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PHASE STUDY AND ELECTRICAL PROPERTIES OF DIVALENT DOPED NON-STOICHIOMETRIC BISMUTH ZINC NIOBATE CUBIC PYROCHLORE

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ABSTRACT

A study of extrinsic doping is essential to elucidate relative ability of the pyrochlore materials to accommodate various dopants in forming new solid solutions and to search for improvement of electrical properties. Much reported stoichiometric cubic pyrochlore $Bi_3Zn_2Nb_3O_{14}$ appears to contain ZnO as secondary phase. Reducing Zn content in $Bi_3Zn_2Nb_3O_{14}$ resulted in $Bi_3Zn_{2-x}Nb_3O_{14-x}$ solid solutions where $0.04 \leq x \leq 0.31$. The phase pure material of composition $Bi_3Zn_{1.84}Nb_3O_{13.84}$ has been indexed on a cubic cell, space group FD3M, with cell constant a = 10.5579 (4) Å. Incorporation of divalent ions Cu^{2+}, Mg^{2+}, Ca^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+} in non-stoichiometric cubic pyrochlore $Bi_3Zn_{1.84}Nb_3O_{13.84}$ has been studied. Extensive solid solutions were observed when copper and cadmium were introduced as dopants where solid solution limits were obtained at x = 0.5 and 0.4, respectively in $Bi_3Zn_{1.84-x}Nb_3M_xO_{13.84}$. Other divalent dopants showed rather narrow solid solutions in the range of x = 0.15 to 0.25. Conductivity Arrhenius plots of all the doped materials are linear and reversible on heat-cool cycles with activation energy of 1.4-1.6 eV (x = 0.1). At the frequency of 100 kHz, these materials exhibit high relative permittivity (ε') and low dielectric loss (tan δ) with values in range of 50-100 and 0.001-0.015, respectively at 28 °C. A slight increase in relative permittivity was observed in the doped materials except where Cd^{2+} and Ni^{2+} were dopants. Dielectric loss generally increases with increasing dopant content. Copper doped solid solutions exhibit higher conductivity which could be associated with lowering of activation energy (1.4-0.8 eV).

INTRODUCTION

Bi_2O_3-ZnO-Nb_2O_5 (BZN) based pyrochlore ceramics were first explored in 1970s by Chinese engineer for low firing temperature multilayer capacitors. It attracts tremendous interest as BZN materials exhibit excellent dielectric properties such as high dielectric constants (ε), relatively low dielectric losses, and compositionally tunable temperature coefficient of capacitance (τ_c) [1]. Currently, BZN materials have been developed for Multilayer Ceramic Capacitors (MLCC) co-firing with low Pd content electrode materials. BZN materials that satisfy the NGO (negative-possitive-zero, that is 0 ± 30 ppm/^{0}C) MLCC specification over the standard -55 ^{0}C to 125 ^{0}C are comparable to commercial materials. There appears to be two structurally-related phases, which are often referred to as cubic and orthorhombic pyrochlores in BZN system, respectively. However, there is considerable uncertainty in the literature as to their precise stoichiometries; in addition, the so-called orthorhombic phase is, in fact, monoclinic [2, 3] and its crystal structure, like pyrochlore, can also be described as an anion-deficient fluorite, is based on the zirconolite structure and not on the pyrochlore structure.

Generally, cubic pyrochlores can be represented by the general formula $A_2B_2O_6O'_{1-\delta}$, indicating oxygen nonstoichiometry in the crystal lattice. Alternatively the pyrochlore structure can be described as an ordered, oxygen-deficient fluorite structure. The properties can possibly be tailored within wide limits by doping on the A and B site. Consequently, pyrochlore oxides exhibit many interesting properties: ionic conduction, electronic conduction, catalytic activity and fluorescence. In doped pyrochlore system, the ionic sizes of the substituted cations should be comparable to those of the A and B site cations and the combination must yield the same average charge as the A and B cations to maintain charge neutrality [4]. The substituted cations should have suitable ionic radii for the pyrochlore structure according to the upper and lower radius limits given by Subramanian et al [5]. These values are given as $0.87 < r_A < 1.17$, $0.58 < r_B < 0.775$ Å and $0.96 < r_A < 1.29$, $0.54 < r_B < 0.76$ Å, respectively for $A_2^{3+}B_2^{4+}O_7$ and $A_2^{2+}B_2^{5+}O_7$. The stability range for the pyrochlore structure has been quantified by the cation radius ratio (r_A/r_B). For $A_2^{3+}B_2^{4+}O_7$ and $A_2^{2+}B_2^{5+}O_7$ systems, the stability ranges are $1.46 < r_A/r_B < 1.80$ and $1.4 < r_A/r_B < 2.2$, respectively [5, 6]. From ionic radii compilations, the weighed r_A/r_B average for cubic pyrochlore BZN (bismuth zinc niobates) is 1.66, which is well within the stability limit for the pyrochlore structure.

