Dielectric and ferroelectric properties of CoCr_2O_4 nanoceramics

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CoCr_2O_4 nanoceramics are prepared by sol–gel auto combustion method. Synchrotron X-ray diffraction analysis affirms the single-phase pristine cubic structure with space group $Fd\bar{3}m$. Debye–Scherrer method estimates the crystallite size of main intense peak to be ~ 27.15 nm. Prominent bands obtained in infrared spectra at 448 and 599 cm^{-1} are due to metal–oxygen stretching bond present at tetrahedral and octahedral sites. Dielectric parameters decrease as frequency increases from 10^3 to 10^6 Hz that can be interpreted by Maxwell–Wagner-type interfacial polarization. Complex impedance spectra (Nyquist plot) reveal arc like behavior, which is mainly due to intergrain (grain boundary) resistance that also exhibits conducting nature of the nanoceramics. Weak ferroelectricity is mainly associated with the partial reversal of the polarization. Leakage current behavior follows the Ohmic and Child square law. Electron conduction process was interpreted by space-charge limited current (SCLC) mechanism. Leakage current behavior observed in cobalt chromite nanoceramics is mainly attributed to the oxygen vacancies.

Keywords: CoCr_2O_4 nanoceramics; synchrotron X-ray diffraction; dielectric spectroscopy; electric polarization; leakage current behavior.

1. Introduction

Pristine CoCr_2O_4 nanoceramics are a type-II multiferroic [two or more ferroic properties exist at the same time] material manifesting magnetoelectric coupling that has recently attracted great interest and much attention. These nanoceramics are more efficient to store charges in electronic memory devices. Despite their large number of advantages, multiferroic materials are rare in nature because the conditions for being simultaneously ferroelectric [FE] and ferromagnetic [FM] are challenging. Therefore, investigation of new multiferroic materials is of huge scientific interest due to its various applications such as electric switches, high frequency resistor, and magnetic field sensors, electronic and nonvolatile memories (NVMs). CoCr_2O_4 nanoceramics are spinel metal oxides. Spinel is one constituent of this family of multiferroic materials with general formula AB_2O_4 that has developed research interest due to its large applications as energy storage materials. Chromium ions require unfilled d orbitals: d^3 [Cr^{3+} , $S = 3/2$]. Normally, chromites [ACr_2O_4 ; $A = \text{Mn, Co, Fe, Zn}$ etc.] reveal many unusual magnetic properties such as ferroelectricity (shifting of charge ordering) and ferrimagnetism (unequal reversed magnetic moments).^{1–4}

Cobalt chromite nanoceramics belong to a class of complex spinel metal oxides, which is a type-II multiferroic

material. In CoCr_2O_4 , Co^{2+} ions exist at A (tetrahedral) sites and Cr^{3+} ions are at B (octahedral) sites. It has been reported that CoCr_2O_4 has shown successive magnetic orders at different temperatures such as ferrimagnetic phase occurs below $T_C \approx 92\text{--}94\text{ K}$, incommensurate conical spiral order below $T_S \approx 26\text{ K}$ and commensurate order below $T_L \approx 26\text{ K}$.^{5–7} Generally, for these type-II multiferroics, the electrical polarization is much smaller ($\sim 10^{-2}\text{ }\mu\text{C}/\text{cm}^2$) than in type-I multiferroics ($\sim 10\text{--}100\text{ }\mu\text{C}/\text{cm}^2$). Particularly in BiFeO_3 ($T_C \sim 1100\text{ K}$, $T_N \sim 643\text{ K}$, $P \sim 90\text{ }\mu\text{C}/\text{cm}^2$) and YMnO_3 ($T_C \sim 914\text{ K}$, $T_N \sim 76\text{ K}$, $P \sim 6\text{ }\mu\text{C}/\text{cm}^2$) the FE Curie temperature (T_C) is much higher than the magnetic ordering temperature (T_N).²

Recently, certain research groups have investigated in detail about the multiferroicity, Raman scattering, magnetodielectric behavior and the electrocatalyst behavior of CoCr_2O_4 system. But the room temperature dielectric properties, electric polarization and leakage current response are not discussed. The main purpose of the present work is to synthesize CoCr_2O_4 nanoceramics and characterize it to better understand the dielectric properties, electric polarization and leakage current behavior observed at room temperature. The space-charge limited current (SCLC) conduction and oxygen vacancies in the form of defects have also been discussed to explain the leakage current.^{8–12}

2. Experimental Details

Spinel CoCr_2O_4 nanoceramics were prepared by sol–gel auto combustion method.^{13,14} The stoichiometry amounts of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were taken as starting materials. All the metal nitrates were dissolved in double distilled water and the molar ratio of metal nitrate to citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was set as 1:2. Ammonia (NH_3) solution was dropwise added to the above solution under hot plate magnetic stirrer. The homogeneous solution was neutralized to $\text{pH} \sim 10$ with the help of digital pH meter. The resulting solution was then heated to $\sim 80^\circ\text{C}$ for 3 h to obtain viscous gel. Increasing the heating temperature up to $110\text{--}120^\circ\text{C}$ leads to the ignition of gel. The dried gel burnt completely and finally it produced a nanocrystalline powder, which was calcined at 800°C for 8 h to obtain the cubic spinel phase. For pelletization, organic polymer (polyvinyl alcohol, PVA) was added in calcined powder and pressed into a circular disk with size 1 mm thickness and 10 mm diameter by applying a pressure of ~ 8 Tons. Sintering of the pellets was done at 800°C for 8 h.

