



Substituted $\text{Bi}_{3.5}\text{Mg}_{1.8}\text{Nb}_{2.7}\text{O}_{13.8}$ pyrochlores with transition metals (Zn, Ni and Cd): Doping mechanism, structure and electrical properties

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Abstract

The influence of transition metals (Zn, Cd and Ni) on bismuth magnesium niobate ($\text{Bi}_{3.5}\text{Mg}_{1.8}\text{Nb}_{2.7}\text{O}_{13.8}$, BMN) pyrochlores was investigated. Considering the difference in their ionic radii, Cd was postulated to substitute Mg at the eight-fold coordinated A-site whereas Zn and Ni were to replace Mg at the six-fold coordinated B-sites of the host structure. Solubility limits in these substitutional pyrochlore solid solutions were determined to be 0.4, 0.1 and 0.3 for Zn, Ni and Cd, respectively. Upon introducing these divalent cation dopants, notable changes in the lattice parameters and grain sizes were observed with increasing dopant concentration. The high dielectric constants, ϵ' of Zn, Cd and Ni doped BMN pyrochlores were discernible with their bulk values of 195–216, 173–195 and 153–195, respectively. The highest ϵ' of 216 was recorded for the composition with Zn = 0.1 in contrast to the lowest value of 153 found in the composition with Ni = 0.1. Meanwhile, these highly insulating divalent cation doped BMN pyrochlores also exhibit low dielectric losses, $\tan \delta$ whose values are in the order of 10^{-3} . The excellent dielectric properties allow these novel pyrochlore phases to be potentially applied for the energy storage applications.

Keywords: Bi/Mg niobate, solid state synthesis, dielectric properties, impedance spectroscopy, capacitors

1. Introduction

High performance functional ceramics are greatly demanded for the miniaturisation of passive electronic

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components, e.g. resonators and multilayer ceramic capacitors (MLCCs). There has been progressive development in MLCCs, and still much research efforts are required for the overall quality improvement. The MLCCs are well-received owing to their excellent dielectric properties, e.g. high capacitance, compact size, high reliability and good frequency characteristics [1–3]. A monolithic multilayer ceramic capacitor requires both buried electrodes, i.e. an internal electrode, an external termination (external electrode) and high permittivity ceramic dielectrics that are highly compatible during the manufacturing process. The high capacitance MLCCs with increasing stacked layers would require expensive electrodes, e.g. Pt or Au. To reduce the cost of internal electrode, alternative low melting point electrode, e.g. Ag-Pd alloy, Ni or Cu are co-fired under the reducing atmosphere [3]. In other words, these dielectrics should have high electrode compatibility, low dielectric loss ($\tan \delta$) and high dielectric constant (ϵ') over a specific temperature range, i.e. extremely low temperature coefficient ($TC\epsilon'$).

In search for high ϵ' ceramics, Bi-pyrochlores appear to be promising candidate attributed to their composition variation, structural flexibility and electrical property tunability. Numerous bismuth-based pyrochlores with the general formulas, $\text{Bi}_2(\text{B}_{2/3}^{2+}\text{B}_{4/3}^{5+})\text{O}_7$ and $\text{Bi}_2(\text{B}^{3+}\text{B}^{5+})\text{O}_7$ where $\text{B}^{2+} = \text{Mg}, \text{Cu}, \text{Zn}$ and Ni ; $\text{B}^{3+} = \text{Sc}$ and In ; and $\text{B}^{5+} = \text{Nb}$ and Ta had been studied systematically [4–12]. The dominant phase had a cubic pyrochlore structure except in some cases small amount of MgNb_2O_6 phase can be found. On the other hand, the B-site substitution with i.e. Cu^{2+} or Nb^{5+} would lead to a structural distortion from the cubic into the tetragonal phase. These bismuth pyrochlores exhibited moderately high ϵ' in the range 67 to 250 and low $\tan \delta$ of <0.011 at room temperature and 1 MHz. Interestingly, lower $\tan \delta$ and ϵ' were found in tantalum analogues, similar to the case of Ta and Nb perovskite microwave dielectrics, i.e. $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ and $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, respectively.

The ionic radii of the substituted cations should be comparable to those of the A and B-site cations while the combination of cations should yield the same average charge in order to maintain the overall charge neutrality [5,6]. The introduction of other cations, e.g. Ti, Cu, Ta, Sn or Sr ions into the bismuth zinc niobate (BZN) pyrochlores caused a huge variation of ϵ' in the range of 60–200, high $\tan \delta$ and large negative temperature coefficient of capacitance, TCc [4,7–12]. As reported by Mergen *et al.* [13–15], Cr, Co, In, Ir, Sm, Nd and Fe were introduced into $\text{Bi}_{1.50}\text{Zn}_{0.92}\text{Nb}_{1.50}\text{O}_{6.92}$ pyrochlore and these doped pyrochlores exhibited varying ϵ' in the range of ~ 60 –240 and low $\tan \delta$ in the order of 10^{-3} . It is also worthwhile highlighting that divalent cation plays a crucial role for the phase formation and dielectric properties of pyrochlores. Notably, bismuth magnesium niobate (BMN) pyrochlores with relatively higher ϵ' and lower $\tan \delta$ were synthesised successfully. The successful doping of Mg in the Bi_2O_3 -MgO- M_2O_5

($\text{M} = \text{Nb}$ and Ta) ternary systems could be due to the comparable ionic radii between Mg^{2+} and Zn^{2+} [8,16–20]. Moreover, MgO has high refractory and low $\tan \delta$ characteristics that are crucial for dielectrics.

