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Dielectric relaxation and magnetic properties of Cr doped GaFeO$_3$

M Bakr Mohamed$^1$, H Wang and H Fuess

Institute for Materials Science, Darmstadt University of Technology, Petersenstraße 23, 64287 Darmstadt, Germany

E-mail: mbm1977@ yahoo.com

$^1$Author to whom any correspondence should be addressed.

Abstract
Polycrystalline Ga$_{1-x}$Cr$_x$FeO$_3$ ($x = 0.05, 0.1$ and 0.15) samples were prepared by solid state reaction. The monophasic compounds crystallize in the orthorhombic space group P $c$ 2$_1$ n and the unit cell volume decreases with increasing Cr content. The saturated magnetization and magnetic transition temperature of the ceramics decrease due to the dilution of the magnetic interaction with Cr concentration. The dielectric properties were investigated from 133 to 353 K at various frequencies (100-10$^3$ Hz). Whereas the dielectric constant decreases with Cr-content an increase of dielectric loss tangent was observed. The activation energy of the compounds (calculated both from loss and modulus spectrum) are the same and have values $\sim 0.22$ and 0.27 eV for Cr=10 and 15%, respectively, and hence the relaxation process may be attributed to the same type of charge carrier. A separation of the grain and grain boundary properties has been achieved using an equivalent circuit model. The capacitance and resistances associated with the grain boundary were found to be higher than that associated with grain.

1. Introduction
The study of multiferroics is a very hot topic. It is interesting not only from the point of view of fundamental physics but also for many potential applications in electronics [1, 2].

GaFeO$_3$ has an orthorhombic crystal structure (space group P $c$ 2$_1$ n) with four different cation sites labeled Ga1, Ga2 (mostly occupied by gallium) and Fe1, Fe2 (mostly occupied by iron). This material has a spontaneous polarization along the $b$ axis and a ferromagnetic structure below room temperature result from unequal distribution of Fe spins of nearly equal magnitude on the sublattices with a magnetic moment of the spin along the $c$ axis [3, 4].

GaFeO$_3$ 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 [5-7] for rare earth orthoferrites. For example, in the lanthanum orthoferrites, partial replacement of Fe by Cr leads to a reduction in the Néel 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 aging effect and the dielectric loss; thus, the effect of doping of Cr$^{3+}$ is that of a stabilizer of the piezoelectric and dielectric properties [8, 9].

In the present work we study the (a) magnetic properties, (b) apply the variable-frequency technique of impedance spectroscopy to the samples over a wide temperature range, and (c) characterize the grain and grain boundary resistance using IS, from which one can calculate their capacitance and can model the equivalent circuit for Cr-substituted GaFeO$_3$ samples.

2. Experimental procedures
The polycrystalline GaFe$_{1-x}$Cr$_x$O$_3$ (x=0.05, 0.1 and 0.15) samples were prepared by solid state reaction method. Appropriate amounts of Ga$_2$O$_3$ (99.99%), Fe$_2$O$_3$ (99.9%), and Cr$_2$O$_3$ (99.9%) were mixed together and ground in an agate mortar till a homogeneous mixture was formed. This mixture was precalcined at 900°C (20h) and then at 1050°C (50h). These powders were reground thoroughly, pelletized and sintered at 1300°C (10h). The crystal structure of the samples was examined by x-ray diffraction using MoK$_\alpha$ with wavelength $\lambda=0.709703$ Å. The lattice constants and structural parameters of the samples were refined by the FULLPROF program package [10]. Magnetization evaluation was executed a SQUID magnetometer in the temperature range of 5–320 K under a magnetic field of 100 Oe. M-vs-H hysteresis curves were measured at 10 K in applied magnetic fields H ranging up to 6 T. For dielectric measurements, the uniaxially pressed powder (heated at 1050°C) was then cold pressed using a “wet-bag” pressing technique in weber presser KIP100E Isostatic press to achieve uniform distribution throughout the pellet and then sintered at 1300°C (10h). Silver electrodes were prepared for the samples and the dielectric measurement was controlled by a programmable electrometer (KEITHLEY 617). The complex dielectric permittivity was investigated using a Novocontrol Alpha-A analyzer (f = 100–107 Hz), in the temperature from 133K- 350K with a ZGS active sample cell. Surface morphologies were investigated on High Resolution Scanning Electron Microscopy (HRSEM).

