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Structural, vibrational and dielectric behavior of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu and x = 0.0, 0.5) spinel chromites

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Abstract:

Low temperature sol-gel auto combustion method is used to synthesize the spinel chromites of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg {non–Jahn Teller (JT) ion}, Cu {JT ion}; x = 0.0, 0.5). Synchrotron, and lab x-ray diffraction pattern confirms the single-phase crystalline nature. Structural features from cubic (space group *Fd3m*) [CoCr₂O₄, Co_{0.5}Mg_{0.5}Cr₂O₄ and Co_{0.5}Zn_{0.5}Cr₂O₄] to tetragonal (space group *I4*₁/*amd*) [Co_{0.5}Cu_{0.5}Cr₂O₄] are reported. SEM micrograph of sintered samples results in less porosity with average particle size distribution of ~ 0.2 – 0.3 µm. Shifting of Raman active phonon modes is seen with doping and an additional Raman active mode is seen at 666.45 cm⁻¹ for Co_{0.5}Zn_{0.5}Cr₂O₄. Dielectric behavior as a function of frequency reveals that dispersion in all these chromites is attributed to hopping mechanism. Higher value of dielectric constant (ε ') and minimum loss tangent (tan δ) for non-JT ion Co_{0.5}Zn_{0.5}Cr₂O₄ is measured inferring effective charge polarization in chromites as compare to doped JT ions. Both grains and grain boundaries are active in Co_{0.5}Zn_{0.5}Cr₂O₄ at lower frequencies as depicted from impedance analysis. Doping does not showed the presence of electric polarization in chromites.



Keywords: Spinel chromites, Synchrotron x-ray diffraction, Raman scattering, Dielectric properties.

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1. Introduction

Various nanosized metal oxides with the spinel structure are focused in solid-state sciences due to their broad range of functions [1]. Chromites are amongst them and belong to a class of complex oxide spinels with general formula AB_2O_4 . Herein, A ions are generally divalent cations (Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Mg²⁺ etc.) occupying tetrahedral (T) sites and B ions are trivalent cations (Cr³⁺) in octahedral (M) sites. In the compound it is *d* elements exhibiting a spacious diversity of physical properties. Cr³⁺ (*d*³) ions are almost always covering octahedral site due to their large crystal field stabilization energy (CFSE) ~224.5 kJ mol⁻¹ [2].

Magnesium, zinc and cobalt chromite are normal type spinel structure are referred as an excellent example of coordination model for the formation of solid solutions with ions substitution in the tetrahedral site. Usually, structural changes, elastic and dielectric responses are witnessed during the physico – chemical mechanisms. The complex spinel type structures (magnetite, chromite etc.) displays variable degree of disorder of the A and B cations over the tetrahedral (T) and octahedral (M) sites. The inversion parameter *i* (defined as the fraction of the B cations at the T sites) is successful in discussing the disorder. The inversion parameter *i* can vary from 0, in the completely normal spinel (${}^{T}A{}^{M}B_{2}O_{4}{}^{2-}$) [3].

Transition metal and alkaline earth metal-doped CoCr_2O_4 crystallize in cubic closed packing with *Fd3m* space group with 56 atoms per unit cell. Co atoms are placed in tetrahedral positions 8*a*, Cr atoms are placed in octahedral positions 16*d* and O atoms of 32*e* position [4]. It is stressed that Jahn-Teller (JT) active cation (A²⁺) such as Ni²⁺ and Cu²⁺ in NiCr₂O₄ and CuCr₂O₄, as well as their solid solutions, provides a decrease in the space group from spinel cubic (*Fd3m*) to tetragonal (*I*4₁/*amd*) crystal structure distortions due to co-operative JT effect in chromites. Needless to mention that it depends on the orbital degeneracy of electronic states in the chromites.

Multiferroic CoCr₂O₄ ($T_{\rm C} = 94$ K) materials, which simultaneously exhibit magnetic and electric charge ordering and the effect of mutual influence of the electric polarization and magnetization. Hence forth, Chromites combining ferroelectric and magnetic properties are of scientific and technological interest for application in novel multifunctional devices. Transition metal and alkaline earth metal-doped CoCr₂O₄ are promising as multiferroic nature in them allows one to reveal the ordering of the magnetic and electrical subsystems. Existence of subsystems with ordered or disordered lattice, charge, spin, orbital ordering and presence of JT ion as [Ni²⁺ and Cu²⁺] and non–JT ion [Zn²⁺ and Mg²⁺] at A – site leads to complex physical properties and unexpected structures [5, 6]. Earlier, it was shown that spinel CoCr₂O₄ also

induces electric polarization apart from spontaneous magnetization leading to multiferroic nature [7].

The cation distribution between A-site and B-site depends on the ionic radii, the type of bonding and the synthesis technique. Altering the variables as temperature, pH and concentration of metal ions may impact the cation distribution. We note that in high temperature solid-state method, the powder of desired sample with relatively smaller surface area is readily achieved by mixing, heat treatment and grinding. Comparatively, much larger surface area and smaller crystallite size of spinel metal oxides have been achieved by wet chemical techniques involving sol-gel auto combustion technique. On the other hand, sol-gel method requires much lower temperatures and shorter calcinations times to obtain the desired product, comparing to conventional solid-state method [8, 9].

Nano particles of spinel possess unique dielectric properties and are effectively used for high frequency device applications. High performance devices require low dielectric loss (tan δ) because the lower it is the higher the efficiency and lower the noise [10]. We must mention that no systematic efforts have been made to probe the dielectric and ferroelectric behaviour of Co-Zn, Co-Mg and Co-Cu chromites. In the present paper, we thus aimed at understanding the structural transformation, lattice and dielectric properties of A-site doped JT ion as [Cu²⁺] and non-JT ion [Zn²⁺and Mg²⁺] at CoCr₂O₄ nanosized samples via low temperature sol-gel auto combustion method. The sol-gel method is easy, cheep, less time taking process, produce products with small crystallites/high surface area and eliminate intermediate impurity phases.