The prepared nanoceramics powders were characterized at room temperature. The Synchrotron X-ray powder diffraction (SXRD) was performed on the angle dispersive X-ray diffraction beamline (BL-12) at Indus 2 synchrotron source, RRCAT, Indore India. The beam line consists of a Si (111)-based double crystal monochromator and two experimental stations, namely, a six circle diffractometer (Huber 5020) with a scintillation point detector and an image plate (Mar 345dtb) area detector. The latter has been used for present SXRD measurements and the image plate data has been processed using Fit2D program. Room temperature Fourier transform infrared (FTIR) spectra were recorded in the ATR mode using a Frontier Perkin–Elmer (SP 10 STD) spectrometer in the frequency range $400\text{--}4000\text{ cm}^{-1}$. Energy dispersive spectrometer (INCA Oxford) confirmed the chemical compositions. Dielectric measurements were carried out using a Wayne–Kerr impedance analyzer (Model-6500B) in the frequency range from $20\text{ Hz--}120\text{ MHz}$ where ac voltage setting was kept in the range of $10\text{ mV--}1\text{ V}$ with a wide temperature range up to 1000°C . High purity silver conducting paste was used to coat on the pellets for better electrical contact for the dielectric measurements. Fe and leakage current properties were tested using Radiant Tech. USA.

3. Results and Discussion

3.1. Structural analysis

Synchrotron X-ray diffraction pattern of CoCr_2O_4 nanoceramics are illustrated in Fig. 1(a). Cobalt chromite shows good crystalline nature with highly ordered hkl planes. Structural analysis confirms the prepared nanoceramics as a single-phase cubic spinel structure with space group $Fd\bar{3}m$. The hkl planes (2 2 0), (3 1 1), (2 2 2), (4 0 0), (2 4 2), (5 1 1),

(4 4 0), (6 0 2), (5 3 3) and (4 4 4) are found associated to the cubic structure. Observed typical SXRD patterns of CoCr_2O_4 nanoceramics were equated with the International Committee on Powder Diffraction data that match well with the file (JCPDS Card No. 780711).¹⁵ Crystallite size (D) of main intense peak is calculated using Debye–Scherrer formula:

$$D = k\lambda/\beta \cos \theta, \quad (1)$$

where k is a structural shape factor and its value for a spherical particle ~ 0.9 . Crystallite size estimated from Debye–Scherrer is $\sim 27.15\text{ nm}$. The strain is calculated using the relation $\beta/4 \tan \theta$ ($\sim 4.2 \times 10^{-3}$). This strain is mainly due to the presence of lattice defects in the form of oxygen vacancies. Lattice strain is also dependent on the porosity and the pore structure of the prepared nanoceramics. Porosity and oxygen vacancy depend on the synthesis technique.^{16,17} Normally, nanoparticles occupy higher surface-to-volume ratio. This ratio depends on the different techniques of synthesis for nanoparticles. These properties are directly related to the average crystallite size and the induced lattice strain in the present CoCr_2O_4 nanoceramics. Co^{2+} ions occur at tetrahedral site and Cr^{3+} ions prefer octahedral site. Hopping probability at tetrahedral site is higher as compared to the octahedral site.

The formation of spinel structure of CoCr_2O_4 nanoceramics is also confirmed by infrared spectra. Fig. 1(b) shows the IR spectra of prepared nanoceramics as a function of wavenumber. The infrared absorption bands in the frequency ranges $400\text{--}700\text{ cm}^{-1}$ are the prominent bands due to the spinel structure. The properties of CoCr_2O_4 nanoceramics mostly depend on the cation distribution of tetrahedral and octahedral sites. Two sharp vibrational frequency bands ν_1 (599 cm^{-1}) and ν_2 (448 cm^{-1}) confirm the formation of CoCr_2O_4 nanoceramics, which arises due to stretching vibration of $\text{Cr}^{3+} - \text{O}^{2-}$ at tetrahedral and octahedral sites. A small band at around 898 cm^{-1} is due to $\text{Co}(\text{II})\text{--O}$ bond, which is in agreement with the earlier observations.^{18,19} Chemical constituents are obtained by the energy dispersive X-ray spectra (EDAX) of CoCr_2O_4 nanoceramics as depicted in Fig. 1(c). The quantitative analysis of EDX spectrum reveals the values of atomic %. Observed atomic mass percentages of Co, Cr and O are ~ 12 , ~ 25 and ~ 61 , respectively.

