Low dielectric constant and signature of ferroelectric nature in transition metal (Co, Ni, Cu)-doped $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ aluminates

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This paper throws light on the preparation of transition metal-doped $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co, Ni, Cu}$) aluminates via solid-state reaction route. The X-ray diffraction characterization analysis confirmed that all the samples have crystallized into the pseudocubic phase having space group $Fd3m$ and were single phased. The incorporation of transition metals viz. Co^{2+} , Ni^{2+} , Cu^{2+} in the $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ matrix does not result in the appearance of new peaks or any considerable shift in diffraction peaks within the limits of XRD experimentation. This infers homogeneous dispersion of dopants at the Mg-site which is attributed to nearly same ionic radii of the dopants to that of Mg-site in $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$. Lattice structure, bonding nature and hence the spinel formation were verified through Raman scattering technique. The compositional verification was carried out via energy dispersive analysis of X-rays (EDAX). The surface morphology and hence the microstructural studies were carried out using field emission scanning electron microscopy (FESEM). The synthesized $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co, Ni, Cu}$) aluminate samples were tested for polarization studies keeping their insulating nature into consideration and they displayed a sign of well-behaved P-E loop.

Keywords: Nanoparticles; structure; morphology; polarization.

1. Introduction

MgAl_2O_4 is a spinel (ternary) oxide of the type AB_2O_4 , where 'A' represents a divalent metal cation which occupies a tetrahedral site and 'B' represents a trivalent metal cation and occupies the octahedral site. Mg–Al spinels have a wide solid solubility range and is the only chemical compound in the binary MgO – Al_2O_3 system that possesses a wide range of solid solutions for spinel-corundum compositions. MgAl_2O_4 spinel has high melting point, high chemical inertness against both acidic and basic slags, low expansion values at elevated temperatures, and is an eco-friendly refractory material.^{1,2} These aluminates being effective refractory materials, have found use in steel ladles, cement rotary kilns, vacuum induction furnaces, continuous casting tundishes, glass industries, etc.^{3–5} The simple way to modify and improve the properties of the materials is to dope the parent lattice by suitable cations. The properties are altered to a great extent by the preparation procedure. Additionally, the unoccupied tetrahedral and octahedral sites along with order–disorder transitions of cations with respect to these sites also increases the possibility to modify these properties. The effect of doping of Zn^{2+} at Mg^{2+} site has been found to be resistive in nature with low dielectric constant and highly reduced dielectric loss usable in electrical insulation, substrates for integrated circuits, and microwave technology.⁶

The conventional method of preparation of MgAl_2O_4 spinel is to calcine the mixture of MgO and Al_2O_3 or other raw materials at high temperature. As it is an important high refractory electro-insulating and constructional material with application in electro-technical, metallurgical, chemical and radio-technical industry, it is accordingly prepared by solid-state route depending on the dispersity of the initial materials, the type and the quantity of the components of the material in the temperature range 1000–1600°C. It is often challenging to prepare support materials that meet all these design criteria. To tune the properties, mixed metal oxides provide the best opportunities, but mostly these materials are heterogeneous multiphase mixtures. These mixed metal oxides can be prepared with a wide range of properties and typically have higher surface areas than magnesia while having greater thermal stability than transition aluminas.^{7–9}

Highly dense spinel ceramics have the potential to be widely used in diverse engineering fields. But dense materials with high-purity characteristics exhibiting stoichiometric composition are difficult to synthesize directly from mixtures of individual Al_2O_3 and MgO powders via conventional solid-state reaction, as the volume expansion (5%) accompanying the spinellization reaction determines the extent of densification.¹¹ Usually, compact materials are prepared by a two-stage firing process viz. calcining the powder mixture at higher temperature to complete the spinellization reaction,

followed by intense grinding and re-firing at further higher temperatures. The successful synthesis of highly dense spinels at reasonable firing temperatures may result in the production of highly reactive, phase-pure spinel powders.^{10,11}