2. Experimental details

2.1 Chemicals

Starting materials used in the present study were cobalt nitrate $(Co(NO_3)_2 6H_2O)$, zinc nitrate $(Zn(NO_3)_2 6H_2O)$, magnesium nitrate $(Mg(NO_3)_2 6H_2O)$, copper nitrate $(Cu(NO_3)_2 3H_2O)$, chromium nitrate $(Cr(NO_3)_2 9H_2O)$, citric acid, ammonia solution (NH_3) and polyvinyl alcohol (PVA). All the chemicals were of analytical reagent grade and used without further purification. Distilled water with lower conductivity was used in all experiments.

2.2 Synthesis

The polycrystalline $\text{Co}_{1-x}\text{M}_x\text{Cr}_2\text{O}_4$ (M = Zn, Mg, Cu; x =0.0, 0.5) chromite samples were prepared by sol-gel auto combustion method [11]. All metal nitrates in their stoichiometry were dissolved in distilled water. The molar ratio of metal nitrate to citric acid was adjusted at 1:2. The mixed solution was added ammonia solution drop wise and pH of the solution was

neutralized at 10 with pH meter. The neutralized solution was evaporated to dryness by heating at 120°C on a hot plate with continuous stirring, until it becomes viscous and finally formed a very viscous gel. The dried gel burnt completely in a self-propagating combustion manner to form a loose powder. Finally the burnt powder was calcined at temperature of 800°C for 8 h. to obtain spinel phase.

For pelletization, calcined powder was used by compacting in uniaxial hydraulic press under a load of 8 Tons. Organic polymer (polyvinyl alcohol, PVA) was added as binder material in this calcined powder. The nanosized powder was pressed into circular disk shaped pellets of size 10 mm in diameter and 1 mm in thickness. The pellets were further sintered at 800°C for 8 h.

2.3 Characterizations

The crystal structure and phase evolution of the samples were examined at room temperature. Lab x-ray powder diffraction (XRD) are recorded using Bruker D8 advance x-ray diffractometer with Cu k α_1 radiation ($\lambda = 1.5406$ Å). The XRD data were collected in the 2 θ range from 10° < 2 θ < 80° by step-scanning 0.02° increments and a scanning rate of 2°/min. generating x-ray by 40 kV and 40 mA power settings. The Synchrotron x-ray powder diffraction (SXRD) has been performed on the angle dispersive x-ray diffraction (ADXRD) beam line (BL-12) at Indus-2 synchrotron source using x-ray of wavelength (0.8042 Å).

The Raman microscopy (LABRAM-HR) with 488 nm LASER has been used to record Raman spectra of the samples. Microstructural features and surface morphology of the samples have been examined by scanning electron microscope [SEM: JEOL-JSM-5600]. Dielectric measurements of the present samples were evaluated with Wayne Kerr impedance analyzer model- 6500B works over the wide range of frequency (20 Hz-120 MHz), ac voltage range (10 mV-1V) and temperature range varies upto 1000°C. The high purity silver conducting pastecoated pellets of sample were used for better electrical contact for dielectric measurement. Ferroelectric properties of synthesized samples were tested using Radiant Tech. USA.

3. Results and discussion

3.1. Structural analysis

The typical lab x-ray diffraction (XRD) and Synchrotron x-ray diffraction (SXRD) pattern of the sintered $Co_{1-x}M_xCr_2O_4$ chromite samples with compositions x = 0.0, 0.5 and M = Mg (alkaline earth metal ion), Zn and Cu (transition metal ions) are shown in Fig. 1 and 2, respectively. The XRD pattern of $CoCr_2O_4$, $Co_{0.5}Mg_{0.5}Cr_2O_4$ and $Co_{0.5}Zn_{0.5}Cr_2O_4$ chromites exhibit a single phase DDV PC CoCrETE JALCOM 15 July 2017 4

without any detectable secondary phase. The observed peaks are indexed as (111), (220), (311), (222) (400), (422), (511), (440) and (533) which are the characteristics planes of single-phase cubic spinel structure (space group Fd3m). The observed XRD pattern of CoCr₂O₄ was compared and is matched with the JCPDS file No. 22-1084 [12]. Substitution by JT ion as Cu²⁺ in CoCr₂O₄ as Co_{0.5}Cu_{0.5}Cr₂O₄ crystallizes in tetragonal structure (space group $I4_1/amd$). Henceforth, only transition metal as Cu²⁺ witnesses a structural transition and non-JT ion $[Zn^{2+}and Mg^{2+}]$ does not alter the cubic spinel structure of chromites.

The lattice constant as calculated from XRD of Co_{0.5}Mg_{0.5}Cr₂O₄ is slightly less as compared to CoCr₂O₄ because smaller ionic radii of Mg²⁺ (0.71 Å) and lattice constant of $Co_{0.5}Zn_{0.5}Cr_{2}O_{4}$ is greater because ionic radii of Zn^{2+} (0.74 Å) as compare to Co^{2+} (0.72 Å) [13]. The unit cell parameters as calculated from SXRD to be a = 6.7410 Å and c = 8.3868 Å for Co_{0.5}Cu_{0.5}Cr₂O₄ was compared tetragonal CuFe₂O₄ ferrite which are compatible with the reported value (JCPDS file No. 34-0425, a = 5.844 Å, c = 8.630 Å, space group $I4_1/amd$) [14 -17]. Tetragonal (c/a > 1) distortions are observed found at octahedral sites, JT ions [Cu²⁺] unless the long – range elastic coupling between tetrahedral and octahedral sites clearly favors another. Volume of the unit cell decreases from cubic (~ 581 Å³) to tetragonal (~ 383 Å³).

Fig. 3 showed the most intense peak (311) slightly shifted with A-site doping ions Mg^{2+} , Zn^{2+} and Cu^{2+} in CoCr₂O₄. Specifically, doubly splitted peaks as observed around $2\theta = 18.5^{\circ}$ in Co-Cu chromite and single broadened peak in Co-Mg and Co-Zn chromite. The tetragonal distortion of $Co_{0.5}Cu_{0.5}Cr_2O_4$ chromite with Cu^{2+} ions and Jahn-Teller effect distorts the CuO_6 octahedra so that the two Cu-O bonds along z are longer then the four Cu-O bonds in the xyplane. $\text{Co}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{O}_4$ with $\text{Cu}^{2+}(3d^9)$ electronic configuration (octahedral site) as $(t_{2g})^6 (e_g)^3$ [17]. Herein, the six electrons with the antiparallel spin occupy the triply degenerate state while the three electrons in e_g orbital are distributed. A strong Jahn-Teller distortion is expected due to its $(e_g)^2$ ground state with c/a > 1 (~ 1.244).

