Synthesis Dependent Structural Magnetic and Electrical Properties of CR-Doped Lead-Free Multiferroic AlFeO₃

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Abstract: Polycrystalline samples AlFe₀.⁹⁵Cr₀.₀⁵O₃ synthetized by a solid state (SR) and a co-precipitation (cop) method show an orthorhombic system in space group Pc21n. It was found that, the cation distribution and magnetic ordering vary toughly on the synthesis conditions. We deployed impedance spectroscopy in studying the dielectric behavior of AlFe₀.⁹⁵Cr₀.₀⁵O₃. The significant results of this work are: for both samples, permittivity and dielectric loss are very sensitive to the temperature and frequency variation. The existence of supplementary imperfections and conducting species in AFCr₅-s ceramics led to important dielectric permittivity in AFCr₅-s. Values of the activation energy determined at low temperature point toward oxygen vacancies motion in slight range, however at high temperature, such a motion turns to long-range one. The dielectric response in case of AFCr₅-s was assigned throw complex impedance plots to the grain as well as grain boundary. Conversely, additional individual pores similarly participate to dielectric belongings of AFCr₅-cop.

Keywords: multiferroic material; Cr-doped AlFeO₃; site disorder; dielectric study

1. Introduction

In recent times, the ABO₃ perovskite type oxide materials displaying ferroelectric and ferromagnetic ordering identified as multiferroics materials have extended noteworthy scientific and technological consideration [1–4]. In such materials, magnetic and electric properties are linked to each other, that promote them to be used in device applications such as sensors, data devices storage, [3–6]. In this setting, the exploration for single phase magnetoelectric materials that have suitable properties for everyday requests is a noteworthy task for material scientists and physicists. Additionally, lead (Pb) or other heavy metals are deployed in the most single-phase magnetoelectric resources [7,8]. Consequently, for ecological as well as communal healthiness aims, the scientists and companies manufacturing devices that deployment of materials having ferroelectric as well as magnetoelectric properties are progressively attracted in sinking or even, in extreme case, fully excluding the heavy metals from such devices in aim to produce lead-free resources [7].

AlFeO₃ (AFO) is a perovskite lead-free material, that crystallize in orthorhombic or in rhombohedral system [9]. The orthorhombic phase (AFO) is built of a dual mixture of cubic and hexagonal closed packing of oxygen ions [9]. This arrangement leads to collinear ferromagnetic structure with magnetic ordering temperature (Tₘ) between 210 and 250 K [10,11]. The asymmetric unit of AlFeO₃ has 4 different cations sites that are denoted as Fe1, Fe2, Al1 and Al2. Fe1 and Fe2 are occupied principally by iron however those of Al1 and Al2 are occupied predominately by aluminum ions. These cations are octahedrally coordinated to oxygen except Al1, that have a tetrahedral oxygen environment [12]. Several researchers
reported on the AFO synthesis conditions in ceramics and thin films samples as well as its multiferroic properties [13–15]. Both, the cation and magnetic ordering depend strongly on the preparation conditions. AFO have a weak magnetoelectric behavior at room temperature. AlFeO$_3$ contains only trivalent metals in the structure like rare earth orthoferrites, making them attractive systems for investigations of isovalent substitutions. In particular, the replacement of Fe$^{3+}$ by Cr$^{3+}$ and its effect on structural, magnetic and other properties have been reported [16,17] for rare earth orthoferrites. For example, in the lanthanum orthoferrites, partial replacement of Fe by Cr leads to a reduction in the Neel temperature from 750 K in LaFeO$_3$ to 280 K in LaCrO$_3$. Moreover, Cr doping is one of the most adopted strategies to tailor the dielectric and piezoelectric properties of ferroelectrics for practical applications. It is well known that Cr is effective in decreasing the ageing effect and the dielectric loss; thus, the effect of doping of Cr$^{3+}$ is that of stabilizing the piezoelectric and dielectric properties [16,17]. Cr-doping of GaFeO$_3$ leads to an increase in the activation energy of conduction, primarily at the grains rendering the material more resistive and hence leading to reduced electrical leakage [18].

In this work we study the magnetic properties, In the present work, we synthesized AlFe$_{0.95}$Cr$_{0.05}$O$_3$ by different preparation (solid state reaction and sol-gel) methods and utilize the techniques of X-ray, dielectric measurement, and dc magnetic measurement in order to throw light on the effect Cr substitution and low temperature annealing methods on the structural, magnetic and dielectric properties of Cr-doped AlFeO$_3$.

