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Cadmium substituted $(Bi_{1.5}ZnNb_{1.5})O_7$ dielectric ceramics

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Abstract The effects of small amounts of Cd substitution for Zn in the low loss dielectric material $Bi_{1.5}ZnNb_{1.5}O_7$ are reported. Solid solution of $(Bi_{1.5}Zn_{0.5-x}Cd_x)(Zn_{0.5}Nb_{1.5})O_7$ was formed in the present ceramics for $x < 0.1$, and β-Bi_2O_3 secondary phase appeared at $x = 0.3$. For $x = 0.5$, another phase $Bi_{1.6}Cd_{0.4}O_{2.8}$ appeared gradually with increasing x. With increasing x, the dielectric constant increased firstly and reached their maximums 168 at 1 MHz, then decreased after $x > 0.2$. High-ε dielectric ceramics with low dielectric loss were created at the composition $x = 0.2$: $\varepsilon = 168$, $\tan\delta = 0.0001$ and $\alpha_\varepsilon = -554$ ppm/° at 1 MHz.

Introduction

Pyrochlore oxides possess the general formula $A_2B_2O_7$. Their structure may be described as an ordered cubic close-packed array of cations with the oxide ions occupying seven-eights of tetrahedral sites between the cations. The pyrochlore structure is related to that of fluorite, AO_2, but with ordered cations and ordered vacancies in one-eight of the tetrahedral anion sites. In spite of the immense flexibility of chemical composition in the pysrochlore system, a cubic structure with eight molecules per unit cell (Z = 8) and space group Fd3m is the predominant phase. Pyrochlore oxides display a remarkable range of physical properties, including (for specific compositions) metallic, semiconducting, or ionic electrical behavior that can be controlled by doping [1–3]. Other properties include dielectric character, ferroelectric behavior, ferrimagnetism, and giant magnetoresistance. The crystal structure of those oxides has been described by many authors [4, 5]. A wide variety of additional cations are commonly found to be incorporated in pyrochlore solid solutions in specimens that occur in nature. For the Bi-based system, more and more researches have been carried out to enhance the properties. Pyrochlore with dielectric constant of approximately 20 and low dissipation factor were reported in the Bi_2O_3–ZnO–Sb_2O_5 (BZN) system. Significantly higher dielectric constant (ε = 200) were reported in the Bi_2O_3–ZnO–Nb_2O_5–TiO_2 system. The temperature coefficients of dielectric constant (α_ε) of those systems can also be tuned by introducing cation substitutions on to the different positions [6–9].

It is reasonable to expect on crystal-chemical grounds that cubic pyrochlore phases may also be remained with partial substitution of Zn^{2+} by Cd^{2+} ions. Such data are however not available in the literature. In this study, a new low sintered system, $(Bi_{1.5}Zn_{0.5-x}Cd_x)(Zn_{0.5}Nb_{1.5})O_7$, was developed for exhibiting promising dielectric properties. In particular, the impacts of Cd on the density, microstructure and electric properties of the BZN ceramics were also investigated.

Experimental details

The starting materials were reagent grade oxide powders of Bi_2O_3, ZnO, Nb_2O_5, CdO, stoichiometric

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mixtures of powders of the base composition ($Bi_{1.5}$ $Zn_{0.5-x}Cd_x$) ($Zn_{0.5}Nb_{1.5}$)O_7 ($x = 0$, 0.1,0.2,0.3, 0.4,0.5) were milled for 4 h in de-ionized water with zirconia media. Those powders were then dried and calcined at 800 °C for 2 h in close alumina crucibles. The powders were remilled and dried before pressing into 12 mm discs. Discs were sintered in air at temperatures range of from 920 °C–980 °C. Both sintered disks and green disks were characterized by a Rigaku D/ Max-2400 diffractometer with Cu Kα radiation. The microstructure of the samples was examined on well-sintered surfaces using an AMARY 1000 scanning electron microscope (SEM). The grain sizes of samples were determined by the intercept method. Apparent densities were determined by the Archimedes method. The densities of the samples were found to be greater than 96% of theoretical density as determined geometrically.

