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Crystal structures, phase stability, and dielectric properties of $(1-x)$ $Bi_{3/2}MgNb_{3/2}O_7-x$ $Bi_2Zn_{2/3}Nb_{4/3}O_7$ ceramics

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ABSTRACT

The preparation, crystal structures, phase stability and dielectric properties of the $(1-x)$ $Bi_{3/2}MgNb_{3/2}O_7-x$ $Bi_2Zn_{2/3}Nb_{4/3}O_7$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) ceramics were investigated systematically. The sol–gel process was employed to produce crystalline, single-phase $Bi_{1.5}Mg_{1.0}Nb_{1.5}O_7$ (BMN) and $Bi_2(Zn_{2/3}Nb_{4/3})O_7$ (β_BZN) pre-nanopowders for the synthesis of the ceramics. X-ray diffraction data indicated that these ceramics presented a phase transition for Bi^{3+} and Zn^{2+}-rich specimens ($x \geqslant 0.6$), from cubic pyrochlore to orthorhombic zirconolite-like structure. The tolerance factor (t) combined with r_A/r_B value and the lattice energy (U) were employed to provide an indication of the structural stability of the $(1-x)$ BMN–x β_BZN cubic pyrochlores ($x \leqslant 0.4$). The tolerance factor (t) calculation contain more structural information, which gives further insight into the details of the structural stability features in the $(1-x)$ BMN–x β_BZN cubic pyrochlores. The relationships between the crystal structures and dielectric properties of the ceramics were determined, and the dielectric loss was related to the phase stability of the system. It is suggested that the dielectric properties are mainly determined by the phase structure, composition and stability in the $(1-x)$ BMN–x β_BZN system.

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1. Introduction

The pyrochlores family with the general formula, $A_2B_2O_7$, is fascinating for the A- and B-sites can be occupied by a broad range of elements that can give rise to a great variety of physical properties, [1] which allow a diverse useful technological applications, such as high frequency dielectric microwave materials for LTCC technique, the electrolyte in solid-oxide fuel cells, host materials for the immobilization of fission products, catalysis, piezoelectricity, ferro- and ferri-magnetism, luminescence, giant magneto resistance, and thermal barrier coatings [2–9].

Bi-based $A_2B_2O_7$-types ternary metallic oxides pyrochlores, Bi_2O_3–MO–Nb_2O_5 (M = Mg, Zn), have received wide attraction for their potential use for multilayer capacitor, electric-field tunable dielectric thin films materials and integrated device applications due to their outstanding dielectric properties, i.e. high dielectric constants (ε) as well as electric-field tunable, relatively low dielectric losses over a considerable frequency range around room temperature, and compositionally tunable temperature coefficients of capacitance (τ_c) combined with low sintering temperatures which enable the possibility of co-firing with Ag electrodes [10–14].

Members of Bi_2O_3–MO–Nb_2O_5 (M = Mg, Zn) pyrochlores family, $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (α_BZN), $Bi_2(Zn_{2/3}Nb_{4/3})O_7$ (β_BZN), $Bi_{1.5}Mg_{1.0}Nb_{1.5}O_7$ (BMN), have received the most particularly attention [14–16]. The crystal structure of the $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (α_BZN) and $Bi_{1.5}Mg_{1.0}Nb_{1.5}O_7$ (BMN) pyrochlores are cubic structure with space group Fd-3 m, while it adopts an orthorhombic distorted pyrochlores structure in the $Bi_2(Zn_{2/3}Nb_{4/3})O_7$ (β_BZN) ceramics [11,17]. Because these two phase pyrochlores have opposite signal of the temperature coefficient of the capacitance (τ_c): negative and positive, respectively, a temperature stable ceramics can be fabricated by mixed in different stoichiometric proportions sintered at suitable temperatures.