3. Results and discussion
3.1. Structure and microstructure
Figure 1(a) shows the XRD patterns of the sintered GaFe$_{1-x}$Cr$_x$O$_3$ (x 0.05, 0.1 and 0.15) samples recorded at room temperature. The Rietveld analysis results reveal that all samples have orthorhombic structure (P c 2$_1$ n) as shown in Figure1(b) for the GaFe$_{0.85}$Cr$_{0.15}$O$_3$ sample. The unit cell volume of the solid solution GaFe$_{1-x}$Cr$_x$O$_3$ slightly decrease from about V = 417.38[4] nm$^3$ to V = 415.55 nm$^3$, when x is changed from 0 to 0.15. This decrease in unit cell volume with increasing Cr substitution is expected since the ionic radius of Cr$^{3+}$ is slightly smaller than that of Fe$^{3+}$. The SEM micrograph of the sintered pellet is shown in Figure 2(a and b). The micrograph revealed a uniform distribution of the grains of varying shape with well defined boundaries with average grain size in the range of ~1-3 μm. The energy dispersive X-ray spectrum in the SEM mode is shown in Figure 2(c and d), which determines the chemical composition of the samples.

3.2. Magnetic properties
The magnetic properties of GaFe$_{1-x}$Cr$_x$O$_3$ (x=0.05, 0.1 and 0.15) samples are shown in Figure 3(a). The temperature dependence of the magnetization (zero field cooling; ZFC and field cooling, FC), measured over the temperature range from 5 to 300 K under 100 Oe field, indicates that the magnetization is decreased by Cr doping. The magnetization of GaFe$_{0.85}$Cr$_{0.15}$O$_3$, which is 3.7 emu/g, is found to be less than that of the undoped sample (6.3 emu/g) at 5 K [4]. The magnetic transition temperatures ($T_C$) calculated from the minimum position of the dM/dT versus temperature curve are around 148, 120 and 104 K for Cr=5, 10 and 15 %. The Curie temperature $T_C$ decreases with increasing Cr content in GaFe$_{1-x}$Cr$_x$O$_3$ as compared to the parent compound where its $T_C$=190K[4]. A similar behavior has been observed in the CoCr,Fe$_2$,O$_4$ system [11]. The lowering of $T_C$ may be related to the weak Cr$^{3+}$($3\mu_B$)-O-Cr$^{3+}$($3\mu_B$) [12] and Fe$^{3+}$($5\mu_B$)-O-Cr$^{3+}$($3\mu_B$) interaction [13] as compared to Fe$^{3+}$($3\mu_B$)-O-Fe$^{3+}$($5\mu_B$).

Figure 3(b) presents the magnetization as a function of field. All samples exhibit hysteresis behavior in the $M$-$H$ curve, indicative of ferrimagnetism. The saturation magnetization ($M_s$), remnant magnetization ($M_r$), and coercivity ($H_c$) of the samples obtained from the hysteresis curves are presented in Table 1. It is seen that $M_r$, $M_s$, and $H_c$ exhibit decreasing trends with increasing x. If the spin of the substituting Cr$^{3+}$ion align with the Fe$^{3+}$ ion, the spin magnetic moment (SMM) of Cr$^{3+}$($d^7$) ion is $3\mu_B$, thus, the net SMM is expected to be reduced by 2 $\mu_B$ per formula unit[14].

3.3. Dielectric properties
The frequency dependence of the dielectric constant, $\varepsilon'$, and the dielectric loss, tan$\delta$, at 353 K for Cr=10 and 15 % are shown in Figure 4. $\varepsilon'$ clearly shows a Debye-like relaxation from a high value at low frequency to a small saturated value at higher frequency for both samples. The decrease of the dielectric constant and the higher dielectric loss as a function of Cr-content may be related with the grain size. In general the dielectric constant and the dielectric polarization are proportional to the grain size [15]. In the present study, however, a different behavior was observed similar to Cr doped $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films [16]. A possible explanation may be a change in concentration of oxygen vacancies and defect related dipoles due to variable oxidation state of both Fe and Cr.

In general, the dielectric constant of any material is due to dipolar, electronic, ionic, and interfacial polarizations [17, 18]. The dipolar and interfacial polarizations contribute significantly to the dielectric constant at low frequencies. Both these polarizations are strongly temperature dependent. In the high frequency region $\varepsilon'$ is almost the same for all samples as the contribution to the dielectric constant arises from electronic and ionic polarizations at high frequencies which are frequency independent. The frequency dependence of dielectric loss spectrum (tan$\delta$) shown in inset of Figure 4 implies that the hopping of charge carriers plays an important role in their transport process because a loss peak is an essential feature of the charge carrier hopping transport [19]. The monotonous increase in the loss factor at low frequency is probably due to the contribution of the d.c. conductivity [20].