We have reported cubic pyrochlore phase formation, subsolidus solid solution and possible mechanisms in the Bi_2O_3-ZnO-Nb_2O_5 system previously. We disclosed a rather narrow trapezium shaped solid solution area that does not include the so-called ideal composition P [7]. Further investigation has been carried out especially on synthesis and characterization of divalent doped Zn-deficient cubic pyrochlore which is discussed in this paper.

METHODOLOGY

High purity oxides Bi_2O_3 (Aldrich, 99.9 %), ZnO (Merck, 99 %), and Nb_2O_5 (Alfa Aesar, 99.9 %) were used as starting materials in the sample preparation. MgO (99 %, Aldrich), CdO (99.99 %, Aldrich), CaO (99.9 %, Aldrich), NiO (99.99 %, Aldrich), PbO (99.99 %, Alfa-Aesar) and CuO (99.9 %, Aldrich) were used as dopants for chemical doping of $Bi_3Zn_{1.84}Nb_3O_{14}$. Stoichiometric quantities of the oxides were weighed and mixed with acetone in an agate mortar. The resulting powder was transferred into a gold boat and pre-fired at 700 °C for 24 h in a furnace. Subsequently, the mixture was fired at temperatures of 800 °C and 950 °C for 24 h with intermediate regrinding. Samples were analyzed by X-ray powder diffraction using an automated Shimadzu diffractometer XRD 6000 in 2θ range of 10-70 ° at 2 °/min. Selected samples were analyzed at a scan rate of 0.1 °/min and the data were used for cell parameter refinement using Chekcell software. Gold electrodes were attached on both faces of the sample pellet. The pellet was then dried and hardened at 600 °C. Electrical properties were studied through measurements performed in the frequency range of 5 Hz-13 MHz, using a Hewlett Packard LF impedance analyzer, HP4192A controlled by a computer. The ac measurements were taken from room temperature to 800 °C at 50 °C increments and 30 minutes equilibration at each temperature. All the measurements were performed in air.

RESULTS AND DISCUSSION

All the literature on chemical doping involved stoichiometric P phase [8, 9, 10]. However, this particular composition was shown to contain excessive ZnO [2]. Phase pure $Bi_3Zn_{1.84}Nb_3O_{13.84}$ was synthesized, refined and indexed on a cubic cell, space group FD3M, with cell constant a = 10.5579 (4) Å. (Fig. 1). This material has been reported as average pyrochlore type, albeit with stoichiometry $(Bi_{1.5}Zn_{\sim0.42})(Zn_{0.5}Nb_{1.5})0_{\sim6.92}$ indicating distribution of Zn over A and B sites and extensive displacive disorder on both the A and O' sites. It was speculated that it could be a host lattice for various dopants due to its Zn and oxygen vacancies in the structure [2, 7, 11]. Extrinsic chemical doping was carried out in the Zn-deficient, phase pure cubic pyrochlore $Bi_3Zn_{1.84}Nb_3O_{13.84}$ in order to elucidate relative ability of the pyrochlore material to accommodate various dopants in forming new solid solutions and in the search for better performance materials.

In this study, Cd^{2+} with ionic radius of 1.10 Å (8-coordinated), Ca^{2+} with ionic radius of 1.12 Å (8-coordinated), $Pb^{2+}$with ionic radius of 1.29 Å (8-coordinated), Cu^{2+} with ionic radius of 0.73 (6-coordinated), Mg^{2+} with ionic radius of 0.72 Å (6-coordinated), Co^{2+} with ionic radius of 0.65 Å (6-coordinated) and Ni^{2+} with ionic radius of 0.69 Å (6-coordinated) appear suitable as dopants because their ionic radii are in the radius limits given by Subramanian for r_A and r_B [5, 6]. Extensive solid solutions were observed in copper and cadmium doped materials where solid solution limits were obtained at x = 0.5 and 0.4, respectively, in $Bi_3Zn_{1.84-x}M_xNb_3O_{13.84.}$ Other divalent dopants showed rather narrow solid solutions in the range of x = 0.15 (Ni), 0.20 (Mg & Co) and 0.25 (Pb and Ca), respectively.