The spinel powders prepared by chemical methods display a higher degree of chemical homogeneity, better control of stoichiometry and improved sinterability,^{11,12} when compared with those synthesized by the conventional solid-state reaction method. But the solid-state reaction may improve the side features of the material, for example, when the density increases, the chances of enhanced dielectric constant increases and often may lead to the introduction of the ferroic properties which is the aim of this study. There is bulk literature available on Mg–Al spinels prepared via chemical methods and according to their nano size, there is scarcity of the data for the exploration of these materials with large grain sizes and that on the effect of dopants with different compositions. In this work, all the attention has been drawn to the physical properties with controlled particle size through the assurance of proper dispersion of the initial materials and intermediate firing temperatures. Ultrafine spinel powders (< 40 nm) were obtained by calcining the precursor in the temperature range of 900–1200°C. Here, we describe the preparation and characterization of the $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) spinel powders, as well as its behavior on densification.

2. Experimental Details

The polycrystalline samples of $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates were synthesized successfully by high temperature solid-state reaction method also known as ceramic method under open atmosphere. According to the nominal compositions of $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates, appropriate amount of highly pure starting reagents such as MgO , ZnO , Al_2O_3 , CuO , NiO , Co_3O_4 , were thoroughly mixed as per the formula and ground for 5 h to obtain the fine powdered sample. After calcining the powdered mixture at 1050°C for 10 h, it was mixed with polyvinyl alcohol (PVA), the polymer matrix that acts as binder for the sample. The mixture of binder and sample was pressed into pellets of the diameter of 10 mm. The pellets were sintered at 1200°C for 10 h to densify them and later, they were silver polished for better electrical contact for dielectric and polarization measurements.

The crystal structure, particle size and type of phase $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminate materials that were acquired were identified by means of X-ray powder diffraction technique at room temperature using Bruker D8-Advance X-ray diffractometer with $\text{CuK}\alpha_1$ (1.5406 Å) radiation. The diffraction data is collected with a step size of 0.02° over the angular range 2θ ($10^\circ < 2\theta < 80^\circ$) generating X-ray by 40 kV and 40 mA power settings. Raman spectroscopy was carried out on the

synthesized samples using Jobin Yvon Horiba Lab RAM (system HR800) spectrometer with a 488 nm excitation source equipped with a peltier cooled charge coupled device detector. Field emission scanning electron microscopic images were obtained using the FESEM instrument model SUPRA 55 with a resolution of 1.4 nm at 1 kV without beam deceleration, magnification power of $\times 12\text{--}900000$ kV and acceleration voltage of 0.1–30 kV. Compositional verification via energy dispersive analysis of X-rays (EDAX) was carried out by recording the energy spectra using the energy-dispersive spectrometer, model INCA Oxford. Dielectric measurements were carried out by Wayne Kerr, Model 6500B, Precision Impedance Analyzer with the frequency range 20 Hz to 1 MHz. The P-E loop, i.e., electrical polarization as a function of field was carried out on commercial ferroelectric loop tracer make of M/s Radiant Instruments, USA with specification of voltage range of ± 100 kV to ± 10 kV, frequency range of ± 100 kHz to ± 0.03 Hz and a minimum leakage current of 2 pAmp.

3. Results and Discussions

3.1. X-ray diffraction analysis

The spinel structured polycrystalline $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminate samples were prepared at high temperature by conventional solid-state reaction route. The crystal structure, phase purity of the prepared samples was examined by X-ray diffraction experiment. The data obtained in the angular range of ($10^\circ < 2\theta < 80^\circ$) is displayed in Fig. 1. The XRD spectra analysis revealed the single phased cubic structure with space group Fd3m for all the samples. The retention of the crystal structure for all the dopants may be attributed to homogeneous distribution of the dopant transition metal ions at the

Fig. 1. X-ray spectra of $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates.