The dielectric constant and the dielectric loss at 100 Hz-10 MHz for the sample of Cr=15% versus temperature (T) are shown in Figure 5. The dielectric constant is high at 1 KHz and decreases very sharply with increasing frequency at temperatures above 350 K. Jen Hsiao et al. found similar situation in Li$_{0.011}$Ni$_{0.94}$Ta$_{0.05}$O composition [21] and they explained the decrease in dielectric constant at higher frequencies in terms of the interfacial space charge polarization. Where the space charge polarization increases with increasing temperature due to the increase in dc conductivity, moreover, it decreases with increasing frequency due to the decrease in ac conductivity [22]. The values of (dielectric constant, dielectric loss) at 1 KHz and 298 K are (22.7, 0.01), (22.8, 0.6) and (16, 0.2) for GaFe$_1$$_x$Cr$_{0.15}$O$_3$ compositions, respectively. Which indicates the dop of Cr decrease dielectric constant and increase the dielectric loss opposite to the situation of Cr doped BiFeO$_3$ [23], where the dielectric constant increase considerably with the Cr doping level. The frequency (f) dependence of the $\varepsilon'$ and tan$\delta$ of GaFe$_{0.85}$Cr$_{0.15}$O$_3$ as a function of temperature are shown in Figure 6 (a) and (b). The peak in tan$\delta$, shifts to a lower frequency on lowering the temperature. The values of the most probable relaxation time $\tau_m$ were obtained from the peak frequencies $\omega_m$ ($\omega_m \tau_m=1$) of tan$\delta$. The variation of $\tau_m$ vs $10^3/T$ shown in Figure 6 suggest that the relaxation time follows the Arrhenius law

$$\tau = \tau_0 \exp(E_a/K_B T)$$

(1)

where $E_a$ is the activation energy for the dielectric response, $K_B$ is the Boltzmann constant and T is the absolute temperature. The activation energy for the dielectric relaxation obtained from the slope of the fitted line is 0.24 and 0.28 eV for Cr=10 and 15%, respectively.

It has to be mentioned that the samples have been synthesized at high temperature $\geq$1200 °C; a slight amount of oxygen loss can occur and may be expressed as by the Kroger-Vink notation [24]:

$$O_{o}^{x}=V_{o}^{x}+1/2O_2 (\text{gas})+2e^{-}.$$ 

where $O_{o}^{x}$ is the loss of lattice oxygen, $V_{o}^{x}$ is the presence of oxygen-ion vacancy and $e^{-}$ is the electron released or captured. The electron release may be captured by Fe$^{3+}$ to generate Fe$^{2+}$ for charge compensation such as in $LaFe_{0.9}Ni_{0.1}O_3$ [25]. The $V_{o}^{x}$ and Fe$^{2+}$, contribute not only to the conductivity but also to the dielectric response. So, the activation energy values obtained above are almost equal to the activation energy of electron hopping between an Fe$^{3+}$ and an Fe$^{3+}$ ion in the oxide [26]. Again the strong increase in the dielectric characteristics
with increasing temperature may be due to thermally induced oxygen ion vacancies and enhancement of hopping conduction as we will see later [27].

Polycrystalline samples may be analyzed by considering the impedance $Z(\omega)$ spectra as an electric modulus $M(\omega)$ spectra in order to emphasize the grain and grain boundary contributions to the electric properties[28]. From the physical point of view, the electric modulus corresponds to the relaxation of the electric field in the materials when the electric displacement remains constant [29].

The logarithmic frequency dependence of the electric modulus $M'$ and $M''$ for various temperature are shown in Figure 7 for GaFe$_{0.9}$Cr$_{0.1}$O$_3$. In terms of the dielectric constant $\varepsilon(\omega)$, the electric modulus is given by

\[
\begin{align*}
M'(\omega) &= \varepsilon'(\omega) + \frac{1}{\varepsilon^*} \\
M''(\omega) &= \varepsilon''(\omega) + \frac{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2}{\varepsilon^*} \\
M''(\omega) &= \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2}
\end{align*}
\]