2. Experimental Section

Polycrystalline AlFe$_{0.95}$Cr$_{0.05}$O$_3$ (AFCr5-s) was prepared by the conventional high temperature solid-state route. High purity Al$_2$O$_3$, Cr$_2$O$_3$ (99.99%) and Fe$_2$O$_3$ (99.99%) were mixed in stoichiometric ratio. The mixture was thoroughly mixed and homogenized in agate mortar. The mixture was calcined at 700 °C for 12 h and 1100 °C for 12 h with in between grinding. The calcined powder was pressed into pellets that were sintered at 1300 °C for 12 h with heating and cooling rate of 250 °C/h. At this temperature, the sintering time was optimized to get maximum dense and proper phase AFCr5-s. The ceramic pellets prepared by solid state route will be designated as AFCr5-s in the manuscript onwards. For co-precipitation, stoichiometric amount of Al$_2$O$_3$, Cr(NO$_3$)$_3$ and Fe(NO$_3$)$_3$·9H$_2$O were mixed under continuous stirring until, reaching a transparent solution. Al to Fe molar proportion was 1:0.95. The pH of the solution was adjusted to 9 by drop wise addition of NH$_4$OH (1M) solution under vigorous stirring. Afterward the solution was toughly washed with methanol to eliminate the contaminations and precipitates were collected. The obtained precipitation was dehydrated at 120 °C for 4 h. in a second step, the obtained powder was heated at 900 °C for 2 h. the obtained sample will hire after designates as AFCr5-cop. The sample purity was examined by X-ray diffraction (XRD) using CuK$_\alpha$ radiation in the 2θ range from 15 to 70 at room temperature. The lattice constants parameters of the samples were refined by the FULLPROF program package. Surface morphology and particles size features of the samples was carried out using a JEOL microscope; JSM-6010LA (W-SEM). The dielectric properties in a wide temperature range (160–400) K and for the frequency of 1·10$^7$ Hz, were carried out on the Ag-electrode ceramic disks by using a Novocontrol Alpha-A broadband dielectric spectrometer. Temperature was controlled with a 0.1°C device by the Novocontrol Quatro Cryosystem in dry nitrogen atmosphere. The M-versus-H hysteresis curves were measured at 5 K in applied magnetic fields $H$ ranging up to 5 T using a LakeShore VSM 7410 magnetometer.

3. Results and Discussion

3.1. Structural Characterization

The XRD patterns measured at room temperature of AlFe$_{0.95}$Cr$_{0.05}$O$_3$(AFCr5-s and AFCr5-cop) are shown in Figure 1.
Both of the samples have an orthorhombic symmetry with space group (Pc2 _1n) no other phases were detected. Compared to AFCr5-s, the XRD peaks of AFCr5-cop were enlarged. The shrinkage of particle size could be at the origin of the widening of the XRD lines.

![Figure 1](image1.png)

**Figure 1.** Rietveld refinement of samples X-ray diffraction (XRD) pattern (a) AFCr5-sd (b) AFCr5-cop.

The lattice parameters are listed in Table 1. The lattice constants a, b and c increase with decreasing annealing temperature. The reduction in particle size relaxes the lattice leading to a cell volume expansion; a similar behavior has been reported for other oxide systems such as GaFeO 3 [19].

|                | a       | b       | c       | V       |
|----------------|---------|---------|---------|---------|
| AFCr5-s        | 8.7427(7)| 9.3875(5)| 5.0803(7)| 416.96(2) |
| AFCr5-cop      | 8.7577(3)| 9.4104(6)| 5.0853(5)| 419.10(5) |

The effect of preparation condition on the microstructures was studied on as sintered samples (crosswise sector of pellets) using SEM is shown in Figure 2. It can be seen for AFCr5-s that the grain and grain boundaries are well established, however, in AFCr5-cop microstructure we can recognize, beside grain and grain boundaries amasses of intra-grain pores. The pore magnitude in AFCr5-cop is around 400 nm. These pores are typically intra-grain ones which are not associated to build pores nets. They ended up inside grains. The grain boundaries breadth is nearly of similar order, in both AFCr5-s and AFCr5-cop. The particle size is 0.8–1.2 μm for AFCr5-s and 0.3–0.6 μm for AFCr5-cop respectively. Pure AFO has non-uniform grains with varying sizes ranging between 1 and 3 μm which becomes smaller with Cr doping.

![Figure 2](image2.png)

**Figure 2.** SEM images of AlFe 0.95Cr0.05O 3 (a) prepared by solid state reaction (b) prepared by coprecipitation.
3.2. Magnetic Properties

Magnetic moment evolution of AFO, AFCr5-s and AFCr5-cop polycrystalline at 5K, by applying an external field (H) up to 50 kOe are depicted in Figure 3.