Research efforts have been focused on composition, stability, and processing windows of the main phases in the Bi_2O_3–MO–Nb_2O_5 (M = Mg, Zn) systems [18–20]. In particular, Wang et al. [15] reported the phase stability of the orthorhombic and cubic pyrochlores in the Bi_2O_3–ZnO–Nb_2O_5 (BZN) system. Nino et al. [18] investigated the Bi_2O_3 solubility in Bi_2O_3–ZnO–Nb_2O_5 pyrochlores system. Based on the results of previous work, excess Bi_2O_3 with respect to the base formulation of the cubic pyrochlores phase in the Bi_2O_3–ZnO–Nb_2O_5 and Bi_2O_3–MgO–Nb_2O_5 system was performed. The differences of the phase stability behavior between these systems were discussed by Nino and co-workers [21]. However, because of the immense flexibility of chemical composition in

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the Bi_2O_3–MO–Nb_2O_5 (M = Mg, Zn) pyrochlores system, many questions still remain to be answered about the phase stability in these systems. In addition, it notes that unlike Bi_2O_3–ZnO–Nb_2O_5 system, there is no stable orthorhombic phase in Bi_2O_3–MgO–Nb_2O_5 system, although Mg^{2+} and Zn^{2+} have similar ionic radii (0.72 and 0.74) in six coordination as well as similar electronegativity (χ_{Mg} = 1.31, χ_{Zn} = 1.65) according to the crystal chemistry [22]. Therefore, the determination of the phase stability of the orthorhombic and cubic pyrochlores in the Bi_2O_3–ZnO–MgO–Nb_2O_5 system are theoretical and technical important.

To expand the knowledge on the processing windows and solubility limits of Bi-based pyrochlores ceramics, single cubic $Bi_{1.5}Mg_{1.0}Nb_{1.5}O_7$ (BMN) and $Bi_2(Zn_{2/3}Nb_{4/3})O_7$ (β_BZN) orthorhombic pyrochlores phase powders were synthesized separately by the sol–gel process, and compositions of the full range (1−x) BMN–x β_BZN (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) between BMN and β_BZN were produced by mixing different amounts of the two ceramics. For these ceramics, the crystal structures and phase stability have not been investigated yet. In this work, for the first time, the tolerance factor (t) combined with r_A/r_B value (the ratio of the ionic radius of A-site over the ionic radius of B-site) and the lattice energy (U) are employed to provide an indication of the structural stability of the (1−x) BMN–x β_BZN cubic pyrochlores. The relationship between the crystal structures, stability, and dielectric properties of the (1−x) BMN–x β_BZN ceramics are determined.

2. Experiment and theory

2.1. Experimental methods

$Bi_{1.5}Mg_{1.0}Nb_{1.5}O_7$ (BMN) and $Bi_2(Zn_{2/3}Nb_{4/3})O_7$ (β_BZN) nanopowders were synthesized by the sol–gel process. For preparation of the precursor solution, analytically pure (AR) $Bi(NO_3)_3{\cdot}5H_2O$ (99.00%), $Mg(NO_3)_2{\cdot}6H_2O$ (99.00%), $Zn(NO_3)_2{\cdot}6H_2O$ (99.00%) and Nb_2O_5 (99.99%) were used as the raw materials. Citric acid (99.00%) and ethylene glycol (99.00%) were used as a chelating agent and reaction medium, respectively. The experimental procedure for preparing the nanopowders is shown in Fig. 1. Firstly, stoichiometric Nb_2O_5 was dissolved in the appropriate amount of HF at 80 °C for 20 h, and then ammonia water was added into the above solutions to form chemical precipitate of niobic acid [$Nb(OH)_5$]. The precipitates were filtered off and washed with distilled water to remove the H^+ and F^+ ions. The $Nb(OH)_5$ precipitates were dissolved completely in citric acid water solution under stirring at 80 °C. Subsequently, stoichiometric amounts of $Mg(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $Bi(NO_3)_3{\cdot}5H_2O$ were added to the niobium citrate solution heated at 60 °C to form the (Bi, Mg, Nb) and (Bi, Zn, Nb) complex precursors, respectively. The solutions was kept under stirring at 60 °C, resulting in clear pale yellow solutions. Ethylene glycol was added to those solutions to promote polymerization of the mixed citrate. By heating in a water bath at 80–90 °C, viscous gels were obtained. Finally, the gels was dried at 200 °C and then calcined at 650 °C in air for 2 h, respectively. Ceramics of the full range (1−x) BMN–x β_BZN (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) between BMN and β_BZN were produced by mixing different amounts of the two ceramics. The samples were uniaxially pressed at 10 MPa and sintered in air at 960 °C, for 4 h.