Consequently, various methods have been used to synthesise BMN or bismuth magnesium tantalate (BMT) pyrochlores using direct solid-state reaction, intermediate method involving pre-synthesised BiNbO_4 , thin film fabrication etc. [4–9,13–17]. BMN pyrochlores showed not only good electrical properties at high temperatures, but they also possessed interesting electrical behaviour at sub-ambient temperatures. $\text{Bi}_4\text{Mg}_{4/3}\text{Nb}_{8/3}\text{O}_{14}$ exhibited a relaxor behaviour wherein a diffused phase transition was involved, i.e. reduced ϵ' and increased T_m (maximum ϵ' at a specific temperature) in response to temperature and frequency. Similar behaviour was also observed in our detailed electrical circuit modelling study of BMN and BMT pyrochlores wherein these pyrochlores were an insulator with resistivity $>10 \text{ M}\Omega \text{ cm}$ at low intermediate temperatures, ~ 240 –623 K, but, transforming into a modest electrical conductor with activation energy 1.07 eV above $\sim 623 \text{ K}$ [18,19].

To date, much research attention has been focused on the electrical performance of the BMN or BMT pyrochlores. These compositions are probably not phase pure and may contain trace amount of other secondary phases. However, it is well understood that the electrical performance of functional ceramics is greatly influenced by the careful control of composition, structure and processing procedure. As such, we undertake a systematic study pertaining to the influence of transition metal dopants on these BMN pyrochlores from the perspectives of their subsolidus solubility, crystallochemical structural change and dielectric performance.

II. Experimental

2.1. Materials

Bi/Mg niobate ($\text{Bi}_{3.5}\text{Mg}_{1.8}\text{Nb}_{2.7}\text{O}_{13.8}$, BMN) doped with Zn^{2+} , Ni^{2+} and Cd^{2+} , having compositions $(\text{Bi}_{3.5}\text{Mg}_{0.5})(\text{Mg}_{1.3-x}\text{Zn}_x\text{Nb}_{2.7})\text{O}_{13.8}$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$), $(\text{Bi}_{3.5}\text{Mg}_{0.5})(\text{Mg}_{1.3-x}\text{Ni}_x\text{Nb}_{2.7})\text{O}_{13.8}$ ($x = 0, 0.1, 0.2, 0.3$) and $(\text{Bi}_{3.5}\text{Mg}_{0.5-x}\text{Cd}_x)(\text{Mg}_{1.3}\text{Nb}_{2.7})\text{O}_{13.8}$ ($x = 0, 0.1, 0.2, 0.3$), were prepared by solid-state reaction. High purity oxides including Bi_2O_3 (Alfa Aesar, 99.99%), MgO, CdO, ZnO and NiO (Aldrich, 99%), Nb_2O_5 and Ta_2O_5 (Alfa Aesar, 99.9%) were pre-heated, weighed out stoichiometrically before mixing homogeneously in acetone by an agate mortar. The platinum boats containing mixed reactants were fired gradually at 300 and 600 °C both for 1 h to form less-volatile intermediate. These pre-treated powders were left at 800 °C overnight followed dwell at 1025 °C for 48 h with intermediate regrinding. All the heat treatments were performed in air using a muffle furnace with programmable heating/cooling rate of 10 °C/min. The thermal equilibrium or phase change was ensured by a prolonged heat

treatment duration and/or subsequent firing at high temperatures.

The phase identification of these divalent cation doped pyrochlores was performed by a Shimadzu powder X-ray diffractometer, XRD 6000, Cu K α radiation over the 2θ range 10–70° at the scan rate 2°/min. Meanwhile, the quantitative study was performed using Chekcell refinement program for the lattice parameter determination. The cold-pressed pellets with dimension of 8 mm diameter and ~1.5 mm thick, achieved a relative density above 90%TD, as calculated from their geometrical and theoretical densities after sintering at 1075 °C for 24 h. Then, the surface morphology of the densified pellets after firing at 1025 °C was examined by a scanning electron microscope (SEM, JOEL JSM-6400) at different magnifications. For the elemental analyses, 400 ppm sample triplicates were prepared by digesting 0.1 g pyrochlore powder in 12.5 ml concentrated HF and 250 ml blank solution containing 5% concentrated HNO₃. These solutions were diluted 5 times and analysed by an inductively coupled plasma-optical emission spectrometer (Perkin Elmer Optima 2000DV). Both thermogravimetric and differential thermal analysers (Perkin Elmer, TGA/DTA 7) were used to characterise the thermal stability of the doped BMN pyrochlores. The electric properties of these pyrochlores were measured using an AC impedance analyser (Hewlett Packard 4192A) with an applied voltage of 0.1 V over the frequency range of 5 Hz to 13 MHz. The conductivity jig with the attached pellet with gold electrodes was inserted into a temperature controlled horizontal tube furnace. The electrical measurements were performed in air for both heat-cool cycles over the temperature range of 30 to 850 °C. The impedance data were corrected for the samples' geometrical factors and the stray capacitance of the empty jig prior to further analysis using Zview software.

III. Results and discussion

3.1. Phase formation analysis

Zn²⁺, Cd²⁺ and Ni²⁺ were selected as dopants for Bi/Mg niobate, and substitution at the A-site or B-site of the pyrochlore. The ratios of ionic radii of these cations are deliberated carefully, wherein the stable pyrochlores follow the upper and lower limits, i.e. $0.87 < r_A < 1.17$ or $0.58 < r_B < 0.775$ Å for the average A₂³⁺B₂⁴⁺O₇ pyrochlores, respectively [5]. In this study, Cd²⁺ with the ionic radii of 1.10 Å (8-coordinated) and 0.95 Å (6-coordinated), Ni²⁺ with the ionic radius of 0.69 Å (6-coordinated), and Zn²⁺ with the ionic radii 0.90 Å (8-coordinated) and 0.74 Å (6-coordinated) appear to be the suitable dopants, which fall within the limits [6]. The larger dopants are likely to substitute at the A-site as these cations are more compatible with Bi³⁺ over the eight-fold coordination. Hence, Cd²⁺ cation is expected to substitute Mg²⁺ at the A-site (Bi_{3.5}Mg_{0.5-x}Cd_x)(Mg_{1.3}Nb_{2.7})O_{13.8}. Note that Cd²⁺

has an ionic radius of 1.10 Å, which is comparable with Bi³⁺ (1.17 Å, 8-coordinated) to share the A-site [20]. Meanwhile, the smaller Zn²⁺ and Ni²⁺ are more compatible with the 6-coordinated Mg²⁺ (0.72 Å) at the B-site. Thus, it is postulated to be a one-to-one replacement of Mg²⁺ by Zn²⁺ or Ni²⁺ based on the formula (Bi_{3.5}Mg_{0.5})(Mg_{1.3-x}M_xNb_{2.7})O_{13.8} (M = Zn or Ni).