![Figure 3. M–H hysteresis loops obtained at 5K for AFCr5-s et AFCr5-cop.](image)

Altogether samples display hysteresis behavior in the M–H curve, revealing of ferrimagnetism. A close inspection of M–H curves reveals a small pinching that could be described by the occurrence of soft and hard magnetic phases in the samples. Such behavior could be related to the cation sites that have diverse magnetic anisotropic energies. In fact, Al2, Fe1, Fe2 have an octahedral oxygen environment and embrace strong anisotropy. Whereas Al1 has a tetrahedral coordination, with less anisotropic energy [20]. The high anisotropy of the material could be evidenced from the fact, that all samples do not demonstration any saturation up to 50 kOe. The Figure 3 shows hysteresis behavior indicating a weak ferromagnetism. The origin of such weak ferromagnetism in Cr-doped AFO samples could be a result of several reasons. The first possibility may be due to the uncompensated canted spins from the surface and also due to internal canted spin. The compounds of metal oxide and perovskite shows such a canted ferromagnetism such as, BiFeO3 and LaFeO3 [16,17]. The second reason is the super exchange interaction. According to Kanamori-Goodenough (KG) rules [21], the Fe-O-Fe and Cr-O-Cr super exchange interactions are antiferromagnetic, while Cr-O-Fe is predicted to be ferromagnetic. Until now no sign of strong ferromagnetism were observed in bulk samples of Cr substituted AFO, as observed in layered growth of LaCrO3-LaFeO3 [22]. Since, Cr substitutions preferentially favor the Cr-Cr coupling on substitution in the host metal ions and also the randomness of Cr ions in the host lattice site show a weak magnetism [22]. Such behavior of Cr-Cr coupling is observed in Cr-doped LaFeO3 [23].

The values of coercivity (Hc), remnant magnetization (Mr), and the saturation magnetization (Ms) of the materials achieved from the hysteresis curves are depicted in Table 2. The saturation magnetization (Ms) was determined by linear extrapolation of the inverse of the applied field (1/H) to zero. We can recognize that Ms and Mr growth with reducing annealing temperature whereas Hc drops. The coercivity declines due to lower crystallinity, whereas the deviations in magnetic properties such as Ms and Mr are generally linked to the effects of the cationic stoichiometry and their distribution on different sites. If the spin of the substituting ion Cr3+(3µB) aligns through that of Fe3+(5µB) ion at that time the total spin magnetic moment is expected to be reduced by 2µB per formula unit [24].
|            | Ms(emu/Fe) | Hc(Oe) | Mr(emu/Fe) |
|------------|------------|--------|------------|
| AFCr5-s    | 0.77       | 6435   | 0.34       |
| AFCr5-cop  | 0.89       | 4035   | 0.49       |

Commonly Hc is affected by grain magnitude as well as rotation of the domain wall. Conversely, several additional effects could amplify Hc such as surface effects (metal–oxide interchange anisotropy) as well as inside imperfections in the material arrangement that leads to magnetic domain movement restriction. Moreover it was proved that as the particle size increases, there is a decrease in the of Fe–O bond length and Fe–O–Fe bond angle [21]. This decrease in Fe–O distance and Fe–O–Fe bond angle, leads to change in single particle band width of oxygen and iron in AFCr5-s structure. The deviation of such band size induces magnetic exchange variation, and accordingly, the magnetic properties change.

3.3. Dielectric Measurements

The $\varepsilon'$ variation with frequency at different temperature is depicted in Figure 4. We can note, that in both samples $\varepsilon'$ exhibits a large value at low frequency (lower than 100 Hz) and step like decrease with increasing frequency. For both samples, $(\varepsilon/\varepsilon')$ increases with temperature in low frequency ranges up to 360 K before decreasing. An associated Debye like relaxation peak is observed in tan($\delta$) in the range of the observed step like frequency dispersion in $\varepsilon'$. The frequency-dependent behavior of the real and imaginary part of the dielectric constant is commonly observed in the case of materials exhibiting colossal dielectric constant ($\varepsilon' = 41,000$) due to extrinsic effects [25,26]. The shift with temperature and frequency supports a Maxwell–Wagner relaxation type, which arises due to the presence of region with different conductivities within the sample [25–27]. In the low frequency domain, the great values of $\varepsilon'$, suggest that the capacitance of grain boundary is greater than the bulk grain capacitance of the material. In fact, at the grain boundaries, the collected charge might provide a Maxwell–Wagner type relaxation behavior [25,26]. The prompt growth in the dielectric constant values (two orders) about 200 K stand up from numerous issues, such as inherent to the system beside extrinsic belongings. In inherent effect case, the sudden increase of ($\varepsilon/\varepsilon'$) within a tiny temperature domain might appear in the vicinity of the beginning of ferroelectric arrangement where the dipoles are exposed to a twofold well energy barrier. In such circumstance, the $(\varepsilon/\varepsilon')$ follows the Curie–Weiss comportment overhead the transition temperature. Such behavior was not observed in AFCr5-s samples. The result is owing to the grain boundary below 200 K however above 200 K a mutual consequence of the grain boundary and the space charge effect ascending owing to the semiconducting performance linked with the interaction effects.