The structural parameters like crystallite size (D_{311}) , microstrain etc. was determined using FullPROF based Rietveld refinement method. We further use Scherer's formula to determine crystallite size or crystallographic domains from high energy Synchrotron source (17 -27 ± 0.0001 nm) data. It reduces as compare to low energy Lab source ($20 - 46 \pm 0.001$ nm). SXRD allows us to select appropriate 2θ angle and perfect analysis of full width half maximum (FWHM) value. The analysis of FWHM value at highest instance peak (311), x-ray density (ρ_x) for each chromites was calculated using relation: $\rho_x = 8M/Na^3$ where, 8 signify the number of molecules per unit cell of spinel structure, M is the molecular weight of chromites, 'a' is the 5

lattice constant of the chromite samples and *N* is the Avogadro's number. Microstrain (ε) and dislocation density (δ) of all the prepared chromite samples was estimated using the equation $\varepsilon = w/4 \tan \theta$ and $\delta = 1/D^2$ (lines/m²), respectively where w is full width half maximum (FWHM) value. Microstructural parameter represented in Table 1 and 2.

The detailed analysis of measured laboratory XRD and SXRD patterns of the samples was simulated based on the Rietveld refinement (using the FullPROF software). The simulations were performed according to The Marquardt least squares methods were used in the Rietveld method to minimize the difference between the observed and calculated powder diffraction patterns. The pseudo-voigt analytical function was used to fit the experimental peak profiles. Fig. 4 and 5 represents the experimentally observed, calculated patterns, reflection Bragg positions along with the difference pattern obtained using Rietveld refinement for CoCr₂O₄, Co_{0.5}Zn_{0.5}Cr₂O₄ and Co_{0.5}Mg_{0.5}Cr₂O₄. The refined crystal parameters obtained from Lab XRD such as lattice parameters, lattice volume, atomic positions, *R*- values and goodness of fit χ^2 mentioned in Table 3. The value of χ^2 comes out to be ~ 1, which may be considered to be very good for estimations.

Chemical composition of prepared chromites depends on site occupancy. Wyckoff position, site occupancy and inversion parameter (*i*) [fraction of the B cations at the T sites] as determined for chromites obtained from Lab XRD and SXRD are documented in Table 4. Usually, occupancy of Cr and O ions in chromites depends on oxygen positional parameter. Occupancy larger than unity for Cr and O ions is consistent with earlier reported data on $CuCr_2O_4$ nanoparticles [9]. Oxygen ions are attached with the octahedral sites. The tetrahedral sites are little to incorporate the metal ions, so the oxygen ions alteration to adjust them. Due to this evolution the octahedral sites diminish by same amount as tetrahedral sites expand. This displacement is interpreted as oxygen positional parameter.

Fig. 6 displays the crystal structure of pristine $CoCr_2O_4$ chromite. Non – JT (Zn²⁺) ions and JT (Cu²⁺) substituted in A-site of $CoCr_2O_4$ such as $Co_{0.5}Zn_{0.5}Cr_2O_4$ and $Co_{0.5}Cu_{0.5}Cr_2O_4$ chromites the refined crystal structure transform cubic to tetragonal.

The morphology of the particles of chromite samples visualized from scanning electron microscopy. The images of the SEM after sintered at 800°C for 8 h are shown in Fig. 7 (a-d). From the micrograph it observed that sintered nanosized chromite particles are non spherical in shape and with little agglomeration and porosity. The average particle size distribution was found to be $CoCr_2O_4$ (0.168 µm) from SEM with imaging software (Image-J). Enhanced average

ACCEPTED MANUSCRIPT particle size with doping non-JT (Zn^{2+} , Mg^{2+}) and JT (Cu^{2+}) ions is observed about 0.207 μ m, $0.253 \ \mu m$ and $0.283 \ \mu m$ for $Co_{0.5}Zn_{0.5}Cr_2O_4$, $Co_{0.5}Mg_{0.5}Cr_2O_4$ and $Co_{0.5}Cu_{0.5}Cr_2O_4$, respectively.

3.2 Vibrational analysis

Room temperature Raman spectra of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu; x = 0.0, 0.5) nanosized chromite samples in the frequency range of 100-800 cm⁻¹ are shown in Fig. 8. Lorentzian line shape was used to fit the Raman spectra and thick smooth lines in red and green color are fits to the Lorentzian function. The resolved Raman modes when assigned to Zn and Mg ions doping in $CoCr_2O_4$ showed a normal spinel cubic structure with (*Fd3m*) space group, which gives rise to 42 normal modes at the Brillouin zone center: three F_{1u} acoustic modes and 39 optical modes, belonging to the distribution $\Gamma = A_{1g} + E_g + F_{1g} + 3F_{2g} + 2A_{2u} + 2E_u + 4F_{1u} + 2F_{2u}$ where, five fundamental modes are Raman active $(A_{1g} + E_g + 3F_{2g})$ and four are IR active $(4F_{1u})$. The rest of modes are both Raman (F_{1g}) and IR $(2A_{2u} + 2E_u + 2F_{2u})$ inactive modes [18].

On the other hand Cu ion doping in $CoCr_2O_4$, structural features from cubic (*Fd3m*) to tetragonal (I4₁/amd) symmetry which can due to occur eventual Jahn-Teller effect. Vibrational representation for tetragonal phase belong to the distribution $\Gamma = 3B_{1g} + B_{2g} + 2B_{1u} + 4B_{2u} + 2A_{1g}$ $+A_{2g}+2A_{1u}+4A_{2u}+4E_{g}+6E_{u}+F_{1g}+2F_{2u}$. In these modes 10 are Raman active $(2A_{1g}+3B_{1g}+2E_{2u})$ $B_{2g} + 4E_g$) while the 10 are IR active $(4A_{2u} + 6E_u)$ and remaining modes are inactive in both spectra [19]. The Raman modes of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu; x = 0.0, 0.5) samples are illustrated in Table 5.