According to the XRD results (Fig. 1) solid solubility range of these chemically modified BMN pyrochlores were determined to be $0 \leq x \leq 0.4$ for (Bi_{3.5}Mg_{0.5})(Mg_{1.3-x}Zn_xNb_{2.7})O_{13.8}, $0 \leq x \leq 0.3$ for (Bi_{3.5}Mg_{0.5-x}Cd_x)(Mg_{1.3}Nb_{2.7})O_{13.8} and $0 \leq x \leq 0.1$ for (Bi_{3.5}Mg_{0.5})(Mg_{1.3-x}Ni_xNb_{2.7})O_{13.8}. Figures 1a-c confirmed that the doped pyrochlores are phase pure and crystallise in the cubic pyrochlore structure with a space group of *Fd3m*. About 22.22 mol% of Mg is possibly replaced by Zn for the (Bi_{3.5}Mg_{0.5})(Mg_{1.3-x}Zn_xNb_{2.7})O_{13.8} pyrochlores. A secondary phase is observed when the ZnO dopant concentration reaches $x = 0.4$ or higher. On the other hand, ~16.67 mol% of Cd²⁺ and ~5.56 mol% of Ni²⁺ could replace Mg²⁺ in the BMN pyrochlores. As a comparison, the Ni doped BMN pyrochlores show the lowest subsolidus solubility, which is probably due to the huge size difference between these replacing and replaceable ions. For the Cd series, more intense peaks of CdO are discernible with increasing dopant concentration. These secondary phases are attributed to Cd_{0.88}Nb₆O₁₆ and CdO phases (not shown here-with). The lattice parameters for all the divalent cations doped BMN pyrochlores are found to be in the range of 10.5795(5)–10.5857(4) Å. Note that the incorporation of these divalent cation dopants in the host structure could cause a slight expansion of the unit cell, i.e. ~0.05% of the BMN pyrochlores. The relatively larger lattice parameters of Zn doped BMN pyrochlores are discernible when the smaller Mg²⁺ is replaced by Zn²⁺ at the B-sites. On the other hand, the Cd series also shows increased lattice parameters and this is due to the compatibility of larger Cd²⁺ (1.10 Å) with Bi³⁺ in sharing the A-site [21]. Interestingly, the Ni doped BMN pyrochlore with the postulated formula of (Bi_{3.5}Mg_{0.5})(Mg_{1.3-x}Ni_xNb_{2.7})O_{13.8} shows a slight increase in the lattice parameter when ~2.5% of Ni is introduced. Ideally, the smaller ionic radius of Ni²⁺ (0.69 Å) may cause a unit cell contraction according to the Vegard's law, if the changes in lattice parameter with composition are governed purely by the relative sizes of the ions. However, such changes are also influenced by other factors including valence state and electron affinity. The increased lattice parameter of Ni doped BMN pyrochlore could be due to its variable valence state and low electron affinity, which causes a relatively longer bond length and an increased lattice parameter. The variations of lattice parameter of these chemically modified BMN pyrochlores are given in Fig. 1d.

The changes of strain value due to the doping of BMN pyrochlores with divalent cations are negligibly small, i.e. in the order of 10⁻⁴ (more information is