Mg²⁺ site as well as to the comparable ionic radii [Mg²⁺ (0.66 Å), Co²⁺ (0.72 Å), Ni²⁺ (0.69 Å) and Cu²⁺ (0.72 Å)] of the host site with those of dopants. The intensity of the characteristic peak reveals the crystalline nature and large FWHM of the characteristic peaks indicates the lower nano size of the crystals in the as prepared samples. The *hkl* values of the reflections in the obtained spectra were indexed as (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (5 3 1), (5 3 3), (6 2 2) and (4 4 4). The lattice parameters obtained are in agreement with the reports^{13,14} and a slight variation in the value of lattice parameter '*a*' may be attributed to the ionic radii difference of the dopants replacing Mg²⁺ site. The average crystallite size of the as prepared samples was calculated in the range of 20–30 nm using classical Scherer formula, $t = k\lambda/\beta \cos \theta$ where ' λ ' is the X-ray wavelength, ' θ ' is the Bragg's angle and '*k*' is the constant. The details of the structural parameters obtained from XRD analysis are demonstrated in Table 1. The crystal structure of the pristine Mg_{0.5}Zn_{0.5}Al₂O₄ with the elements occupying their sites has been displayed in Fig. 2.

3.2. Raman spectroscopy

The number of expected Raman peaks for MgAl₂O₄ spinel can be determined from group theory.¹⁵ The factor group analysis predicts that the following modes are observed for ordered spinel (*Fd3m*): $1A_{1g} + 2A_{2u} + 1E_g + 2E_u + 1F_{1g} + 4F_{1u} + 3F_{2g} + 2F_{2u}$. Among these, only five Raman active modes are available $1A_{1g} + 1E_g + 3F_{2g}$. It has been reported that four modes of vibration are generally observed for MgAl₂O₄ and the fifth mode corresponding to *F*_{2g} (2) has been reported elsewhere.¹⁶ But in this study, out of the Raman spectra displayed in Fig. 3, only two Raman bands are observed corresponding to 417 cm⁻¹ assigned as *E*_g mode and 670 cm⁻¹ assigned as *F*_{2g} mode which are the intrinsic to the normal spinel structure. Raman spectroscopy probes the local structural environments and is very sensitive to note the M–O bond (Al–O versus Mg–O) that is helpful in gauging structural order. The band at 417 cm⁻¹ assigned as *E*_g mode is a characteristic peak and is generally the most intense Raman band in ordered spinels. However, these peaks are broader and less intense in disordered spinel and achieve

Table 1. Details of parameters obtained from XRD patterns of the Mg_{0.5-x}TM_xZn_{0.5}Al₂O₄ (*x* = 0, 0.05 and TM = Co, Ni, Cu) aluminates.

Parameters	Values obtained at room temperature			
	Mg _{0.5} Zn _{0.5} Al ₂ O ₄	Mg _{0.45} Cu _{0.05} Zn _{0.5} Al ₂ O ₄	Mg _{0.45} Ni _{0.05} Zn _{0.5} Al ₂ O ₄	Mg _{0.45} Co _{0.05} Zn _{0.5} Al ₂ O ₄
Space group	<i>Fd-3m</i>	<i>Fd-3m</i>	<i>Fd-3m</i>	<i>Fd-3m</i>
<i>a</i> = <i>b</i> = <i>c</i> (Å)	8.0792	8.0799	8.0758	8.077
<i>V</i> (Å ³)	527.3632	527.5013	526.691	526.6175
Density (g/cm ³)	14.992	15.258	13.109	12.302

Fig. 2. (a) Top view and (b) 3D cell structure of pristine Mg_{0.5}Zn_{0.5}Al₂O₄ aluminate.

Fig. 3. Raman spectra of the as prepared samples.

sharpness and intensity with increasing structural ordering. The peak of the E_g mode has been attributed to the bending mode for Al^{3+} ions in the tetrahedral sites, and thus to cation disordering.^{17–20}

3.3. Composition and morphology

After successful preparation of single-phased $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ -based materials at high temperature, a curiosity for the presence of comprising elements of the synthesized samples compelled us for EDAX characterization. The EDAX spectra of the samples under investigation is displayed in Fig. 4 and it is obvious from the spectra that all the integrated components of the samples are present and there is no loss in the limits of the experiment. Also, the spectra clarifies that there is absence of any foreign element. The displaying of the peaks and their intensities are indicative of the energy of the elements in the samples and hence their composition.