It can be clearly seen that values of $M'(\omega)$ increase with frequency and reach a constant value at higher frequencies [Figure 7(a)], while $M''(\omega)$ exhibits a maximum ($M''_{\text{max}}$) [Figure 7(b)] centered at the dispersion region of $M'(\omega)$. It may be noted from Figure 7(b) that the position of the peak $M''_{\text{max}}$ shifts to lower frequencies as temperature decreased. The frequency region below the peak maximum ($M''_{\text{max}}$) determines the range in which charge carriers are mobile on long distances. At frequency above peak maximum the carriers are confined to potential wells, being mobile on short distances [30]. Figure 7(c) shows the frequency dependence of normalized $M'/M''_{\text{max}}$ peaks for GaFe$_{0.9}$Cr$_{0.1}$O$_3$. The $M'/M''_{\text{max}}$ curves are overlap for all the temperatures into a single master curve, indicating that they describe the same mechanism at various temperatures relaxations. The temperature dependence of the characteristic relaxation time was determined and plotted in Figure 7(d), which follows the Arrhenius law [31]. From the least square fitting, the activation energies are calculated, and are found to be 0.22 and 0.27 eV for Cr=10 and 15%, respectively. The nearly equal values of activation energy (calculated from loss and modulus spectrum) suggests that the relaxation process may be attributed to the same type of charge carriers.

Figure 8 shows Complex impedance ($Z'$ vs. $Z'$ ) plot for GaFe$_{1-x}$Cr$_x$O$_3$ samples measured at 353 K. The impedance diagrams clearly demonstrate that Cr influences the values of impedance, the real and imaginary components of the impedance decrease with an increase of Cr amount. Impedance spectra have been analyzed by an equivalent circuit, as displayed in the inset of Figure 8. The two sub-circuits represent the grain (g) and grain boundary (gb) effects. The impedance spectra reveal semicircles whose centres do not lie on the abscissa of the axis, suggesting departure from ideal Debye-type behavior[33]. Hence, in the equivalent circuit, the constant phase elements (Q) capacitance $Q(\omega) = B (i\omega)^{n-1}$ are assumed to describe the depressed semicircle [32], where B is constant. The exponent n varies between 0 and 1 (n= 1 for an ideal capacitor and n=0 for ideal resistor). The best fitting of equivalent RC circuit at 353 K using the software“ZsimpWin” are $R_g = 0.7$ and 3.51 MΩ, $R_{gb} = 88.81$ and 40.89 MΩ, $C_g = 8.186 \times 10^{12}$ and $6.506 \times 10^{12}$ F, $C_{gb} = 0.995 7 \times 10^{-9}$ and $4.779 \times 10^{-9}$ F for Cr=10 and 15 %, respectively. Thus, the impedance spectroscopy analysis clearly demonstrates that the grain boundaries are more resistive than the grain in GaFe$_{1-x}$Cr$_x$O$_3$ system.

In order to further elucidate the transport mechanism in this system, the electric conductivity at different temperatures is studied. Electric conductivity can be calculated from the dielectric data as

\[
\sigma(\omega) = \varepsilon_0 \varepsilon' \tan \delta,
\]

where $\omega$ is the angular frequency and $\varepsilon_0$ is the vacuum permittivity. Figure 9(a) shows frequency dependence of a.c. conductivity $\sigma_{\text{a.c.}}$ at various temperatures for GaFe$_{1.85}$Cr$_{0.15}$O$_3$. It can be seen that at low frequencies and above room temperature plateaus of $\sigma_{\text{a.c.}}$ (frequency independent values of conductivity) exist which corresponds to d.c. conductivity.

The observed frequency dependent conductivity can be described by the equation

\[
\sigma(\omega) = \sigma_{\text{d.c.}} + A \omega^n,
\]

[17]
where \( n \) is the frequency exponent in the range of \( 0 < n < 1 \) and for an ideal Debye-type behavior it is equal to 1, \( A \) and \( n \) are thermally activated quantities, hence electrical conduction is a thermally activated process[33]. Extrapolating these curves towards low frequency gives the dc conductivity \( (\sigma_{dc}) \). The resulting \( \sigma_{dc} \) is plotted as a function of reciprocal temperature in Figure 9 (b) and it well obeys the Arrhenius law,

\[
\sigma = \sigma_0 \exp \left( \frac{E_{\text{cond}}}{k_B T} \right),
\]

where \( \sigma_0 \) is the pre-exponential term, \( E_{\text{cond}} \) is the conduction activation energy, and \( k_B \) is the Boltzmann constant. From the fitting \( E_{\text{cond}} \) are 0.22 and 0.28 eV, for Cr=10 and 15%, respectively. This thermal activation energy of the intragrain conductivity is very close to that obtained from the dielectric relaxation, which suggests that the conductivity may play a very important role in these materials.