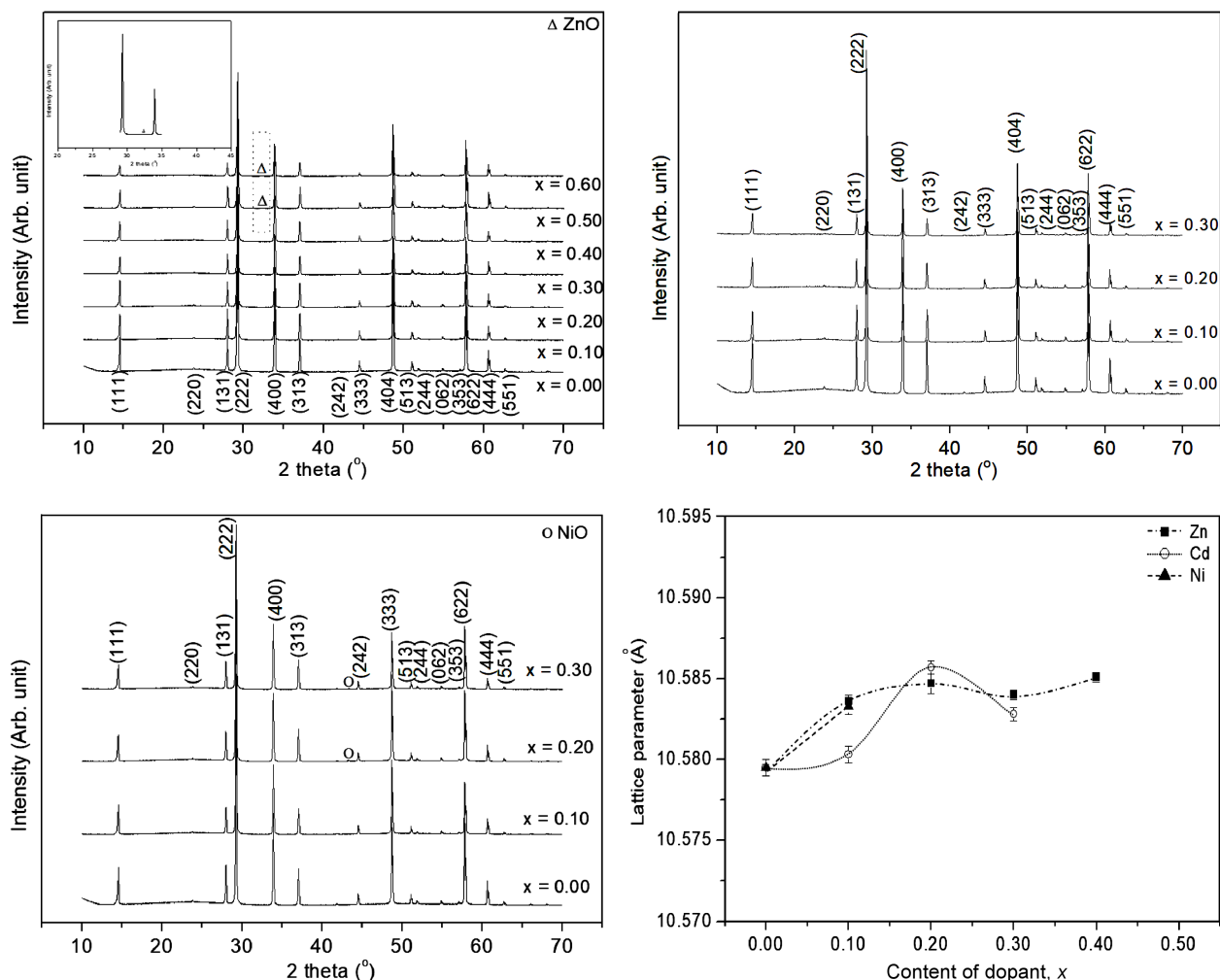


Figure 1. XRD patterns of chemically modified BMN pyrochlores: a) Zn series ($0.0 \leq x \leq 0.6$), b) Cd series ($0 \leq x \leq 0.3$), c) Ni series ($0.0 \leq x \leq 0.3$) and d) lattice parameters versus dopant concentration

given in Supporting Information⁸ in Table S1). This implies that the incorporation of these dopants does not lead to a drastic structural change wherein all ions are still comfortably in their preferred coordination environment. This is also further supported by the absence of peak shift or broadening as shown by the intense (111) and (222) planes' reflections (Figs. 1a-c).

3.2. Microstructural study

The SEM micrographs of Zn, Cd and Ni doped BMN pyrochlores are shown in Fig. 2. All the samples appear to be dense with their relative densities generally higher than 90%TD (percentage of their theoretical value). This observation is well aligned with the SEM results as only a few pores are seen. The grain sizes are generally larger when these divalent cation dopants are introduced into the BMN pyrochlores. The polyhedral grains of only a few microns, but mostly in the range from 10 to 85 μm can be seen, which is much larger than that of the undoped BMN pyrochlore. It appears that these divalent oxides may provide an eutectic melt with Bi_2O_3 and MgO below the sintering temperature, thus improving the overall sinterability [22].

The elemental composition of these divalent cation doped pyrochlores were also analysed (data are given in Supporting Information in Tables S2 and S3). The obtained results are close to the calculated values, thus confirming the correct chemical stoichiometry of these pyrochlores. In addition, there is no evidence of any systematic deviation from the stoichiometry which could be attributed to the loss of volatile Bi_2O_3 . Note that the Ni doped pyrochlore is not analysed herewith due to the difficulty of sample digestion.

3.3. Thermal analyses

The thermal analyses of these divalent cations doped pyrochlores are shown in Figs. 3a-f. No weight loss and phase change are observed in the doped BMN pyrochlores over the studied temperature range (Figs. 3a-c) Hence, all the doped BMN pyrochlores are concluded to be thermally stable and impervious to any thermal events.

3.4. Electrical properties

The electrical properties of the Zn, Cd and Ni doped BMN pyrochlores are characterised by AC impedance