Powder X-ray diffraction analysis (Rigaku, D/MAX-2500, Tokyo, Japan) was used to analyze the crystal structure of sintered ceramics. A Hewlett-Packard 4278A capacitance meter was used to test capacitance (C) and dielectric loss ($\tan\delta$) at 1 MHz. The dielectric constant (ε_r) was calculated by the equation $\varepsilon_r = (14.4Cd)/D^2$, where D and d are the average diameter and the thickness of the sample, respectively. The temperature coefficient of the capacitance (τ_c) was calculated by the equation $\tau_c = (C_{85}-C_{25})/60{*}C_{25}$, where C_{85} and C_{25} are the capacitances of the samples at 85 and 25 °C, respectively. Archimedes' principle was used to test the bulk density (ρ_v) of all the samples using the equation $\rho_v = (m_0/m_1-m_2)\ \rho_{water}$, where m_0, m_1, and m_2 are the weight after drying, the weight in the air, and the weight in water, respectively.

2.2. Theory development

The tolerance factor (t) combined with r_A/r_B value (the ratio of the ionic radius of A-site over the ionic radius of B-site) and the lattice energy (U) are employed to provide an indication of the structural stability of the (1−x) BMN–x β_BZN ceramics.

2.2.1. The tolerance factor (t)

It is reported that the tolerance factor is an useful tool to determine the stability field of the ceramics [23]. The tolerance factor (t) concept was introduced to analyze structure–property relations of ceramics with the perovskite crystal structure

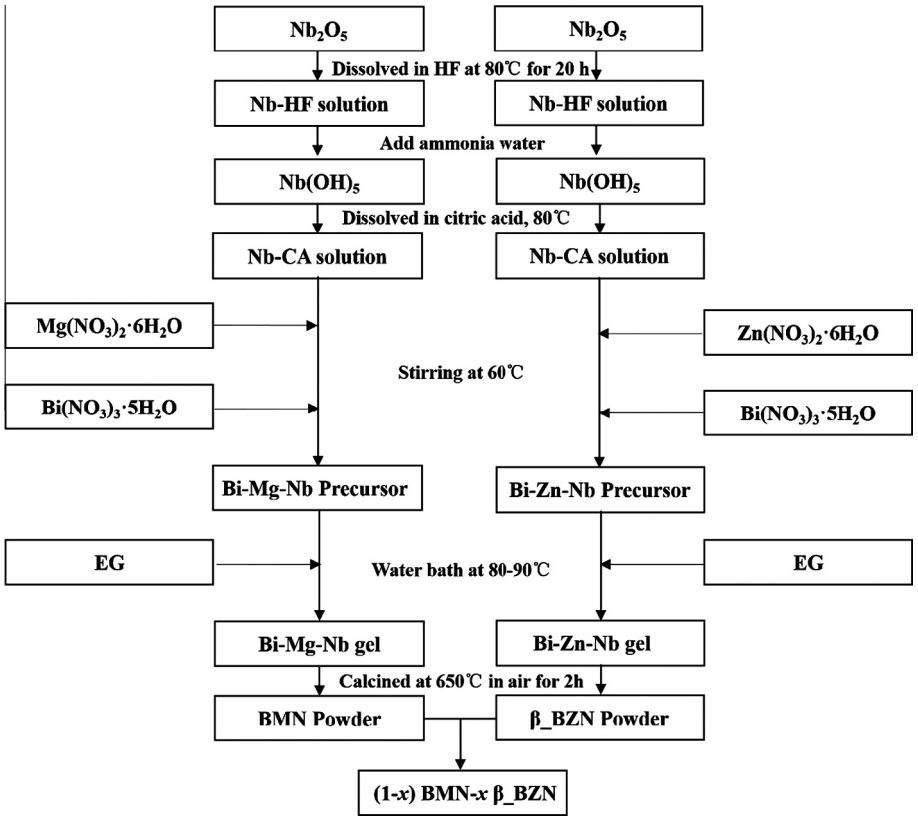

Fig. 1. Flow chart for preparing the (1−x) BMN–x β_BZN ceramics by the sol–gel process.

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