In general, the dielectric constant and the dielectric polarization are proportional to the grain size [15], which was the case in this study. In fact, dielectric constant for AFCr5-s at a given temperature is much higher than the dielectric constant for AFCr5-cop. A ferroelectric hysteresis as a function of temperature was observed for the Al(Fe0.98Nb0.02)O3 ceramic, suggesting that both ferrimagnetic and ferroelectric states coexist in AlFeO3-based compositions below 160 K [28]. Also, a room temperature ferroelectric hysteresis loops was observed in GaFe1-xCrX3O3 samples. With the incorporation of Cr content in GFO, shape of the loops becomes better with enhanced value of polarization and this is attributed to lowered leakage current with Cr doping in GFO [19]. The enhanced value of polarization may be due to increase in the orthorhombic distortion in GFO with the incorporation of Cr content resulting in lowering the electrical leakage in Cr-doped samples [21]. We believe that a similar situation could be observed in our samples.
Figure 4. Evolution of $\varepsilon'$ and loss tangent with frequency at different temperature in AFCr5-s and AFCr5-cop.

Figure 5 illustrates the evolution of $M''$, (imaginary part of electric modulus) against log ($f$) at diverse temperatures. We recognize an asymmetric peak that moves to the greater frequency region with growing temperature. It is noteworthy that at the same temperature the relaxation in AFCr5-s appear at higher frequency compared to AFCr5-cop. at low temperature (200–300 K), the observable anomalies are those that fit to grain relaxation which move out of the measurement range above 320 K [28]. The changeover from long- to short-range movement through by increasing frequency is assumed by area wherever anomaly happens. Such a comportment of $M''$ spectrum is evocative of temperature-dependent hopping kind mechanism for electrical conveyance (charge transport) in the structure. Moreover, the peaks enlargement is a distinctive of diverse mean time relaxation.

Figure 6 displays the frequency dependence of $(Z'')$ measured at selected temperatures. This spectrum recommends the comportment of the greatest resistive part in the sample. A deep examination of the spectrum shows the existence of two relaxation mechanisms that have diverse relaxation times. The grain effect is recognizable on high frequency region [29], through a peak that moves to upper frequency with growing temperature which line with the dielectric loss behavior in the same frequency range. From the time when the loss tangent and the imaginary part of the impedance are interconnected respectively, the grain boundary effect comes out in the low-frequency part.

Figure 7 shows the room temperature frequency evolution of $(Z'')$ and $(M'')$ spectrum for AFCr5-s and AFCr5-cop systems. It can be realized that, for AFCr5-s, the impedance has three relaxations one sharp around 1000Hz, and two small, at lower and higher frequencies. However, in AFcr5-cop, shows a sharp relaxation in the low frequency range and a broadened one at higher frequency. It is noteworthy, that these relaxations appear at lower frequency than in AFCr5-s. The pure AlFeO$_3$ sample does not display any relaxation at high frequencies. Moreover, the maximum values of impedance $(Z''_{\text{max}})$ and modulus $(M''_{\text{max}})$ do occur at different frequency with broadened modulus spectra which are a
symptom of the varied spreading of relaxation times. Based on West et al. [30] analysis, the contribution of grain boundary appears at low frequency and have a high relaxation time as in the case of relaxation with great R and C. however relaxation that appear at high frequency with lower values of R and C are characteristic of the grain contribution. A closely look on the. Impedance imaginary part $(Z'')$ reveals that peak maximum is broadened at low frequency side. however, a peak broadness appears in $M''$ spectra on the high frequency region. We can assume at the designated temperature, that a higher resistive part is dominating the impedance plots, however a lower capacitance is monitoring the modulus plot $(M'')$ with high frequency disposition.