4. Conclusion
Polycrystalline \( \text{GaFe}_{1-x}\text{Cr}_x\text{O}_3 \) (\( x=0.05, 0.1 \) and 0.15) was prepared by solid state reaction. X-ray diffraction of the samples confirmed the orthorhombic crystal structure. The surface morphology of the compounds is studied through SEM, which gives the average grain size as the order of \( \sim 1-3 \) \( \mu \)m. The magnetic properties decrease due to the weakening of the \( \text{Fe}^{3+}-\text{O}--\text{Fe}^{3+} \) superexchange interaction strength when the \( \text{Cr}^{3+} \) ions replaces some of the \( \text{Fe} \) ions. The frequency dependent maxima in the imaginary electric modulus at various temperatures are found to obey Arrhenius law with activation energies of \( \sim 0.22 \) and 0.27 eV, for \( \text{GaFe}_{1-x}\text{Cr}_x\text{O}_3 \), \( x=0.1 \) and 0.15, respectively, which has been interpreted by hopping of electrons between ions of the same element but in different oxidation states. The scaling behavior of the imaginary part of electric modulus (\( M'' \)) suggests that the relaxation describes the same mechanism at various temperatures. Impedance spectroscopy along with the equivalent circuit model was used to determine the resistance and capacitance associated with the grain and grain boundary.

Acknowledgements
One of us (M.Bakr Mohamed) would like to thank the Egyptian Ministry of Higher Education, Scientific Research and Technology for a research grant.
Figure 1. (a) XRD patterns of GaFe$_{1-x}$Cr$_x$O$_3$ (x = 0.05, 0.1, 0.15) ceramic samples. (b) Rietveld analysis results of XRD pattern at RT for the GaFe$_{0.85}$Cr$_{0.15}$O$_3$ sample. Solid circles indicate the experimental data and the calculated data are the continuous line overlapping them. The lowest curve shows the difference between experimental and calculated patterns. The vertical bars indicate the Bragg reflection positions.

Figure 2. The SEM surface images of GaFe$_{1-x}$Cr$_x$O$_3$ samples: (a) x = 0.1, (b) x = 0.15, (c and d) Energy dispersive X-ray spectrum of Cr=10 and 15% doped samples.

Figure 3. (a) Temperature dependence of magnetization for ZFC (open) and FC(solid) modes measured at 100 Oe (b) Magnetic hysteresis loop M(H) measured at 10K for the GaFe$_{1-x}$Cr$_x$O$_3$ samples.

Figure 4. Frequency dependence of (a) $\varepsilon'$ and (b) tan $\delta$ of GaFe$_{1-x}$Cr$_x$O$_3$; x=0.1 and 0.15 at 353 K

Figure 5. Variation of dielectric constant ($\varepsilon$) and tangent (tan $\delta$, inset) with temperature in GaFe$_{0.85}$Cr$_{0.15}$O$_3$ at selected frequencies.

Figure 6. Frequency dependence of (a) $\varepsilon'$ and (b) tan $\delta$ of GaFe$_{0.85}$Cr$_{0.15}$O$_3$ at different temperature, and the inset is ln $\tau$ vs. 1000/T.

Figure 7. Frequency dependence of (a) real and (b) imaginary part of the electrical modulus for GaFe$_{1.9}$Cr$_{0.1}$O$_3$ at several temperature values. (c) Normalized modulus (M/M$_m$) as a function of frequency at different temperatures, (d) Arrhenius plot of the peak frequencies $f_m$ for GaFe$_{1-x}$Cr$_x$O$_3$, x=0.1 and 0.15.

Figure 8. Nyquist plots of GaFe$_{1-x}$Cr$_x$O$_3$ samples at 353 K, inset represents the proposed circuit model.

Figure 9. (a) Frequency dependent electric conductivity at various temperature for GaFe$_{0.85}$Cr$_{0.15}$O$_3$, (b) Arrhenius plot of dc conductivity for GaFe$_{1-x}$Cr$_x$O$_3$, x=0.1 and 0.15 samples, read color represent linear fit.
Figure 1
GaFe\textsubscript{0.85}Cr\textsubscript{0.15}O\textsubscript{3}  

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Figure 2
Figure 3.
Dielectric constant ($\varepsilon'$) and dielectric loss (tan $\delta$) as a function of log(f).

Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9
Table 1. Details of structure refinements with error bar and magnetic properties GaFe$_{1-x}$Cr$_x$O$_3$.

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Reliability factors

| Rp   | 10.3         | 9.90         | 10.1         |
| Rwp  | 9.34         | 8.30         | 8.73         |
| Rf   | 4.84         | 4.56         | 5.06         |
| $\chi^2$ | 3.61       | 3.45         | 4.19         |

Magnetic properties

| $H_c$(Oe) | 4325         | 3142         | 1938         |
| $M_s$(emu/g) | 11.43       | 5.67         | 3.43         |
| $M_r$(emu/g) | 26.53       | 15.83        | 15.22        |
### References


[8] Li J H and Sun Q C 2008 Rare Metals 27 362.