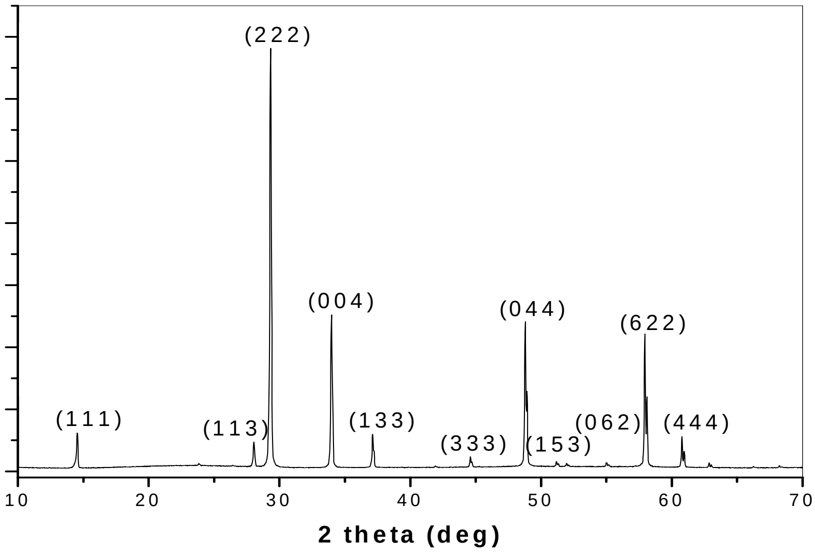


Figure 1: XRD diffraction pattern and peak indexing, $Bi_3Zn_{1.84}Nb_3O_{13.84}$

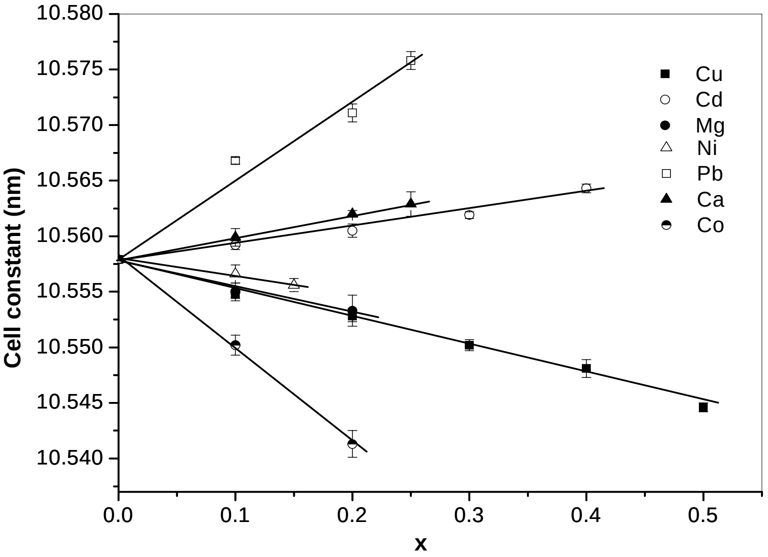


Figure 2: Cell constants vs x of divalent doped BZN pyrochlore

The question immediately arises as to the mechanism of substitution either into the A or B site. Generally, dopants with larger ionic radii are most likely to replace Zn at the A site where they are more compatible to the Bi at the A site under eight coordination environment where B_2O_6 and A_2O' interpenetrating networks are formed. Zn was preferentially displaced off-centre from the A-sites [2, 11], whereas the Bi was essentially located in the central-site position in the pyrochlore. Given that Cd^{2+}, Pb^{2+} and Ca^{2+} have larger ionic radii than Zn^{2+}, they are more compatible with Bi^{3+} when sharing the same site and thus more likely to substitute for Zn^{2+} on the A site (larger site) rather than B site [4, 6]. As Cd, Pb and Ca are incorporated into the BZN pyrochore structure, the cell constants of pyrochlore increase (Fig. 2). The linear-plots indicate that well–behaved solid solutions exist within this range according to Vegard's law which states that the lattice parameters of the solid solutions are directly proportional to the atomic percent of solute present.