Observed Raman active modes $F_{2g}(1)$, E_g , $F_{2g}(2)$ and A_{1g} of Co_{0.5}Zn_{0.5}Cr₂O₄ are shifted toward the lower wave number, red shift is attributed because atomic weight of Zn (65.39 amu) is higher as compare to Co (58.933 amu). However, observed modes of $Co_0 {}_5Mg_0 {}_5Cr_2O_4$ are shifted higher wave number, blue shift is arises because atomic weight of Mg (24.305 amu) is lower compare to Co ion. The Raman active modes were also observed in nanosized $Co_{0.5}Cu_{0.5}Cr_2O_4$ chromites located at 139.91 cm⁻¹ ($F_{2g}(1)$), 483.89 cm⁻¹ (E_g), 551.69 cm⁻¹ $(F_{2g}(2))$, 636.51 cm⁻¹ $(F_{2g}(3))$ and 684.65 cm⁻¹ (A_{1g}) as earlier reported nanocomposites CuCr₂O₄/SiO₂ and CoCr₂O₄/SiO₂ [16]. Other possibilities of a shift in peak position might be due to different synthesis temperatures, the strain caused in the lattice, imperfections due to structure, loss in stoichiometry and reduced size to quantized lattice vibrations.

The strong band 684.65 cm⁻¹ (A_{1g}) of Co_{0.5}Cu_{0.5}Cr₂O₄ is shifted toward the lower wave number of CoCr₂O₄ at 687.67 cm⁻¹ (A_{1g}), red shift is attributed because atomic weight of Cu (63.546 amu) is higher as compare to Co ion. The Raman spectra show also a number of weak

bands in the 520-600 cm⁻¹ range which can be most likely recognized to a little impurity. The Raman bands are assigned to $F_{2g}(1)$ mode involves the tetrahedral cation (O – Co/M – O) vibration, where M is non-JT [Zn²⁺, Mg²⁺] and JT [Cu²⁺] ions. The other high frequency modes are assigned to $F_{2g}(3)$ and A_{1g} , which mainly belongs to stretching vibration (Cr – O) at octahedral site. Vibration bond at A- and B-site reveals the spinel nature of chromites as earlier reported Co_{1-x}Mg_xCr₂O₄ nanoparticles [20].

We note that the thermodynamical variable as temperature led to a significant enhancement of the disorder effect of two cations (A^{2+} and B^{3+}) over the tetrahedral (T) and octahedral (M) sites. In addition, one Raman mode is observed only for Co_{0.5}Zn_{0.5}Cr₂O₄ chromites at 666.45 cm⁻¹ and is attributed to the disorder of the two ions (Co²⁺/Zn²⁺ and Cr³⁺) over the tetrahedral (T) and octahedral (M) sites in the spinel structure consistent with earlier data [21]. Structural analysis also confirms the Co_{0.5}Zn_{0.5}Cr₂O₄ chromite is normal type spinel at room temperature and the degree of disorder (fraction of the B cations at the T sites) is ~ 0.007 (Lab XRD) and 0.011 (SXRD) interpret the inversion parameter (*i*) of chromite spinel structures [22]. Site disorder of Co_{0.5}Zn_{0.5}Cr₂O₄ chromite is higher obtained from SXRD refinement and this higher disorder value attributed one additional Raman modes at 666.45 cm⁻¹. Site disorder depends on oxygen positional parameter and this value calculated from crystallographic structure obtained by Lab XRD and SXRD Rietveld refinement as shown in Table 4.

3.3 Dielectric constant and loss tangent

The variations of frequency dependence dielectric permittivity (ε ') and dielectric loss (tan δ) at room temperature for Co_{1-x}M_xCr₂O₄ (M = Zn, Mg, Cu; x = 0.0, 0.5) chromite samples are showed in Fig. 9 and 10, respectively. It has been observed that all samples exhibit a decline in dielectric constant (ε ') and loss (tan δ) as the frequency increases from 20 Hz to 1 MHz. Quite generally, in different frequency regions four ways of polarization influences dielectric response. Important are dipolar, electronic, ionic and interfacial polarization depending upon frequency of applied external field. The observed dielectric response is usually interpreted in the space charge polarization and charge transferring mechanism. Dipolar and interfacial polarizations is mainly responsible of spinel chromite structure can be interpreted by electrical conduction process. The electrical conduction process in chromites is mainly due to electron transfer mechanism leading to spinel formation [20].

Polarization is also affected by factors such as calcination temperature, stoichiometry, phase homogeneity, grain size and porosity of the chromites. Applied electric field polarization

at lower frequency region (20 Hz – 1 kHz) is seen to be important in electron transfer between $Cr^{3+} \leftrightarrow Cr^{2+}$ ions for spinel chromites. The polarization suppresses with rising frequency and reaches a constant value. In other words, at resonance frequency $\omega = 1/\tau$, where ω is the field frequency and τ is relaxation time of external field, the electron transfer $Cr^{3+} \leftrightarrow Cr^{2+}$ cannot pursue changes in the applied field.

The room temperature dielectric constant and loss value at different frequencies calculated for chromites are documented in Table 6. Measured dielectric constant (loss factor) at 10 kHz of nanosized CoCr₂O₄ is 110 (5.28) is higher, when a comparison is made with CoCr₂O₄ ceramic samples as prepared with high temperature synthesis of 3.2 (0.05) [23]. Measured dielectric constant at 20 Hz for ZnCr₂O₄ (~ 8×10⁴) [24] and CuCr₂O₄ (~ 1×10³) [9]. In our results at long wavelengths, the dielectric constant of Co_{0.5}Zn_{0.5}Cr₂O₄ is enhanced as compare to other doped chromites. Observed dielectric constant of non-JT ion (Zn²⁺) as Co_{0.5}Zn_{0.5}Cr₂O₄ is enhanced ~ 25 × 10⁴ as compare to JT ion (Cu²⁺) as Co_{0.5}Cu_{0.5}Cr₂O₄ is ~ 5 × 10³. It implies that non-JT ion as Zn²⁺ leads to effective charge polarization as compare to JT ion as Cu²⁺ in doped chromites.