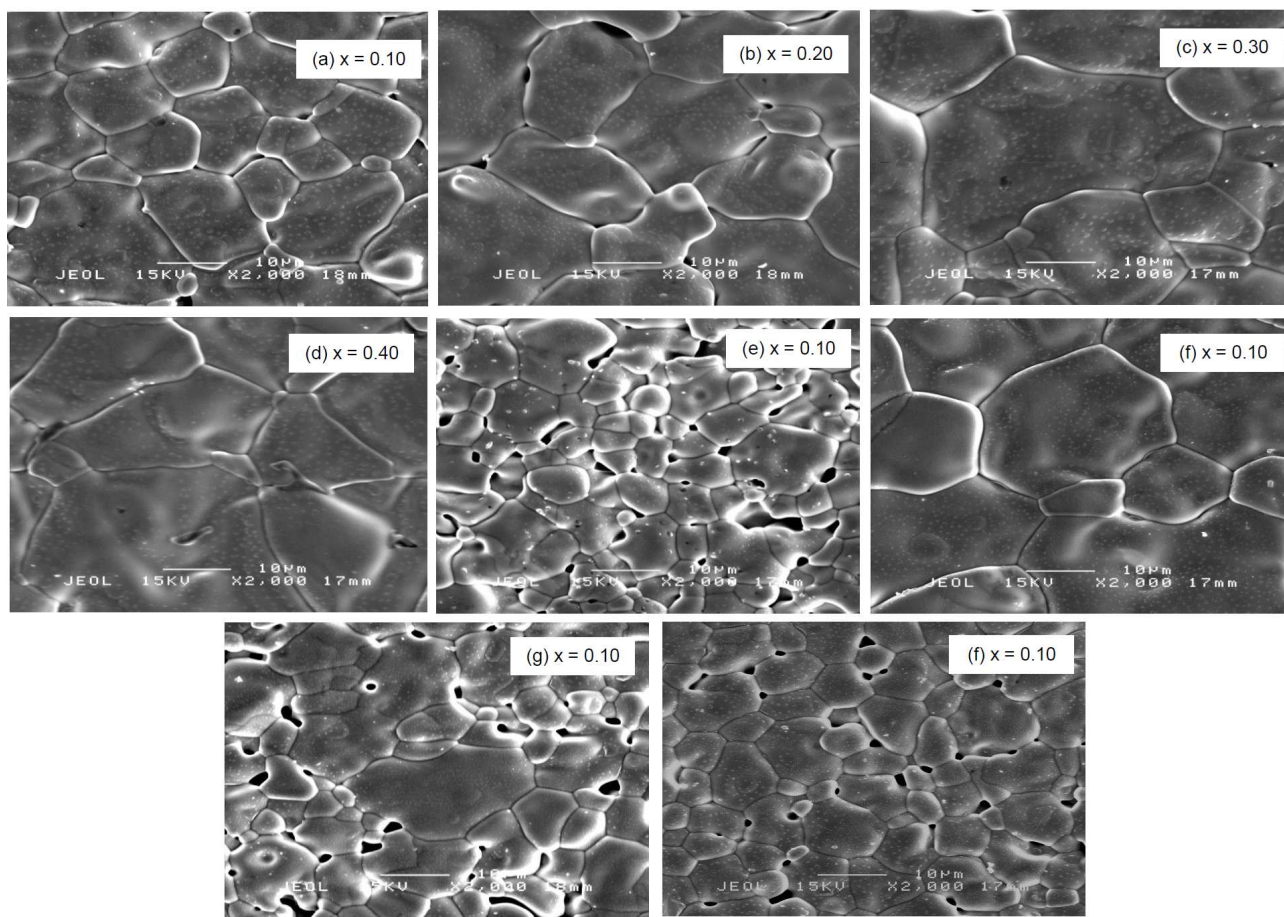


Figure 2. SEM micrographs of chemically modified BMN pyrochlores of Zn series [$x = 0.1$ (a), $x = 0.2$ (b), $x = 0.3$ (c) and $x = 0.4$ (d)], Cd series [$x = 0.1$ (e), $x = 0.2$ (f) and $x = 0.3$ (g)] and Ni series [$x = 0.1$ (h)]

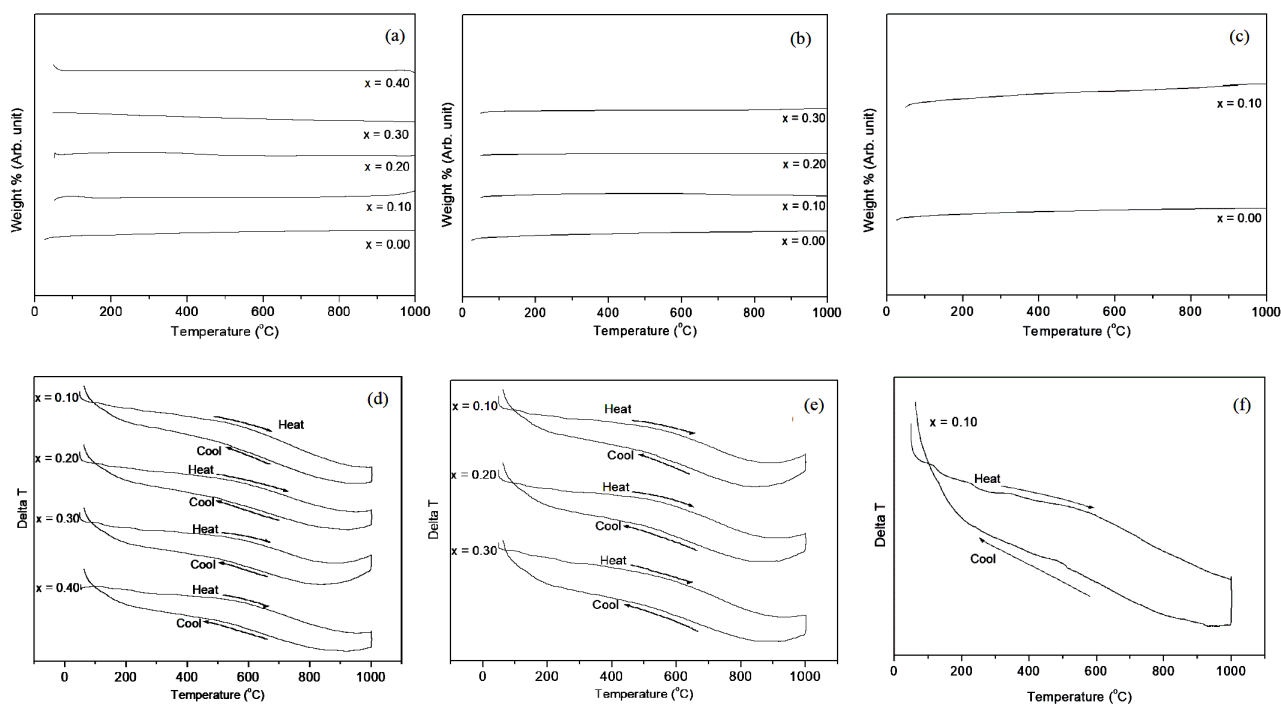


Figure 3. TGA thermograms of chemically modified BMN pyrochlores: a) Zn series, b) Cd series, c) Ni series; and DTA thermograms of: d) Zn series, e) Cd series and f) Ni series