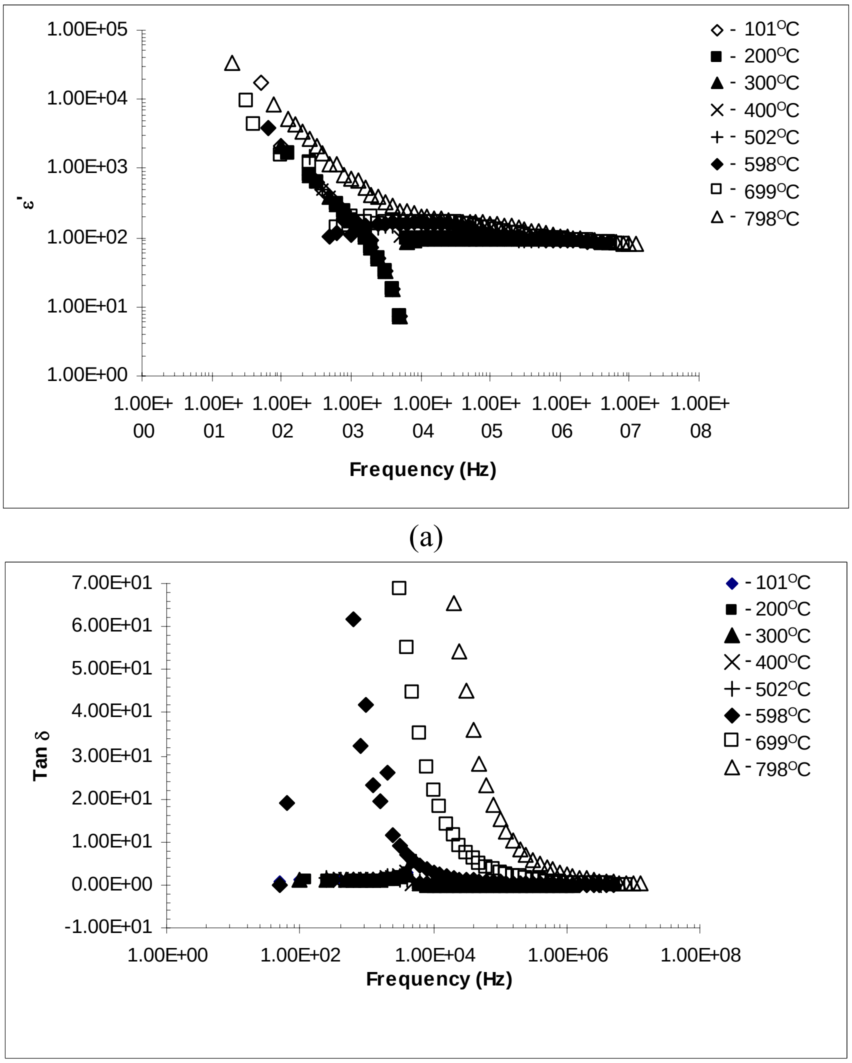
It is postulated that Cu, Co, Mg and Ni with similar ionic radii as Zn occupied B-site replacing Zn in the pyrochlore structure. The formation of extensive Cu doped solid solutions (x = 0.5) is probably due to the close similarity in their ionic sizes; 0.74 Å for Zn^{2+} and 0.73 Å for Cu^{2+} when octahedrally coordinated. However, Ni, Mg and Co doping only results in single phase pyrochlore at limits of x = 0.15 and 0.2, respectively. This indicates that ionic size is not the only variable affecting the stability of the pyrochlore structure. The cell constants of the Mg, Co and Ni-doped BZN materials decrease with increasing dopant concentration, probably a result of their slightly smaller size.

Electrical properties

The divalent doped phase pure samples $Bi_3Zn_{1.84-x}M_xNb_3O_{13.83}$ (x = Cu, Cd, Pb, Ca, Mg, Ni & Co) were characterized by a.c impedance spectroscopy over the frequency range of 5 Hz to 13 MHz. The samples were reversible in heat-cool cycle from room temperature to 850 ^{0}C in air. Perfect semicircles were observed in the complex plane plots and their bulk resistances were considerably high with values ranging from 0.9 to 1.8 MΩ cm at 550 ^{o}C. Conductivities of doped samples were lower than that of the parent material except for Cu doped samples. Cu doped samples exhibited highest conductivity probably due to lower activation energy. Similarly, decrease in conductivities for other divalent doped materials could be associated with higher activation energy required to overcome the energy barrier for the transport of charges.

Figure 3a shows a high degree of dispersion of the permittivity of $Bi_3Zn_{1.84}Nb_3O_{13.84}$ ceramic at low frequencies (<1 kHz) and above 600 ^{o}C (high temperatures). In the range of 100-600 ^{o}C, non-frequency dependence was observed. In Figure 3b, all the curves show an increase of the loss magnitude below 10 kHz. Dielectric losses decreased with frequencies when temperature was above 600 ^{o}C. In the range of 100-600 ^{o}C, non-frequency dependence was observed. All divalent-doped materials showed similar phenomena as BZN pyrochlore. They appear to be dielectric materials, in which a conduction mechanism of the hopping type was present. The dispersions may be associated with the presence of atomic defects in the structure which exhibits a large number of unoccupied atomic sites. In cubic pyrochlore, the occurrence of oxygen vacancies is an intrinsic defect [12].