The morphological study of the as prepared samples has been carried out via field emission scanning electron microscopy (FESEM). The micrographs so obtained are displayed as insets of the EDAX spectra of the corresponding

samples in Fig. 4. As all the samples are insulating with energy bandgap > 3 eV, they are expected to be good dielectric nature. The samples under investigation were sintered at 1200°C but well-defined grain boundaries with highly grown grains are reported at 1500°C ,²¹ so no clear grains or grain boundaries were distinguished. However, a signature of few small grains is obvious that may develop at higher temperature treatment. Generally, the grains seem embedded together to make small and big clusters, consisting of many grains of microsize. The close observation reveals that the porosity of the samples is not so high, as only a few blank spots were visible which witnesses the samples under observation to be mechanically very strong. The micrographs also reveal the uniform distribution of constituents of the samples.^{22,23}

3.4. Dielectric studies

The dielectric constants of the $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates have been measured in a frequency range of 20 Hz to 1 MHz as shown in Fig. 5. The plot reveals that the dielectric constant decreases with an increase in frequency and attains a constant value at higher frequency, showing dispersion behavior. At higher frequencies, the dielectric constant remains unchanged which may be due to the inability of electric dipoles to follow the fast variation of the applied alternating electric field. Consequently, the occurrence of friction between dipoles results in energy dissipation in the form of heat.²⁴ The dielectric constant is calculated by using the following relation:

$$\epsilon = Ct/\epsilon_0 A,$$

where 'C' is capacitance, 't' is the thickness of pellets, 'A' is an area of the pellet used and ' ϵ_0 ' is the permittivity of free space $= 8.854 \times 10^{-12} \text{ F/m}$.

The variation of ϵ' with $\log f$ (Hz) as displayed in Fig. 5 reveals that the samples exhibit strong frequency dispersion at low frequency. The observed frequency dispersion of ϵ' is well explainable in the light of Maxwell–Wagner²⁵ type interfacial polarization and it agrees well with Koop's phenomenological theory.²⁶ The higher value of dielectric constant at low frequencies may be due to the interfacial dislocations, oxygen vacancies, charged defects, grain boundaries effect and interfacial/space charge polarization due to heterogeneous dielectric structure.²⁷

At lower field values, charge accumulation occurs at interface giving rise to the net polarization of the ionic medium enhancing space charge region at electrode–electrolyte interface that in response increases the dielectric constant ϵ' . The higher dielectric constant at lower frequency and lower dielectric constant at higher frequency values are explained on the basis that in a dielectric medium, the good conducting grains are well separated by low conducting grain boundaries. Thus on the application of field, there is free movement of carriers within the grains of the medium but these charges

Fig. 4. FESEM images and EDAX spectra of $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates.

accumulate at the grain boundaries. The extent of accumulation determines the value of dielectric constant in proportional manner. The charges reaching the grain boundaries and hence their accumulation diminishes with increase in ac field,

thereby reduces the extent of polarization and hence the dielectric constant value decreases. The results displayed by the as prepared samples are in agreement with the reports elsewhere.^{28–31}

Fig. 5. Dielectric constant of the above solid state synthesized aluminates.

Fig. 6. Dielectric loss of $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates.

Table 2. Particle size and dielectric parameters of $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates.

Sample name	Particle size (nm)	Dielectric constant		Dielectric loss		<i>ac</i> conductivity	
		20 Hz	1 MHz	20 Hz	1 MHz	20 Hz	1 MHz
$\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$	22.39	88.188	4.76	0.995	0.029	9.76×10^{-8}	7.9×10^{-6}
$\text{Mg}_{0.45}\text{Co}_{0.05}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$	25.18	15.615	5.567	1.933	0.014	3.35×10^{-8}	4.32×10^{-6}
$\text{Mg}_{0.45}\text{Ni}_{0.05}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$	21.472	205.742	4.986	1.108	0.016	2.2×10^{-7}	1.9×10^{-5}
$\text{Mg}_{0.45}\text{Cu}_{0.05}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$	29.81	15.118	4.77	0.957	0.068	1.9×10^{-8}	4.15×10^{-6}