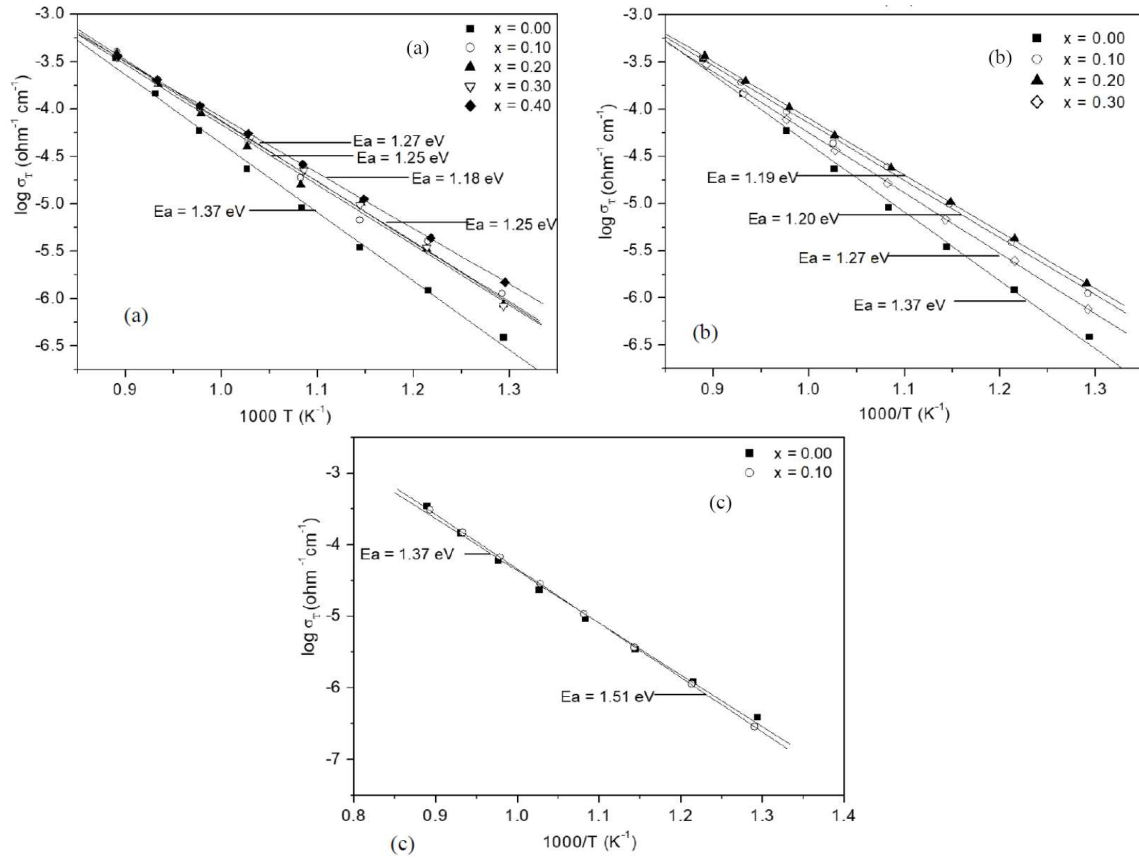


Figure 4. Conductivity Arrhenius plots of chemically modified BMN pyrochlores: a) Zn series, b) Cd series and c) Ni series

spectroscopy over the frequency range of 5 Hz–13 MHz. The conductivity values were deduced from the high intercept of real impedance of typical complex Cole-Cole plots at different temperatures. The conductivities of the Zn and Cd doped BMN pyrochlores are found to increase with increasing Zn and Cd concentration, respectively. This may be due to the decrease in activation energy (Figs. 4a-c). It is proposed that the replacement of Mg^{2+} by Zn^{2+} or Cd_{62}^{+} may cause more local breaks in the symmetry of the host structure due to the presence of different cations at both A-sites and B-sites. This could give rise to the reduced volume of coherent polarising unit, thus lowering the required activation energy in the Zn and Cd doped BMN pyrochlores [23]. The activation energies of the Zn and Cd doped BMN pyrochlores

are found to be in the range of 1.18–1.37 eV and 1.19–1.37 eV, respectively. On the other hand, the Ni doped BMN pyrochlore shows a decrease in conductivity with the activation energy of 1.51 eV (Fig. 4c). All the doped pyrochlores show high activation energy, i.e. higher than 1.0 eV, which is probably due to the electronic hopping mechanism [24–26].

The dielectric constants (ϵ') of the Zn, Cd and Ni doped BMN pyrochlores as a function of temperatures are shown in Figs. 5a-c, respectively. The gradual decrease in ϵ' with increasing temperature is observed for all the divalent cations doped materials. Such phenomenon could be the result of the thermal disruption of dipoles in the BMN pyrochlores. The temperature coefficients of dielectric constant ($TC\epsilon'$) of the Zn

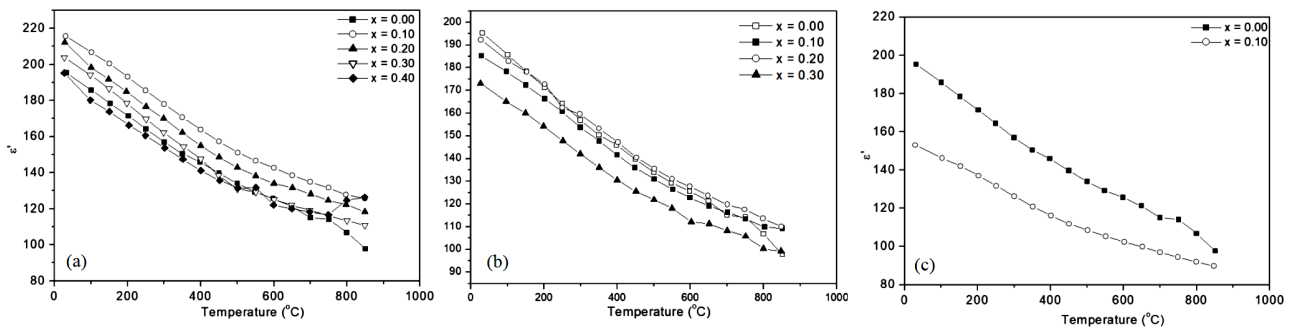


Figure 5. Temperature dependence of dielectric constants at 1 MHz of the chemically modified BMN pyrochlores: a) Zn series, b) Cd series and c) Ni series

