. The identified atomic displacements involve atoms participating in the lowest-frequency O′-A-O′ bending mode, and therefore are likely responsible for both the high dielectric constant and low temperature dielectric relaxation. With the increase of x, vacancies in A-sites will increase. Therefore ions displacive disorder in the A-sites (Bi, Zn, or vacancy), O′-A-O′ bending and the lowest-frequency O-A-O bending mode would have significant changed, which would result in the change of dielectric constant and the shift of the maximum in the dielectric constant to lower temperature.

4 Conclusions

The structure and dielectric properties of $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ceramics with cubic pyrochlore structure were investigated. The lattice parameter slightly decreased and the grain size decreased with the increase of x, which resulted from Bi deficiency in A-sites of cubic pyrochlore $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ceramics. Only cubic pyrochlore phase existed in samples when x is less than 0.4. But some $ZnNb_2O_6$ and $Zn_3Nb_2O_8$ appeared in samples when $x \geq 0.4$. The dielectric constant decreased with the increase of x because of the deficiency of Bi with big polarizabilty. The dielectric relaxational character in $Bi_{1.5-x}ZnNb_{1.5}O_{7-1.5x}$ ceramics was discussed. The maximum in the dielectric constant at 1 MHz was shifted to lower temperature as x increased, which may result from ions displacive disorder in the A-sites (Bi, Zn, or vacancy), O′-A-O′ bending and the lowest-frequency O-A-O bending mode.

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