The dielectric loss ($\tan\delta$) measured as a function of $\log f$ (Hz) at room temperature is shown in Fig. 6. Figure 6 shows decreasing trend in dielectric loss as the applied field value increases. The graph shows higher values of dielectric loss at lower frequency. At high frequencies, the dielectric loss decreases due to the suppression of domain wall motion. The maximum dielectric loss at lower frequencies can be attributed to the hopping frequency of electrons (nearly equal to the applied frequency) between different ionic sites. The dielectric loss arises if the polarization lags behind the applied alternating field which is introduced by the presence of impurities and structural inhomogeneities.^{28–31} In the pristine and Ni-doped $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ samples, the dielectric loss reaches a maximum value at a particular frequency in the low frequency region. This characteristic is attributed to the resonance between the applied electric field and the polaron hopping frequency.⁶

A hump (shoulder) observed in pristine $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ and Ni-doped $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ in low frequency region is assigned to the resonance effect. At resonance frequency, the dielectric loss decreases abruptly approaching to the relaxation process whereas at frequency greater than resonance frequency, the electric dipoles change their direction very fast which in turn hinders the alignment of charge carriers and reduces the accumulation of charges at grain boundaries in the material under observation. This diminished charge

accumulation at the grain boundaries weakens the space-charge polarization as a result of which the value of loss value decreases with further increase in frequency. The dielectric constant, dielectric loss and *ac* frequency values at 20 Hz and 1 MHz are given in Table 2.

The *ac* conductivity of $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates samples is displayed in Fig. 7. The *ac* conductivity was found to be constant initially which after certain threshold value of applied field increases with further increase in frequency. This behavior could be due to activation of hopping of charge carriers between different localized states due to increase in the applied field. The applied electric field de-traps the carriers which is very difficult at the lower values of the field but after the threshold field, the de-trapping enhances with further increase in the magnitude of the applied field. This results in the enhancement of the immigration of electrons and thus leads to the increase in the conductivity at higher frequency values.^{27–32}

3.5. Polarization (P-E loop) studies

Since the $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates exhibit distorted cubic structure called as pseudo-cubic possessing a space group $Fd3m$ and presence of diamagnetic materials like Cu, Zn, etc., we suspected the materials for ferroelectric nature. Though P-E studies to the best of our knowledge have not been reported, we took the initiative and went for the P-E measurements. The data obtained has been plotted and is represented in Fig. 8. As said above, the materials with majority of the concentrations of diamagnetic materials present higher values and more clear P-E loops compared to the loops with other dopants, but in both the cases, the overall character is weak and have no clear saturation. Pristine and Cu-doped $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ have remnant polarization (P_r) values of the order of $0.05 \mu\text{C}/\text{cm}^2$ and $0.15 \mu\text{C}/\text{cm}^2$ and coercive field (E_c) of the order $2.16 \text{ kV}/\text{cm}$, $3.32 \text{ kV}/\text{cm}$, respectively while that of Ni and Co-doped $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ exhibit $P_r = 0.02 \mu\text{C}/\text{cm}^2$, $0.004 \mu\text{C}/\text{cm}^2$ and $E_c = 2.8 \text{ kV}/\text{cm}$ and $1.17 \text{ kV}/\text{cm}$, respectively. The results are intriguing and appeal for the modification in the sense of particle size, preparation process, doping concentration and sintering temperature.^{32,33}

Fig. 7. *ac* conductivity of the above prepared aluminates.

Fig. 8. P-E measurements of $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates.

4. Conclusions

The polycrystalline, single-phased $\text{Mg}_{0.5-x}\text{TM}_x\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ ($x = 0, 0.05$ and $\text{TM} = \text{Co}, \text{Ni}, \text{Cu}$) aluminates were synthesized by solid-state reaction method. The type of phase and crystal structure was confirmed via XRD data revealing cubic structure ($Fd3m$). Raman spectroscopy witnessed lattice structure and bonding in the as-prepared samples and hence confirmed the results of the XRD. EDAX confirmed the presence of all the integrated constituents of the samples under investigation and FESEM revealed crystalline nature without the presence of well-defined grains and grain

boundaries. Dielectric measurements revealed disappearance of relaxation in the Co- and Cu-doped $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$. The synthesized samples also present good looking P-E loop character though they appear very weak.