It might also be due to heterogeneity of dielectric structure may be stoichiometry and grain boundaries. On the other hand, at short wavelengths the variation of dielectric constant is similar for all Co_{1-x}M_xCr₂O₄ (M = Zn, Mg, Cu; x = 0.0, 0.5) chromites. Herein, the polarization is mainly electronic and ionic in origin and polarizability is frequency independent. All of the four chromite samples signify a declining trend in ε ' and tan δ with rising frequency and approximately frequency independent behavior in broad frequency region (~ 1 MHz). The above variation of dielectric constant can be implicit on the origin of hopping mechanism correlated to interfacial space charge polarization in harmony with Koop's theory [25].

From Fig. 10, we detect an abnormal peak in dielectric loss and is attributed to the resonance effect ($\omega = 1/\tau$). The dielectric constant (\mathcal{E} ') decline abruptly due to relaxation process. Whenever the frequency of applied electric field matches well with the hopping frequency of the charge transporters, the maximum electrical energy is transmitted to the oscillating ions, leading to an observation of peak as outcome of power loss. Dielectric loss is higher at lower frequency region as the capacity of storing charge is minimal The loss tangent (tan δ) is lowest for Co_{0.5}Zn_{0.5}Cr₂O₄ and Co_{0.5}Cr₂O₄ measured at a frequency of 10 kHz at 300 K as compared to other chromites as shown in Table 6. Henceforth, substitution by non-JT ion as Zn²⁺ and Mg²⁺ in CoCr₂O₄ as compare to JT ion doped as Cu²⁺ are promising materials for high frequency circuits and other device applications.

Fig. 11 depicts frequency dependent *ac* conductivity (σ_{ac}) behaviour of doped chromite samples. The σ_{ac} is calculated using dielectric data taken at room temperature over a frequency range 20 Hz - 1 MHz. The electrical conductivity in chromites is mainly responsible due to the hopping length (*L*) of the charge transporter. Hopping length (*L*) of the A- and B-sites is calculated from the relation: $L_A = a$ (0.4330) and $L_B = a$ (0.3535), where *a* is lattice constant. Values of hopping length are found to be $L_A = 3.6159$ Å, $L_B = 2.9520$ Å for Co_{0.5}Zn_{0.5}Cr₂O₄ chromites. The distance between two metal ions on the B-site (2.9520 Å) is smaller than the distance between two metal ions on the A-site (3.6159 Å). Therefore, the electron hopping between A \leftrightarrow B sites has a very less probability compared to the electrons hopping in between B \leftrightarrow B sites.

The charge drift under the influence of the applied electric field contributes to the electrical conductivity of the chromites and is earlier documented for ferrites [26]. At higher wavelengths, σ_{ac} is nearly constant but in the low wavelength region, a dispersive nature of conductivity is observed. It is attributed to the fact that with improved frequency of the applied field, the mobility of charge carriers enhances leading to active growth of conductive grains supporting the electron conduction mechanism. The *ac* conductivity of nanosized non-JT doped Zn^{2+} ion: $Co_{0.5}Zn_{0.5}Cr_2O_4$ (~ 4 × 10⁻³ S/m) measured at 10 kHz at 300 K is high when a comparison is made with other doped chromites, consistent with previously reported nanoparticles $ZnCr_2O_4$ (~ 10⁻⁴ S/m) [24] and chromium (II) oxide (Cr_2O_3) is 10⁻⁵ S/m [27]. At high frequency region (1 kHz – 1 MHz) the dominant contribution of *ac* conductivity in ionic conducting materials is due to frequency independent dielectric loss (nearly constant) [28].

The temperature dependent dielectric constant (ε ') and loss tangent (tan δ) of Co_{1-x} M_xCr₂O₄ (M = Zn, Mg, Cu; x = 0.0, 0.5) chromite samples at 10 kHz are showed in Fig. 12. It has been confirmed that both the dielectric constant and loss factor are rising with growing of temperature. This increment is supported by hopping of charge transporters under the thermally activated Cr³⁺ \leftrightarrow Cr²⁺ and Co²⁺ \leftrightarrow Co³⁺ dipoles responsible for the relaxation with increase of temperature. In addition the offerings of space charge polarization (interfacial polarization) are manifesting at higher temperatures. Co_{0.5}Zn_{0.5}Cr₂O₄ chromite is higher dielectric constant as compare to for all prepared chromite samples at 550 K. Such dielectric response, loss and *ac* conductivity behaviour is earlier observed in spinel ferrites [29-31].

3.4 Impedance analysis

The impedance measurement is a powerful method in identifying the interparticle interactions like grains and grain boundaries. The complex impedance formalism is usually defined as DDV PC CoCrETE JALCOM 15 July 2017 10

imaginary part of impedance (*Z*'') versus real part of impedance (*Z*'), which is usually referred as Nyquist plot. Fig. 13 discerns the Nyquist plot of Co_{1-x} M_xCr₂O₄ (M = Zn, Mg, Cu; x = 0.0, 0.5) chromites at room temperature. Typically, the plot would be collected of three semicircles, build upon the electrical properties of the material. Each semicircle indicating a diverse route whose time constant is adequately split from the others over the range of measurement frequencies. The semicircles at lower frequency characterize the sum of resistance of grains and grain boundaries, while that at higher frequency it is the grains only. Third semicircle is moreover presence in some materials, which might be due to the electrode effect [32].

In the present analysis, semicircle for each chromite samples is observed in the frequency range 20 Hz – 1 MHz. The size of the semicircle changes with grain size and the amount of grains also changes with different doping ions in $CoCr_2O_4$. Nanosized $Co_{0.5}Cu_{0.5}Cr_2O_4$ chromite sample showed a large and flat semicircle at higher frequency where the electrical conduction is mainly by the internal grains. We note that nanosized JT doped Cu^{2+} ion showed the largest semicircle. While in case of other prepared $Co_{0.5}Mg_{0.5}Cr_2O_4$, $CoCr_2O_4$ and $Co_{0.5}Zn_{0.5}Cr_2O_4$ (shown in the inset of Fig. 13), a small semicircle is observed at lower frequency and is attributed to the sum of resistance of grain and grain boundaries.