For dielectric measurements, both sides of disks were ground parallel and coated with a layer of silver conducting paint. The frequency dependences of dielectric properties were determined on high precision LCR meter (HP 4284A). The measuring frequency range was from 1 KHz to 1 MHz. The temperature dependence of the dielectric constant and loss was measured from – 70 to 160 °C by placing the discs in an automated measurement system consisting of a PC computer, a HP 4284A LCR meter and a temperature chamber.

Results and discussion

The calcined powder has good sinterability and the dense ceramics were obtained easily at the temperature from 920 to 1040 °C. After the Cd^{2+} was introduced in BZN ceramic, the sintering temperature of the substituted sample was lower down significantly. The SEM analysis revealed the dense structure can be obtained after the substitution at the sintering temperature as lower as 920 °C (Fig. 1). The grain size is about 0.1–0.3 μm, but the grain crystallized perfectly. The grain has straight boundary and regular shape. Therefore, doping with CdO in BZN results in the improvement of grain growth and perfectly crystallized grains in the sample.

Fig. 2 shows the XRD patterns for the original and Cd-doped BZN samples. Solid solution member for $x = 0.1$ and 0.2 could be identified as single phase materials (cubic pyrochlore). However, when $x \geq 0.3$, β-Bi_2O_3 (JCPDS 27–52) started to form and increased in amount with x when sintered at 920 °C. Only low dopant concentrations of Cd were characterized as single phase. Partly replacement of Zn in A-site with Cd led to one single phase (cubic pyrochlore) but distorted the cubic lattice due to its higher ionic radius. In addition, for the totally substitution composition ($x = 0.5$), a bismuth cadmium compound, $Bi_{1.6}$ $Cd_{0.4}O_{2.8}$(JCPDS 41–544), forms as well as pyrochlore and β-Bi_2O_3. Line splitting was observed when $x \geq 0.4$, indicating that there was a distortion from cubic symmetry. In a cubic crystal structure, any distortions of the unit cell which decrease its symmetry increase the number of lines in the pattern [10].

The temperature dependence of dielectric constant of ($Bi_{1.5}Zn_{0.5-x}Cd_x$) ($Zn_{0.5}Nb_{1.5}$)O_7 ceramics are shown in Fig. 3. The dielectric constant of all five samples decreases to some extent with increasing temperature. The tendencies of the dielectric behavior versus temperature for all samples are similar, with the large negative temperature coefficients and low level loss.

The Cd-doped ceramics have excellent dielectric properties same as the original BZN composition, which has a dielectric constant around 150 and rather low dissipation factor (0.0001 at 1 MHz). The small amount of Cd incorporation ($x \leq 0.2$) causes a slight increase of dielectric constant and a decrease of temperature coefficient. With increasing amount of Cd ions substitution ($0.2 < x \leq 0.5$), the dielectric constant decrease and the dielectric temperature

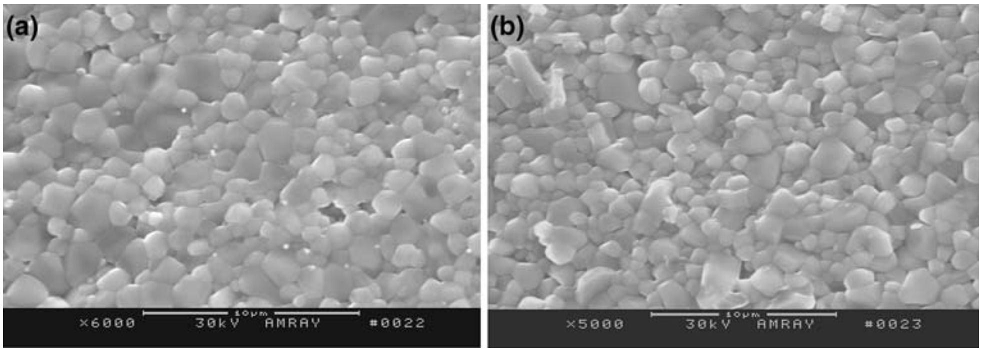


Fig. 1 SEM micrograph of the samples with (**a**) Cd=0.1 mol and (**b**) Cd = 0.4 mol (sintered at 920 °C for 2 h)