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References

- K. Miyakara, Y. Murata, I. Toyoshima, Y. Tanaka and T. Ž. Yokoyama, Varieties of MgO catalysts for 1,3-butadiene hydrogenation, *J. Catal.* **68**, 186 (1981).
- A. A. Bhattacharyya, G. M. Woltermann, J. S. Yoo, J. A. Karsh and W. E. Cornier, Catalytic SOx abatement: The role of magnesium aluminate spinel in the removal of SOx from fluid catalytic cracking (FCC) flue gas, *Ind. Eng. Chem. Res.* **27**, 1356 (1988).
- S. Kohjiya, T. Sato, T. Nakayama and S. Yamashita, Polymerization of propylene oxide by calcined synthetic hydrotalcite, *Makro. Mol. Chem. Rapid Commun.* **2**, 233 (1981).
- W. Bakker and J. G. Lindsay, Reactive magnesia spinel, preparation and properties, *J. Amer. Ceram. Soc. Bull.* **46**, 1094 (1967).
- R. J. Braton, Sintering and grain-growth kinetics of MgAl_2O_4 , *J. Amer. Ceram. Soc.* **54**, 141 (1971).
- J. Ahmad, M. Q. Awan, M. E. Mazhar and M. N. Ashiq, Effect of substitution of Co^{2+} ions on the structural and electrical properties of nanosized magnesium aluminate, *Physica B* **406**, 254 (2011).
- J. S. Yoo, A. A. Bhattacharyya and C. A. Radlouski, De-SOx catalyst: An XRD study of magnesium aluminate spinel and its solid solutions, *Ind. Eng. Chem. Res.* **30**, 1444 (1991).
- J. Rathousky, A. Zukal and J. Starek, Stabilized magnesia as a support for nickel methanation catalysts, *Appl. Catal. A: Gen. Z.* **94**, 167 (1993).
- M. Waqif, O. Saur, J. C. Lavalley, Y. Wang and B. A. Morzrow, Evaluation of magnesium aluminate spinel as a sulfur dioxide transfer catalyst, *Appl. Catal.* **71**, 319 (1991).
- J. Hatanic-Popovic, N. Miljevic and S. Zec, Spinal formation from coprecipitated gel, *Ceram. Int.* **17**, 49 (1991).
- M. Sindel, N. A. Travitzky and N. Claussen, Influence of magnesium-aluminum spinel on the directed oxidation of molten aluminum alloys, *J. Am. Cer. Soc.* **73**(9), 2615 (1990).
- G. Baudin, R. Martinez and P. Pena, High-temperature mechanical behavior of stoichiometric magnesium spinel, *J. Am. Cer. Soc.* **78**(7), 1857 (1995).
- O. Padmaraj, M. Venkateswarlu and N. Satyanarayana, Structural, electrical and dielectric properties of spinel type MgAl_2O_4 nanocrystalline ceramic particles synthesized by the gel-combustion method, *Ceram. Int.* **41**, 3178 (2015).
- K. Izumi, T. Mizukawa and E. Hanamura, Optical response and electronic structure of Zn-doped MgAl_2O_4 , *J. Appl. Phys.* **102**, 053109 (2007).