Table 1. Temperature coefficient of dielectric constant ($TC\epsilon'$) and activation energy (E_a) of doped BMN pyrochlores

x	$TC\epsilon'$ for 30–300 °C [ppm/°C]	E_a [eV]	r_A/r_B
Zn series			
0.0	–742	1.37	1.704
0.1	–645	1.25	1.703
0.2	–732	1.25	1.702
0.3	–753	1.27	1.700
0.4	–773	1.18	1.699
Cd series			
0.0	–742	1.37	1.704
0.1	–628	1.20	1.712
0.2	–630	1.19	1.720
0.3	–659	1.27	1.728
Ni series			
0.0	–742	1.37	1.704
0.1	–643	1.51	1.706

doped BMN pyrochlores are in the range from –645 to –773 ppm/°C. The $TC\epsilon'$ of the Zn doped pyrochlores drops when $x = 0.10$, but increases thereafter with higher Zn concentration. This agrees with the proposed correlation between the ratio of the ionic radii (r_A/r_B) and $TC\epsilon'$, i.e. higher $TC\epsilon'$ was expected with decreasing $r + A/r_B$ in the chemically substituted α -BZN pyrochlore [27]. Higher Zn concentration was claimed to cause a decrease in r_A/r_B ratio due to the larger ionic radius of Zn^{2+} (Table 1). However, lower $TC\epsilon'$ values are also found when Ni and Cd are introduced into the BMN pyrochlores. The $TC\epsilon'$ values of the Cd doped BMN pyrochlores are found to be in the range from –628 to –742 ppm/°C, whilst, a similar value of –643 ppm/°C is also discernible in the Ni doped pyrochlore. In other words, the smaller magnitude of $TC\epsilon'$ of the Cd and Ni doped BMN pyrochlores are due to their larger r_A/r_B ratio (Table 1).

Figures 6a–c show the dielectric losses as a function of temperature of the Zn, Cd and Ni doped BMN pyrochlores at room temperature and frequency of 1 MHz, respectively. The $\tan \delta$ is independent of temperature below 600 °C, but increases appreciably at higher temperatures. This is due to the thermally activated drift mo-

bility of the electric charge carriers that could cause increase in real admittance and this contributes towards higher $\tan \delta$ in conduction mechanism [12,24–26].

Both ϵ' and $\tan \delta$ of the divalent cations doped pyrochlores with varying x at room temperature and fixed frequency of 1 MHz are shown in Figs. 7a,b, respectively. Generally, the ϵ' of the Zn doped BMN pyrochlores increases to a maximum at $x = 0.10$ ($\epsilon' = 216$), but decreases thereafter. The ϵ' of Zn doped BMN pyrochlores with $x = 0.20, 0.30$ and 0.40 are determined to be 212, 204 and 195, respectively. In the Cd doped pyrochlores, the ϵ' shows a slightly decrease with increasing Cd dopant concentration whose ϵ' are found in the range of 173–192. Meanwhile, the doping with Ni ($x = 0.1$) shows ~20% decrease in ϵ' if compared to that of the undoped BMN pyrochlore. The variation of ϵ' could be associated with the lattice imperfections and boundary defects caused by the incorporation of dopants [8].

In our study, Zn^{2+} is postulated to substitute Mg^{2+} at the B-site of the pyrochlore structure as Zn^{2+} (0.74 Å) has a comparable ionic radius with Mg^{2+} (0.72 Å) for the 6-coordination environment. Hence, the higher polarisability of Zn (2.04 Å³) than that of Mg (1.32 Å³) at the B-site of pyrochlore structure may contribute to the higher ϵ' [26,28]. This is due to the key role played by the B ion located at the centre of BO_6 octahedra. The strong correlation of high polarisable octahedra, i.e. ZnO_6 or NbO_6 at the B-site could give rise to high ϵ' in the Zn doped BMN pyrochlores [9]. Accordingly, the substitution of smaller Mg^{2+} by larger Zn^{2+} could result in longer bond distance between the centre cation and its neighbouring octahedral anions. This could provide more flexibility for the movement of B ion within the BO_6 octahedra, thus yielding higher ϵ' [26,28]. However, ϵ' of the Zn doped BMN pyrochlores are found to decrease with higher dopant concentration, i.e. $x \geq 0.20$. One possibility for the ϵ' drop could be due to the randomly distributed Zn^{2+} over the A-site and B-site of the pyrochlore structure with increasing Zn content. The replacement of Mg^{2+} by Zn^{2+} at A-site will cause more Mg^{2+} to occupy the B-site. As a result, the weaker polarisation of MgO_6 and/or NbO_6 may cause lower ϵ' . At this stage, the distribution of the ions in the Zn doped pyrochlore structure is still conjecture. The exact local crystal chemistry of the Zn doped BMN