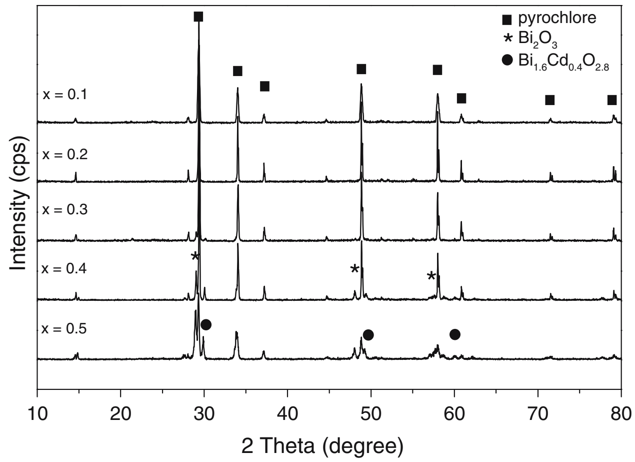


Fig. 2 X-ray diffraction patterns of $(Bi_{1.5}Zn_{0.5\text{-}x}Cd_x)(Zn_{0.5}Nb_{1.5})O_7$ with different *x*

coefficient increase. At room temperature the highest dielectric constant is exhibited by the low substitution of Cd ($x = 0.2$, $\varepsilon = 168$). For the higher *x* compositions, where the concentration of Zn decrease, the dielectric constant decreases to 121 for $x = 0.5$. The dielectric losses are rather low across the entire region of Cd substitution (*x* from 0 to 0.5).

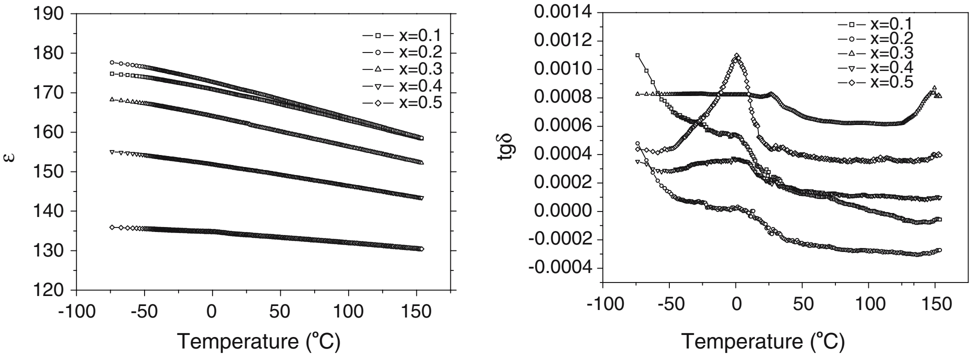
The formation of additional phase and the microstructure influence the dielectric properties of samples, especially the temperature coefficient α_ε. Fig. 4 shows the dielectric constant and temperature coefficient of dielectric constant of samples versus the amount of Cd. The dielectric constant for the end composition $x = 0$ is 150, and it increases up to 158 and 168, respectively, when 10 mol% and 20 mol% of Cd is substituted for Zn at A site. The increase in ε is associated with the larger ion polarizability of Cd than that of Zn at A site due to forming limited solid solutions. The values of ε decrease again with the increase of Cd incorporation further, because the impurity phase plays more important role in determining the dielectric properties of the series system and the ε values decrease linearly from 168 to 121.

It is interesting that the variation trend of α_ε with composition across the series looks like "v" type. The two sides of samples exhibit opposite trends at temperatures from –70 to 160 °C. The temperature dependence of dielectric constant varies systematically with x in the series of compositions. For the lower Cd content ($x \le 0.2$), α_ε decrease from – 470 ppm/°C to – 526 ppm/°C accompany by the increase of ε.