3.5 Electrical modulus analysis

The dielectric modulus spectrum is widely used to study the electrical relaxation in ionic and electronically conducting materials. Fig. 14 shows real part of the electrical modulus (*M*') as a function of frequency for prepared nanosized chromite samples measured at room temperature. The continuous lines are for the fitted curves, whereas the symbols signify the observed data. The observed values of stretched exponent parameter β for all the samples is less than unity and are initiate to be 0.87, 0.34, 0.45 and 0.92 for CoCr₂O₄, Co_{0.5}Zn_{0.5}Cr₂O₄, Co_{0.5}Mg_{0.5}Cr₂O₄ and Co_{0.5}Cu_{0.5}Cr₂O₄, respectively. For an ideal dielectric, the value of β is equivalent to 1, for which the dipole–dipole interaction (Debye type) is insignificant. However, for a system in which dipole–dipole interaction is considerable, the β value for all time less than 1 (non – Debye type) [33]. We thus comment that the CoCr₂O₄, Co_{0.5}Zn_{0.5}Cr₂O₄, Co_{0.5}Mg_{0.5}Cr₂O₄ and Co_{0.5}Cr₂O₄ showed non-Debye type of dielectric relaxations.

Usually, the space charge polarization and electron transfer contributes to relaxation process for Non – Debye type ($\beta < 1$) behavior. Such response needs to be interpreted in terms of electrical modulus (M'). We note that in the low frequency region (20 Hz – 1 kHz), the electrical modulus (M') is nearly zero inferring that the minor electrode polarization contribution for dielectric modulus with rising frequencies. The relaxation process is mainly due to dipolar DDV PC CoCrETE JALCOM 15 July 2017 11

relaxation as interfacial polarization is weak to be probed. M' behaviour documents a continuous increase in dispersive dielectric response and reaches to a maximum value in the high frequency range (1 kHz - 1 MHz) and is an outcome of relaxation mechanism. Such dielectric modulus response infers that the electron conduction process is due to the short range mobility of charge transporter. Nevertheless, such response originates due to the absence of restoring force under the influence of an induced electric field.

We note that the resonance frequency ($\omega = 1/\tau$) is significant for the transition from long range to short range mobility of charge carriers. We may refer to a pioneering work on dielectric relaxation [34], where high dielectric constant (~ 10^4) in the low frequency region (20 Hz – 1 kHz) is argued to depend on dipolar and interfacial polarizations. This is mainly due to dipoledipole interaction (Non – Debye type, $\beta < 1$). Such mechanism is due to space charge polarization and electrical conduction and is viable in spinel chromites.

3.6 Ferroelectric (P-E) loop

We have also made attempts to measure ferroelectric hysteresis loop at room temperature for $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu; x = 0.0, 0.5) chromite samples as shown in Fig. 15. It has been observed from the graph that CoCr₂O₄ sample represent ferroelectric (FE) behaviour whereas doped Chromites looses ferroelectric loop behaviour. The pristine CoCr₂O₄ represents ferroelectric loop without any saturation value. This is attributed to the fact that CoCr₂O₄ is highly conductive at room temperature which results in the partial reversal of the polarization. Co^{2+} has a more-than-half-filled d shell, while Cr^{3+} has a less-than-half-filled shell, suggesting that Co-Cr and Cr-Cr bonds have the opposite sign of spin-orbit interaction, resulting in the opposite directions of electric dipole moments, P_{Co-Cr} and P_{Cr-Cr} from the different bonds [35]. The obtained values of remnant polarization and coercive field for $C_0Cr_2O_4$ are about ~ 0.05 μ C/cm² and 6.12 kV/cm. We end up by commenting that doping of JT ion as [Cu²⁺] and non-JT ion $[Zn^{2+}and Mg^{2+}]$ in ferromagnetic spinel CoCr₂O₄ losses the electric polarization.

4 Conclusions

The nanosized doped chromites $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu and x = 0.0, 0.5) is synthesized by low temperature sol-gel auto combustion. Substitutional effect of JT ion as [Cu²⁺] and non–JT ion $[Zn^{2+}and Mg^{2+}]$ on structural, lattice and dielectric properties of CoCr₂O₄ has been studied. Synchrotron and lab x-ray powder diffraction confirms the formation of single-phase crystalline nature. Structural transition from cubic (space group Fd3m) [CoCr₂O₄, Co_{0.5}Mg_{0.5}Cr₂O₄ and $Co_{0.5}Zn_{0.5}Cr_2O_4$ to tetragonal (space group $I4_1/amd$) [$Co_{0.5}Cu_{0.5}Cr_2O_4$] structure is observed. Cubic to tetragonal structure transition is attributed to substitution by JT ion (Cu^{2+}) causing a DDV PC CoCrETE JALCOM 15 July 2017 12

cooperative Jahn-Teller distortion. Volume of the unit cell decreases from cubic to tetragonal. Non-JT doped ion as Zn^{2+} and Mg^{2+} retains the highly symmetric cubic spinel structure of chromites. Crystallite size of nanosized chromites as calculated from Synchrotron x-ray (high energy) source is about 17 – 27 nm. SEM micrograph of sintered samples results in less porosity with greater densification and an average particle size distribution of ~ 0.2 – 0.3 µm.