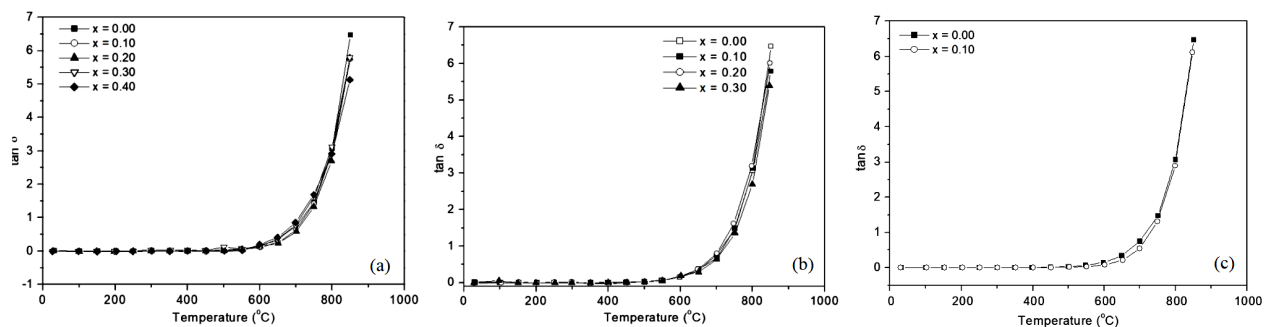


Figure 6. Temperature dependence of losses at 1 MHz of the chemically modified BMN pyrochlores: a) Zn series, b) Cd series and c) Ni series

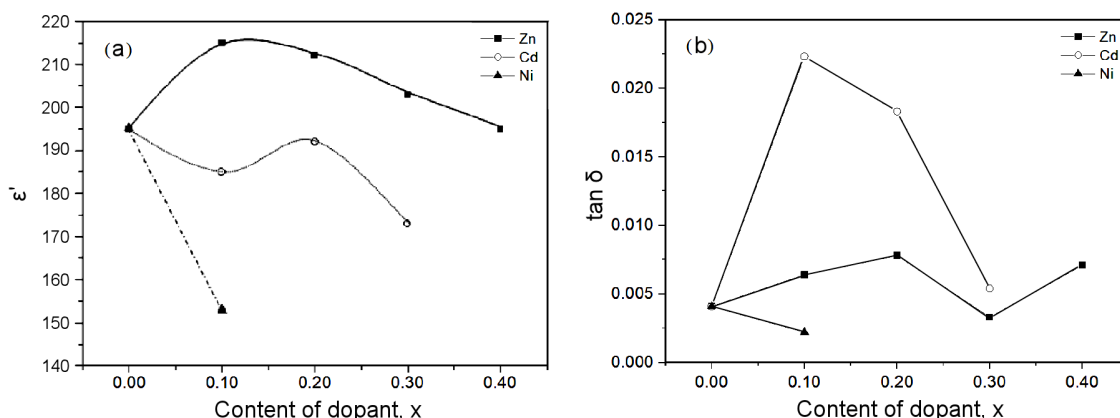


Figure 7. Variation of dielectric properties as a function of dopant concentration at frequency of 1 MHz and room temperature: a) dielectric constants and b) dielectric losses

pyrochlores should be further determined using careful structural study, i.e. neutron diffraction or electron microscopy.

On the other hand, the Cd doped BMN pyrochlores do not show a systematic trend in ϵ' values with varying x . This could be due to the fact that the larger Cd^{2+} is more likely to substitute the Mg^{2+} at the A-site. The incorporation of Cd^{2+} could possibly cause the disorder at the A- and O'-sites of the BMN pyrochlore due to the relatively smaller ionic radius of Cd^{2+} than that of Bi^{3+} . The Cd^{2+} also shows relatively higher ionic polarisability, i.e. $3.40 \text{ \AA}^3$ than that of Mg^{2+} ($1.32 \text{ \AA}^3$) at the A-site of pyrochlore. It has been claimed that if the replacing ions have a smaller ionic radius or greater polarisability than the replaceable ions, they tend to favour an off-centring displacement in ferroelectrics and dipolar glasses [30]. This could be linked to the loosening of the cations situated at the centre of octahedra. Thus, the difference in ϵ' of the Cd series could be attributed to the disorder of the A- and O'-sites of the BMN pyrochlores [30,31].

Finally, the Ni doped BMN pyrochlore shows a decrease in ϵ' , which could be due to the lower polarisability of Ni ($1.23 \text{ \AA}^3$) than that of Mg. Hence, the weak correlation of NiO_6 octahedron with lower polarisability at the B-site could cause a relatively lower ϵ' . Nevertheless, the $\tan \delta$ of these divalent cations doped pyrochlores are retained in the order of 10^{-3} except for the Cd doped pyrochlores ($x = 0.10$ and 0.20) whose $\tan \delta$ are 0.0223 and 0.0183, respectively. Higher $\tan \delta$ could be due to the increased real admittance of Cd doped BMN pyrochlores.

IV. Conclusions

Divalent cations, including Zn^{2+} , Cd^{2+} and Ni^{2+} , were successfully introduced into the BMN pyrochlore host structure. According to the XRD results, solid solubility range of these chemically modified BMN pyrochlores were determined to be $0 \leq x \leq 0.4$ for $(\text{Bi}_{3.5}\text{Mg}_{0.5})(\text{Mg}_{1.3-x}\text{Zn}_x\text{Nb}_{2.7})\text{O}_{13.8}$, $0 \leq x \leq 0.3$ for

$(\text{Bi}_{3.5}\text{Mg}_{0.5-x}\text{Cd}_x)(\text{Mg}_{1.3}\text{Nb}_{2.7})\text{O}_{13.8}$ and $0 \leq x \leq 0.1$ for $(\text{Bi}_{3.5}\text{Mg}_{0.5})(\text{Mg}_{1.3-x}\text{Ni}_x\text{Nb}_{2.7})\text{O}_{13.8}$. The lattice parameters, grain sizes and electrical properties of the doped BMN pyrochlores are found to vary with different dopant concentrations. These BMN pyrochlores exhibited considerably high bulk ϵ' in the range of 195–216, 173–195 and 153–195, for Zr, Cd and Ni series, respectively. It is also worthwhile highlighting that all these doped BMN pyrochlores retained their low $\tan \delta$ in the order of 10^{-3} – 10^{-2} . Hence, these highly insulating BMN pyrochlores with excellent dielectric performance could be potentially applied for multilayer ceramic capacitors.

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§ Supplementary data can be downloaded using following link: <https://t.ly/2rQT8>

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