- ¹⁵D. Rousseau, R. Bauman and S. Porto, Normal mode determination in crystals, *J. Raman Spectrosc.* **10**, 253 (1981).
- ¹⁶M. O'Horo, A. Frisillo and W. White, Lattice vibrations of MgAl_2O_4 spinel, *J. Phys. Chem. Solids* **34**, 23 (1973).
- ¹⁷H. Cynn, High-temperature Raman investigation of order-disorder behavior in the MgAl_2O_4 spinel, *Phys. Rev. B* **45**, 500 (1992).
- ¹⁸H. Bliz and W. Kress, Phonon dispersion relations in insulators, in *Solid State Science*, Vol. 10 (Springer, Berlin, 1979).
- ¹⁹S. Mo and W. Ching, Electronic structure of normal, inverse, and partially inverse spinels in the MgAl_2O_4 system, *Phys. Rev. B* **54**, 16555 (1996).
- ²⁰M. Carpenter, R. Powell and E. Salje, Thermodynamics of non-convergent cation ordering in minerals: An alternative approach, *Am. Mineral.* **79**, 1053 (1994).
- ²¹T. Shiono, H. Ishitomi, Y. Okamoto and T. Nishida, Deformation mechanism of fine-grained magnesium aluminate spinel prepared using an alkoxide precursor, *J. Am. Ceram. Soc.* **83**, 645 (2000).
- ²²E. H. Walker, J. W. Owens, M. Ettaiene and D. Walker, The novel low temperature synthesis of nanocrystalline MgAl_2O_4 spinel using "gel" precursors, *Mater. Res. Bull.* **37**, 1041 (2002).
- ²³M. Saleem and D. Varshney, Structural thermal and transport properties of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ nanoparticles synthesized: Via the sol-gel auto-combustion technique, *RSC Advances* **8**, 1600 (2018); E. N. Alvar, M. Rezaie and H. N. Alvar, Synthesis of mesoporous nanocrystalline MgAl_2O_4 spinel via surfactant assisted precipitation route, *Powder Technology* **198**, 275 (2010).
- ²⁴B. K. Bammannavar, L. R. Naik and B. K. Chougule, Studies on dielectric and magnetic properties of $(x)\text{Ni}_{0.2}\text{Co}_{0.8}\text{Fe}_2\text{O}_4(1-x)$ barium lead zirconate titanate magnetoelectric composites, *J. Appl. Phys.* **104**, 0641231 (2008).
- ²⁵K. W. Wagner, The distribution of relaxation times in typical dielectrics, *Ann. Phys.* **40**, 817 (1913).
- ²⁶C. G. Koops, On the dispersion of resistivity and dielectric constant of some semiconductors at audio-frequencies, *Phys. Rev.* **83**, 121 (1951).
- ²⁷C. M. Kanamadi and S. R. Kulkarni, Dielectric and magnetic properties of $(x)\text{CoFe}_2\text{O}_4 + (1-x)\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ magnetoelectric composites, *Mater. Chem. Phys.* **116**, 6 (2009).
- ²⁸M. Saleem and D. Varshney, Influence of transition metal Cr^{2+} doping on structural, electrical and optical properties of Mg-Zn aluminates, *J. Alloys Compd.* **708**, 309 (2017); S. M. Hosseini, Structural, electronic and optical properties of spinel MgAl_2O_4 oxide, *Phys. Status Solidi B* **245**, 2609 (2008).
- ²⁹M. J. Iqbal, B. Ismail, C. Rentenberger and H. Ipsen, Modification of the physical properties of semiconducting MgAl_2O_4 by doping with a binary mixture of Co and Zn ions, *Mater. Res. Bull.* **46**, 2271 (2011).
- ³⁰M. J. Iqbal and S. Farooq, Effect of doping of divalent and trivalent metal ions on the structural and electrical properties of magnesium aluminate, *Mater. Sci. Eng. B* **136**, 140 (2007).
- ³¹D. Ravinder and K. Vijayakumar, Dielectric behaviour of erbium substituted Mn-Zn ferrites, *Bull. Mater. Sci.* **24**, 505 (2001).
- ³²M. Saleem, A. Mishra and D. Varshney, High-temperature firing effect on the structure and dielectric properties of $(0.5)\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) + $(0.5)\text{Ba}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BKT) composite, *J. Supercond. Nov. Magn.* **32**(4), 1475 (2019).
- ³³N. Rezlescu and E. Rezlescu, Dielectric properties of copper containing ferrites, *Phys. Stat. Solidi. A* **23**, 575 (1974).