A small amount of foreign element is able to modify drastically the properties of a material but the understanding of these modifications is not always well established. When a partial substitution on a cation site is carried out in a crystalline material the substituting cation may differ from the substituted cation by the mass, the volume, the electric charge, the oxide reduction potential. In Cd doped BZN, although the formula we designed simply is the substitution of Cd cations into A-site to replace the Zn cations. We know that Cd^{2+} ion have the size of 1.10Å, just between Zn^{2+} (0.90 Å) and Bi^{3+} (1.17 Å) [11], it can replace either Zn^{2+} or Bi^{3+} in A site. Cd ion can change its site according to the variation of the chemical compositions in the microzone it locates during mass transfers of the sintering, so several kinds of structural defects can be envisaged as $Cd^{\times}_{Zn}$, Cd'_{Bi}, $V^{\bullet}_{O}$, $V^{\bullet\bullet}_{O}$, V'''_{Bi}, V''_{Zn}. Schottky disorders can be easily produced due to the high chemical activity of Cd ion and the volatility of CdO at high temperature, which would promote the mass transfer and densification of samples in the sintering process [12]. The higher the total concentration of all kind vacancies, the easier the sintering and lower sintering temperature needed.

According to Gangull's report [13], the dielectric constant shows a maximum for the $x = 0.5$ in the $Ba_2Zn_{1\text{-}x}Cd_xTa_2O_9$ ceramics, which could be due to the presence of larger amounts of ordered structures as evidenced by electron microscopy. That means the partial substitution Zn by Cd will lead to the formation of the ordered structure. As for pyrochlore structure, such substitution increases the size difference between

Fig. 3 Temperature dependence of dielectric constant and dissipation factor at 1 MHz of BZN ceramics doped with Cd



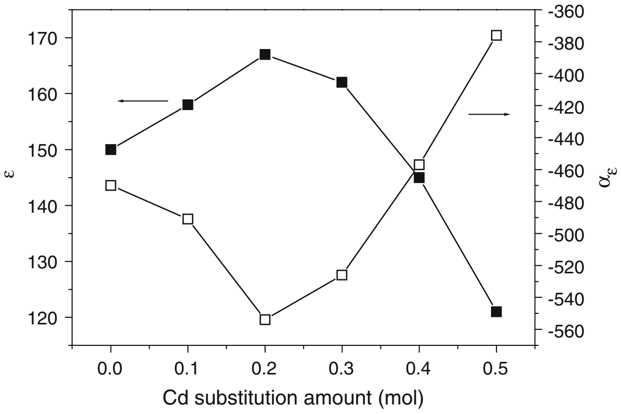


Fig. 4 The variation of dielectric properties as a function of compositions in the $(Bi_{1.5}Zn_{0.5\text{-}x}Cd_x)$ $(Zn_{0.5}Nb_{1.5})O_7$ system

the average radius of the A and B species. This was quite understandable as previous studies of pyrochlore crystal chemistry showed that a pyrochlore structure forms only above a critical value of the radius R_A/R_B. A difference in cation size thus appears to be the driving force for ordering [14]. In present studied, the maximum dielectric constant obtained for the sample corresponding to $x = 0.2$. It may be attributed to the high dielectric polarization arising due to the presence of ordered structure. Further experimental evidence is required to achieve a better understanding.

At the present time it is impossible to give a full explanation of the modifications of the properties of the material resulting of the various substitutions with reference to the above features only. Nevertheless we would like to show, on bismuth zinc niobate pyrochlore as an example, how some of these features could be taken into account to influence the properties of a material. It will be shown and explained how some of the dielectric properties of $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$ are modified with various substitutions. Particularly, with reference to some of the above features, the manufacture of Bi-based pyrochlore material able to be considered with a non noble metal will be described.

Conclusions

We report the modification of dielectric properties for $(Bi_{1.5}ZnNb_{1.5})O_7$ ceramic through Cd partial substitution for Zn in A-site. Addition of Cd lowers the sintering temperature to 920 °C. In the vicinity of ambient temperature, the dielectric constants are about 120–170 for various compositions, and the dielectric loss keeps low level, with the temperature coefficient of dielectric constant (α_ε) remain negative values (– 560~ – 350 ppm/°C). The composition $x = 0.2$ showed the following data: $\varepsilon = 168$, $\tan\delta = 0.0001$ and $\alpha_\varepsilon = -554$ ppm/°C at 1 MHz. The dielectric properties are found to be systematically dependence on compositions and processing conditions.

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