An additional Raman active mode is observed at 666.45 cm⁻¹ for $Co_{0.5}Zn_{0.5}Cr_2O_4$ chromite inferring an disorder (i = 0.011) of the two ions (Co^{2+}/Zn^{2+} and Cr^{3+}) over the tetrahedral and octahedral sites. The dielectric constant of $Co_{0.5}Zn_{0.5}Cr_2O_4$ at lower frequencies is enhanced as compare to other doped chromite samples. It implies that Non-JT ion as Zn^{2+} leads to effective charge polarization as compare to JT ion as Cu^{2+} in doped chromites. The impedance analysis showed that both grains and grain boundaries are active in $Co_{0.5}Zn_{0.5}Cr_2O_4$ at lower frequencies. On the other hand, JT ion Cu^{2+} doped chromites witness's only active grains at higher frequencies. The electrical modulus analysis reveals that the $CoCr_2O_4$, $Co_{0.5}Zn_{0.5}Cr_2O_4$, $Co_{0.5}Mg_{0.5}Cr_2O_4$ and $Co_{0.5}Cu_{0.5}Cr_2O_4$ showed non-Debye type of dielectric relaxations. The doping in ferromagnetic spinel chromites does not favour ferroelectricity, a requirement for chromites as multiferroic material. We end up by commenting that the multiferroic, $CoCr_2O_4$ doped by non-JT ion [Zn^{2+} and Mg^{2+}] are promising materials for high frequency microelectronic applications as compare to doped as [Cu^{2+}] JT ion.

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Table 1 : Crystallite size (for most intense peak 311: D_{311}), lattice constant, inter planar spacing (d)), x-
ray density (ρ_x), micro strain (ε) and dislocation density (δ) calculated from Lab XRD source.	

Sample	2θ (°)	FWHM	$D_{311}\pm$	lattice c	constant	d	ρ_x	3	$\delta \times$
		(°)	0.001	a (Å)	c (Å)	(Å)	(g/cm^3)		10^{14}
			(nm)	~ /					(m^{-2})
CoCr ₂ O ₄	35.757	0.204	42.61	8.321	-	2.509	5.230	0.158	5.507
$Co_{0.5}Zn_{0.5}Cr_2O_4$	35.755	0.418	20.84	8.322	-	2.509	5.303	0.324	23.02
$Co_{0.5}Mg_{0.5}Cr_2O_4$	35.754	0.245	35.49	8.318	-	2.508	4.829	0.190	7.939
$Co_{0.5}Cu_{0.5}Cr_2O_4$	35.555	0.186	46.73	6.858	8.145	2.522	2.760	0.145	4.579

Table 2: Crystallite size (for most intense peak 311: D_{311}), lattice constant, inter planar spacing (*d*), x-ray density (ρ_x), micro strain (ε) and dislocation density (δ) calculated from SXRD source.

<u> </u>		~ /							
Sample	2θ (°)	FWHM	$D_{311} \pm$	Lat	tice	d	ρ_x	З	$\delta \times$
		(°)	0.0001	cons	stant	(Å)	(g/cm^3)		10^{14}
			(nm)	<i>a</i> (Å)	<i>c</i> (Å)				(m^{-2})
$CoCr_2O_4$	18.420	0.159	27.43	8.332		2.512	5.210	0.246	13.28
$Co_{0.5}Zn_{0.5}Cr_2O_4$	18.424	0.245	17.90	8.334	-	2.513	5.287	0.377	31.17
$Co_{0.5}Mg_{0.5}Cr_2O_4$	18.398	0.175	25.01	8.324	-	2.510	4.790	0.270	15.98
$Co_{0.5}Cu_{0.5}Cr_2O_4$	18.343	0.157	27.85	6.741	8.386	2.522	3.994	0.243	12.89

Table 3: Rietveld refined Lab XRD parameters of as synthesized chromites samples.

	1		1
Parameters	$CoCr_2O_4$	$Co_{0.5}Mg_{0.5}Cr_2O_4$	$Co_{0.5}Zn_{0.5}Cr_2O_4$
2θ range (deg.)	10° - 80°	10° - 80°	10° - 80°
Step size (deg.)	0.02°	0.02°	0.02°
Wavelength	1.5406 Å	1.5406 Å	1.5406 Å
Space group	Fd3m	Fd3m	Fd3m
Co (<i>x</i> , <i>y</i> , <i>z</i>)	(0.0, 0.0, 0.0)	(0.0, 0.0, 0.0)	(0.0, 0.0, 0.0)
Mg (<i>x</i> , <i>y</i> , <i>z</i>)	-	(0.0, 0.0, 0.0)	-
$\operatorname{Zn}(x, y, z)$	-	-	(0.0, 0.0, 0.0)
$\operatorname{Cr}(x, y, z)$	(0.6250,	(0.6250,	(0.6250,
	0.6250,	0.6250,	0.6250,
	0.6250)	0.6250)	0.6250)
O(x, y, z)	(0.3877,	(0.3823,	(0.3895,
-	0.3877,	0.3823,	0.3895,
	0.3877)	0.3823)	0.3895)
<i>a</i> (Å)	8.3488 (4)	8.3481 (4)	8.3509
<i>b</i> (Å)	8.3488 (4)	8.3481 (4)	8.3509
<i>c</i> (Å)	8.3488 (4)	8.3481 (4)	8.3509
Bond length (Å)	/		
Co – O	1.9593 (4)	1.9577 (4)	1.9613 (4)
Cr – O	1.9881 (4)	1.9887 (4)	1.9878 (4)
Zn/Mg – O	-	1.9577 (4)	1.9613 (4)
Volume (Å ³)	581.932	581.785	582.371
$R_{\rm Bragg}$	5.58	5.48	3.77
$R_{ m F}^{}$	5.70	5.15	4.48
χ^2	1.16	1.17	1.10

Samples	Ions	Wyckoff	Lab XRD		SXRD	
		site	Occupancy	i	Occupancy	i
CoCr ₂ O ₄	Co ²⁺	8 <i>a</i>	1.01	<mark>0.011</mark>	<mark>1.02</mark>	<mark>0.011</mark>
	Cr^{3+}	16 <i>d</i>	1.99		<mark>1.99</mark>	
	O^{2-}	32 <i>e</i>	4.01		<mark>4.52</mark>	
$Co_{0.5}Mg_{0.5}Cr_2O_4$	Co^{2+}	8a	0.52	<mark>0.015</mark>	<mark>0.46</mark>	<mark>0.006</mark>
	Mg^{2+}	8a	0.86		<mark>0.35</mark>	
	Cr^{3+}	16 <i>d</i>	1.88		<mark>2.13</mark>	7
	O^{2-}_{2-}	32 <i>e</i>	3.74		<mark>4.33</mark>	
$Co_{0.5}Zn_{0.5}Cr_2O_4$	Co^{2+}	8a	0.55	<mark>0.007</mark>	<mark>0.49</mark>	<mark>0.011</mark>
	Zn^{2+}	8a	0.48		<mark>0.49</mark>	
	Cr^{3+}	16 <i>d</i>	2.10		<mark>2.00</mark>	
	O ²⁻	32 <i>e</i>	4.64		<mark>4.03</mark>	

Table 4: Wyckoff site, occupancy and inversion parameter (*i*) of $Co_{1-x}M_xCr_2O_4$ (M= Zn, Mg; x = 0, 0.5) chromites.