3.2. Dielectric properties

Frequency-dependent behaviors of the dielectric parameters [capacitance (C), permittivity or dielectric constant of real (ϵ') and imaginary (ϵ''), loss factor ($\tan \delta$) and ac conductivity (σ_{ac})] observed in the frequency ranges from 10^3 to 10^6 Hz at different stable ac bias voltages [0.1, 0.5 and 1V] for CoCr_2O_4 nanoceramics are illustrated in Figs. 2(a)–2(d). It is well known that the dielectric behavior exhibits four different polarizations i.e., electronic, ionic, dipolar and atomic polarization which appears at very less intervals of

Fig. 1. (a) Synchrotron X-ray diffraction, (b) Infrared spectra and (c) EDAX spectrum of prepared CoCr_2O_4 nanoceramics.

time. The evolution of ionic polarization exists in the range of seconds, while the dipole polarization takes relatively longer time duration. Dielectric materials can be polarized by applying external electric field or *ac* bias voltage that shifts the charge carriers from their mean position. In lower frequency range ($< 10^4$ Hz), only electron charge carrier is leading in this polarization (Ionic polarization). Dipolar polarization is the reorientation of electric dipoles, when a bunch of atoms with a permanent dipole adjust in the presence of alternating field. In frequency region $\sim 10^4$ – 10^6 Hz, the dipolar or orientation polarization effect is more active.

Dielectric parameters strongly depend on the frequencies at different *ac* bias voltage as shown in Figs. 2(a)–2(d). Capacitance, dielectric permittivity and dielectric loss decreases with increasing frequency. This behavior arises because the interfacial (grains) dipoles have very less time to orient them in the direction of the applied *ac* electric field. Dielectric constant (ϵ') has been estimated using the relation

of parallel plate capacitor:

$$\epsilon' = \frac{Ct}{\epsilon_0 A}, \quad (2)$$

where C is the capacitance, t is the thickness of prepared pellet, ϵ_0 is the permittivity of free space and A is the cross sectional area of the flat surface of pellets. The observed value of C is $\sim 5.35 \times 10^{-12}$ farad, $\epsilon' \sim 8.8$, $\tan \delta \sim 0.17$ at 10^3 Hz with fixed *ac* bias voltage of 0.1 V. As the value of bias voltage increases from 0.1 to 1 V, the corresponding dielectric parameters go down as a function of applied frequency. Voltage-related study also exhibits the dielectric properties because dielectric permittivity (ϵ') depends on the capacitance where the value of capacitance is inversely proportional to the applied voltage. Henceforth, as the applied bias voltage increases, the dielectric parameters decrease.^{20–23} Dielectric permittivity also depends on the synthesis methods, calcination temperature and the dimension of prepared

Fig. 2. Room temperature frequency-dependent (a) capacitance, (b) real part of permittivity (ϵ'), (c) imaginary part of permittivity (ϵ'') and (d) dielectric loss ($\tan \delta$) behavior of CoCr_2O_4 nanoceramics at different bias voltage.

pellets. Dielectric loss also illustrated a nonmonotonous response in the higher frequency region. We observe that the value of $\tan \delta$ increases very less beyond $f > 50$ kHz and the dielectric loss is obtained as ~ 0.07 at 10^6 Hz. This trend of loss can be related to the strong relationship between dielectric loss and the conduction mechanism. High frequency energy storage and microwave devices require low value of dielectric loss (~ 0.1) in oxide-based nanomaterials. In the present work, we obtained low value of dielectric loss ~ 0.07 at 10^6 Hz, which is smaller than the required value ~ 0.1 .

Frequency-dependent ac conductivity of CoCr_2O_4 nanoceramics exhibits the hopping of charge carrier mechanisms. Figure 3(a) shows the ac conductivity (σ_{ac}) response of CoCr_2O_4 nanoceramics with different bias voltage at room temperature. The ac conductivity with frequency of prepared

nanoceramics has been estimated using the following equation:

$$\sigma_{ac} = \epsilon' \epsilon_0 \omega \tan \delta, \quad (3)$$

where ϵ' is dielectric constant, ϵ_0 is the permittivity of free space, $\omega (= 2\pi f)$ is angular frequency and $\tan \delta$ is observed loss value. We observe that σ_{ac} gradually increases in higher frequency region (10^5 – 10^6 Hz) because the mobility of charge carriers in grain boundary increases very fast in high frequency region.⁵