Figure 5. Frequency evolution of $M''$ at different temperature for AFCr5-s and AFCr5-cop.

Figure 6. Frequency dependent imaginary part of impedance $Z''$ plot of prepared samples.

Figure 7. (a) variation of imaginary part of the impedance $Z''$ and (b) imaginary part of the modulus $(M'')$ for AFCr5-s and AFCr5-cop.
The Nyquist plots ($Z'$ vs. $Z''$) at selected temperatures are depicted in Figure 8. The complex impedance schemes are branded by the consecutive semicircular arcs reflecting contribution of grain, grain boundary and electrode. Every arc is characterized by a correspondent circuit component build of resistance and capacitance. The grain effect alone appears as single semicircle in $Z'$ versus $Z''$ plot. The existence of second semicircle suggests the presence of grain boundary effects. When a third semicircle is present, it designates the electrode effects. These effects are observed in AFCr5-s spectra and not in AFCr5-cop. At a given temperature (320 K) the grain in AFCr5-s effect is two times higher than that observed in AFCr5-cop.

Figure 8. Nyquist plots evolution with temperature for AFCr5-s and AFCr5-cop.

Evolution of $\sigma_{\text{ac}}(\omega)$ with frequency and temperature is depicted in Figure 9. We can recognize the increase of the conductivity with temperature, characteristic of a semiconductor behavior of the prepared samples. Contrary to impedance spectra, the conductivity plots show different behavior in low temperature ($\leq 300$ K) area and high temperature region ($\geq 300$ K). In low temperature domain (up to 200 KHz) the conductivity is almost frequency independent. At higher frequency ($\sim 200$ kHz–5 MHz) the conductivity turns to a strong frequency variant. This variation is more pronounced for AFCr5-s as compared to AFCr5-cop. The grain boundary effect could be at the origin of such differences.

Figure 9. Frequency evolution of the conductivity at different temperature for AFCr5-s and AFCr5-cop.

In the high temperature domain the conductivity can be considered as built of three distinct sections: the first at small frequency area ($\leq 10$ kHz), in which the conductivity is frequency independent. The second region is regarded as a weak frequency-variant conductivity (10 kHz–1 MHz). The third region ($\nu > 1$ MHz) is a fast frequency-variant region.
We assume that the Maxwell–Wagner mechanism is present in the high-temperature, low-frequency conductivity which is principally owing to the effects of grain boundary. However, intermediary high-temperature and high frequency region can be described by bulk conductivity. The variation in the slope among the low-frequency domain (≤10 kHz) and intermediate-frequency region (from 10 kHz up to 1 MHz) suggests the presence of diverse conduction mechanisms.

$\sigma_{ac}$ dependence with $(10^2/T)$ at a designated frequency is given in Figure 10. The slope of the plot is found to show three temperature regions, 160–200 K, 200–290 K and 300–410 K correspondingly. In the low-temperature regions, the activation energies very comparable, however in low and middle temperature region the activation energy in AFCr5-cop are higher than those calculated for AFCr5-s. A hopping charge carrier’s mechanism could be associated to the obtained higher activation energy. For AFCr5-s, the energy activation calculated at small temperature was 80 meV. This assumes that at low temperature, the conduction could be related to a charge defect at boundaries, moreover, rules out the probability of macroscopic conduction [31–33]. At higher temperature, the sample conductivity upsurges quickly and the estimated energy activation is about 180 meV, that can be also assigned to oxygen vacancies motion at elevated temperature. This energy activation is very slight for the displacement of ions inside grain (inherent conduction).

![Figure 10](image-url)

**Figure 10.** Variation of log ac conductivity with inverse of the absolute temperature for selected frequency for AFCr5-s and AFCr5-cop.

### 4. Conclusions

Particle size dependent studies on structural, magnetic and dielectric properties of Cr-doped AlFe0.95Cr0.05O3 have been investigated. The magnetic structure was found to be ferromagnetic. The Fe$^{3+}$ ions distribution among different sites seems to be related to the preparation methods. The, saturation magnetization (Ms), remanent magnetization (Mr), are enhanced as the particle size decrease, however, coercivity (Hc) decreases. Temperature and frequency electrical impedance and modulus analysis reveal that permittivity in Cr-doped AFO is strongly dependent on microstructure and preparation condition of the samples. Two relaxation processes are detected: high-frequency grain conduction and the low-frequency grain boundary conduction. The grain boundary activation energy was estimated to be higher than that of grain, both grain and grain boundary conduction activation energies increase with decreasing particle size making AFCr5-cop samples better insulators.

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