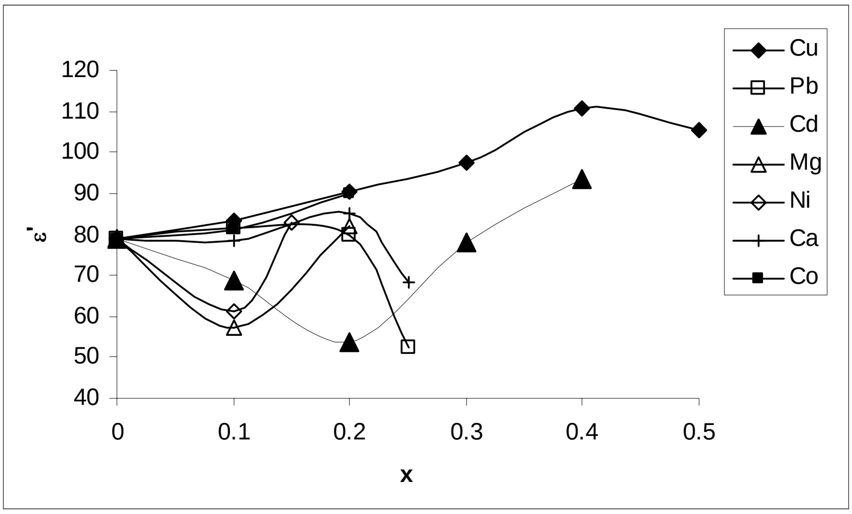
In Figure 4a, no significant increase is observed in dielectric constants of all doped materials except when Cu was used as a dopant at 100 kHz at 600 °C. For Cu doped materials, the dielectric constant appeared to increase with dopant concentration. The increase in ε' is associated with the larger ion polarizability of dopant than that of Zn. For the other doped materials, the dielectric constant appeared to decrease then increase. Work is currently in progress to confirm if the variations are associated with pellet density and sintering condition. Dielectric losses generally increase with increasing dopant content (Fig. 4b).



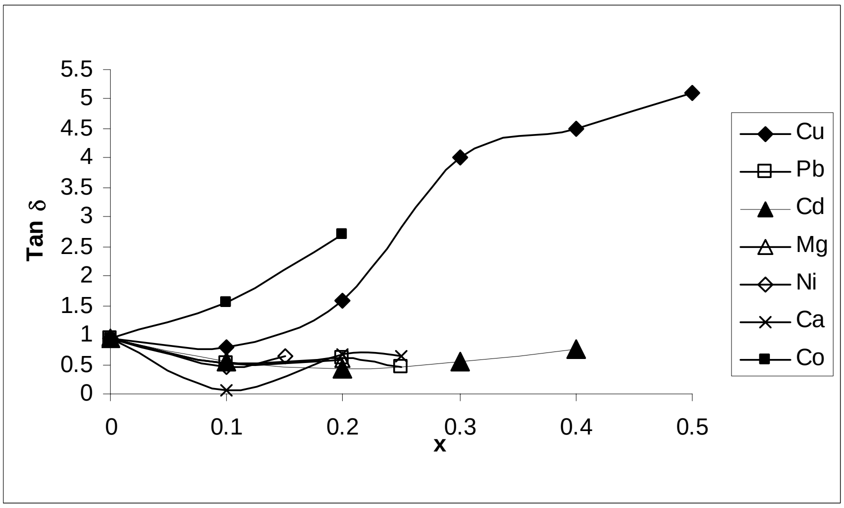
(a)

(b)

Figure 3a & b: Relative permitivity, ε', dielectric loss as a function of frequency at various temperatures



(a)



(b)

Figure 4a & b: Relative permittivity, ε', dielectric losses vs dopants concentration (100 kHz at 600 ^oC)

CONCLUSION

The phase pure material of composition $Bi_3Zn_{1.84}Nb_3O_{13.84}$ has been indexed on a cubic cell, space group FD3M, with cell constant a = 10.5579 (4) Å. Extensive solid solutions were observed in copper and cadmium doped materials where solid solution limits were obtained at x = 0.5 and 0.4 respectively in $Bi_3Zn_{1.84-x}Nb_3M_xO_{13.84.}$ Other divalent dopants showed rather narrow solid solutions in the range of x = 0.15 to 0.25. No clear trend in real permittivity was observed.

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