3.3. Complex impedance properties

Complex impedance structure (CIS) confirms the relaxation and conducting mechanism of the prepared samples. Real (Z') and imaginary (Z'') impedances of CoCr_2O_4

Fig. 3. Room temperature frequency dependent (a) *ac* conductivity, (b) real part of impedance (Z'), (c) imaginary part of impedance (Z'') and (d) Nyquist plot response of CoCr₂O₄ nanoceramics at different bias voltage.

nanoceramics as a function of frequency ranging from 10³ to 10⁶ Hz at different bias voltages are shown in Figs. 3(b) and 3(c). It has been observed that the response of Z' and Z'' decreases fast in lower frequency region (10³–10⁴ Hz) for the applied frequency greater than 10⁴ Hz the response is nearly constant. The value of Z' at 10³ Hz and bias voltage is 0.1 V is $\sim$ 450 k Ω . The dispersive nature of Z' and Z'' observed in our nanoceramics is in positive compliance.¹⁶

The complex impedances Z' and Z'' (Cole–Cole or Nyquist plot) describe the conducting mechanism of the prepared nanoceramics. This research also studies the complex electrical modulus. The complex impedance spectra are generally interpreted by a resistance (R) and capacitance (C) values. The equivalent parallel RC model is broadly used to show the grains and grain boundary structure in metal

oxide-based nanoceramics. Dielectric relaxation mechanism encountered by CIS is originated only in the grains and grain boundary regions. This is the simplest case to be known in terms of double layered model, where each combination or grain contribution is interpreted by one RC circuit element, where R and C are in parallel. This circuit model function works especially for the wide bandgap of materials such as dielectrics, where the capacitor is associated with the ability of the materials to store the charge carriers. Here, parallel resistor defines the leakage current, which is mainly due to un-trapped charges that deviate from the ideal charge storage element. RC component gives rise to a semicircle in the Nyquist plot. The frequency-dependent impedance response in the present system is in a better condition in comparison to the earlier reported results of metal oxide-based ferrite

system.¹⁶ The response of semicircle increases with increased *ac* bias voltage.

3.4. Polarization and leakage current behavior

Generally, FE ceramics reveals nonlinear relationship between electric polarization (*P*) and applied electric field (*E*). Room temperature FE behavior of nanoceramics is observed in the form of *P*–*E* loop. Figures 4(a) and 4(b) show the response of electric polarization without and with coating of silver, respectively. We analyzed the test data and observed that the loop in the presence of silver layer shows nearly circular behavior, whereas without silver layer prepared nanoceramics show very weak polarization loop at 50 V. Circular polarization loop does not show true electric polarization and it is associated to conductive nature.²⁶ Figure 4(c)

shows *P*–*E* loop behavior at 500 V. This behavior is attributed to weak ferroelectricity in the present nanoceramics due to the partial reversal of the polarization. We observed small amount of leakage current present in the polarization loop [as shown inset of Fig. 4(c)]. Leakage current behavior in the positive voltage region is replotted in a logarithm scale ($\log(J)$ – $\log(E)$) as shown in Fig. 4(d).

The *J*–*E* response curve can be well fitted as linear segment with two types of nature: Ohmic and non-Ohmic. First region shows the Ohmic behavior, which can be mostly attributed to Ohmic conduction in low voltage value. While in the high voltage value (second region) the conduction is dominated by Child's square law (non-Ohmic nature). High voltage region contributes to large leakage current in nanoceramics, which greatly exceeds the density of free electrons due to the carrier injection. Electron tunneling process is

Fig. 4. Electric polarization studies of (a) without coating of silver paint, (b) with coating of silver paint, (c) *P*–*E* loop at 500 V. Inset shows the leakage properties and (d) leakage current plot as a function of applied electric field observed at room temperature.

attributed to space charge limited current (SCLC) mechanism. It has been noted that in metal oxide-based nanoceramics, traps are mainly attributed to the oxygen vacancies. The trap control mechanism is directly responsible for transition between two different voltage regions due to the trapping/de-trapping of oxygen vacancy.^{24,25}

4. Conclusions

CoCr₂O₄ nanoceramics were successfully prepared by sol-gel auto combustion method. Synchrotron X-ray diffraction confirms the formation of single-phase cubic spinel nature with space group *Fd3m*. Infrared study reveals two prominent absorption bands in low wavenumber side, which confirms the formation of spinel nanoceramics. Frequency-dependent dielectric parameter response is attributed to Maxwell–Wagner-type interfacial polarization. Nyquist plot exhibits the conducting properties of the prepared nanoceramics. Polarization loop reveals the weak ferroelectricity. *J–E* behavior confirms the Ohmic and non-Ohmic nature. In this work, we obtained very low value of dielectric loss ~ 0.07 observed at 1 MHz, which is smaller than the required value ~ 0.1 for any microwave device. This indicates that a CoCr₂O₄ nanoceramic is beneficial for making such devices.

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