Table 5: Observed Raman active phonon modes for $Co_{1-x}M_xCr_2O_4$ (M= Zn, Mg, Cu; x = 0, 0.5).

Obser		Ram	an shift (cm			Symmetry	
ved		CoCr ₂ O ₄		Co-Zn	Co-Mg	Co-Cu	
mode	Present	Reported	Reported	chromite	chromite	chromite	
	work	[4]	[6]				
$F_{2g}(1)$	195.68	195	196	192.15	195.97	139.91	$\delta (O - Co/M - O)$
E_g	470.91	451	450	469.74	472.15	483.89	$v_s (Cr - O)$,
							$v_s (Co/M - O)$
$F_{2g}(2)$	515.96	516	515	514.50	529.68	551.69	v (Cr – O)
	538.78	541		544.06	545.24		
	560.79	560		567.54	564.90		
	589.91	586		592.20	596.18		
$F_{2g}(3)$	626.51	639	603	639.16	641.80	633.87	$v_s (Cr - O)$
	-	-	-	666.45	-	-	
A_{1g}	687.67	688	685	686.20	688.84	684.65	$v_s (Cr - O)$

Table 6: Dielectric parameters of $Co_{1-x}M_xCr_2O_4$ (M= Zn, Mg, Cu; x= 0, 0.5) at selected frequencies

Sample	At frequency 20 Hz		At freque	ncy 10 kHz
	ε'	tan δ	ε'	$\tan \delta$
CoCr ₂ O ₄	20465	17.4	110	5.28
$Co_{0.5}Zn_{0.5}Cr_2O_4$	252175	1.99	1585	3.59
$Co_{0.5}Mg_{0.5}Cr_2O_4$	94338	8.02	140	10.1
$Co_{0.5}Cu_{0.5}Cr_2O_4$	5193	11.5	43	3.37

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Fig. 1	Laboratory x-ray diffraction pattern of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu and x = 0.0,
	0.5) chromites.
Fig. 2	Synchrotron x-ray diffraction pattern of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu and $x = 0.0$,
	0.5) chromites.
Fig. 3	Shifting of 311 peaks as function of doping concentration in $Co_{1-x}M_xCr_2O_4$.
Fig. 4	The Rietveld refined Lab XRD pattern of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg and x = 0.0,
	0.5) chromites.
Fig. 5	The Rietveld refined SXRD pattern of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg and x = 0.0, 0.5)
	chromites.
Fig. 6	Crystal structure of $CoCr_2O_4$, $Co_{0.5}Zn_{0.5}Cr_2O_4$ and $Co_{0.5}Cu_{0.5}Cr_2O_4$ chromites.
Fig. 7	SEM micrographs of (a) $CoCr_2O_4$, (b) $Co_{0.5}Zn_{0.5}Cr_2O_4$, (c) $Co_{0.5}Mg_{0.5}Cr_2O_4$ and (d)
	$Co_{0.5}Cu_{0.5}Cr_2O_4$ chromites.
Fig. 8	Room temperature Raman shifts of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu and x = 0.0, 0.5)
	chromites.
Fig. 9	Dielectric permittivity (ε ') of Co _{1-x} M _x Cr ₂ O ₄ (M = Zn, Mg, Cu and x = 0.0, 0.5)
	chromite samples as a function of frequency at room temperature.
Fig. 10	Loss tangent (tan δ) of Co _{1-x} M _x Cr ₂ O ₄ (M = Zn, Mg, Cu and x = 0.0, 0.5) chromites as
	a function of frequency.
Fig. 11	Variation of ac conductivity (σ_{ac}) for Co _{1-x} M _x Cr ₂ O ₄ (M = Zn, Mg, Cu and x = 0.0,
	0.5) chromites with function of frequency.
Fig. 12	Temperature dependence dielectric constant (ε ') of Co _{1-x} M _x Cr ₂ O ₄ (M = Zn, Mg, Cu
	and $x = 0.0, 0.5$) chromite samples measured at 10 kHz. Inset shows the variation of
	loss tangent (tan δ) with temperature.
Fig. 13	Nyquist-plot of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu and x = 0.0, 0.5) chromites.
Fig. 14	Real part of electric modulus (M') of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu and x = 0.0,
	0.5) chromites as a function of frequency.
Fig. 15	Ferroelectric loop of $Co_{1-x}M_xCr_2O_4$ (M = Zn, Mg, Cu and $x = 0.0, 0.5$) chromites at room temperature.

Fig. 1



























Fig. 7

















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Fig. 15



Research highlights

- ✓ Synchrotron and lab XRD confirms single phase crystalline nature of $Co_{1-x} M_x Cr_2 O_4$ (M = Zn, Mg, Cu; x = 0.0, 0.5).
- ✓ Structural phase transition occur when moving from $CoCr_2O_4$ (cubic, *Fd3m*) to $Co_{0.5}Cu_{0.5}Cr_2O_4$ (tetragonal, *I4*₁/*amd*).
- ✓ Enhancement of the dielectric constant has been observed for Zn²⁺ ion substitution at Co - site in CoCr₂O₄.
- ✓ Complex impedance analysis shows a large semicircle of Co_{0.5}Cu_{0.5}Cr₂O₄ at higher frequency.
- ✓ Electrical modulus studied reveals the presence of non-Debye type of dielectric relaxation in the chromite materials.