Dielectric relaxation and magnetic properties of Cr doped GaFeO₃

M Bakr, Mohamed , Hui Wang, H Fuess

► To cite this version:

M Bakr, Mohamed , Hui Wang, H Fuess. Dielectric relaxation and magnetic properties of Cr doped GaFeO₃. Journal of Physics D: Applied Physics, 2010, 43 (45), pp.455409. 10.1088/0022-3727/43/45/455409 . hal-00569744

HAL Id: hal-00569744

<https://hal.science/hal-00569744>

Submitted on 25 Feb 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Dielectric relaxation and magnetic properties of Cr doped GaFeO₃

M Bakr Mohamed¹, 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 GaFe_{1-x}Cr_xO₃ (x= 0.05, 0.1 and 0.15) samples were prepared by solid state reaction. The monophasic compounds crystallize in the orthorhombic space group $Pc2_1n$ 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 (100-10⁷ 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 ~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].

GaFeO₃ has an orthorhombic crystal structure (space group $Pc2_1n$) 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 ferrimagnetic 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].

GaFeO₃ 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 Fe³⁺ by Cr³⁺ 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 LaFeO₃ to 280 K in LaCrO₃. 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 Cr³⁺ 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 GaFeO₃ samples.

2. Experimental procedures

The polycrystalline $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x=0.05, 0.1$ and 0.15) samples were prepared by solid state reaction method. Appropriate amounts of Ga_2O_3 (99.99%), Fe_2O_3 (99.9%), and Cr_2O_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, palletized and sintered at 1300°C (10h). The crystal structure of the samples was examined by x-ray diffraction using MoK_α with wavelength $\lambda=0.709703\text{ \AA}$. 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 ($f = 100\text{--}10^7\text{ Hz}$), 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 $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x=0.05, 0.1$ and 0.15) samples recorded at room temperature. The Rietveld analysis results reveal that all samples have orthorhombic structure ($Pc2_1n$) as shown in Figure1(b) for the $\text{GaFe}_{0.85}\text{Cr}_{0.15}\text{O}_3$ sample. The unit cell volume of the solid solution $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ slightly decrease from about $V=417.38[4]\text{ nm}^3$ to $V=415.55\text{ nm}^3$, 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 $\sim 1\text{--}3\text{ }\mu\text{m}$. 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 $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x=0.05, 0.1$ 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 $\text{GaFe}_{0.85}\text{Cr}_{0.15}\text{O}_3$, 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 $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ as compared to the parent compound where its $T_C=190\text{K}$ [4]. A similar behavior has been observed in the $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ system [11]. The lowering of T_C may be related to the weak $\text{Cr}^{3+}(3\mu_B)\text{--O--Cr}^{3+}(3\mu_B)$ [12] and $\text{Fe}^{3+}(5\mu_B)\text{--O--Cr}^{3+}(3\mu_B)$ interaction [13] as compared to $\text{Fe}^{3+}(5\mu_B)\text{--O--Fe}^{3+}(5\mu_B)$.

Figure 3(b) presents the magnetization as a function of field. All samples exhibit hysteresis behavior in the $M\text{--}H$ 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_s , M_r 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 $\text{Cr}^{3+}(d^3)$ 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, ϵ' , and the dielectric loss, $\tan\delta$, at 353 K for Cr=10 and 15 % are shown in Figure 4. ϵ' 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 $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ 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 ϵ' 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 $\text{Li}_{0.01}\text{Ni}_{0.94}\text{Ta}_{0.05}\text{O}$ 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 $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x=0.0$ [4], 0.1 and 0.15), respectively. Which indicates the doped 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 ϵ' and $\tan\delta$ of $\text{GaFe}_{0.85}\text{Cr}_{0.15}\text{O}_3$ 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 τ_m were obtained from the peak frequencies ω_m ($\omega_m \tau_m=1$) of $\tan\delta$. The variation of τ_m vs $10^3/T$ shown in Figure 6 suggest that the relaxation time follows the Arrhenius law

$$\tau = \tau_0 \exp(E_a/K_B T) \quad (1)$$

where E_a is the activation energy for the dielectric relaxation, 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 ≥ 1200 °C; a slight amount of oxygen loss can occur and may be expressed as by the Kroger-Vink notation [24]:

where O_o^x is the loss of lattice oxygen, $\text{V}_o^{\bullet\bullet}$ 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 $\text{LaFe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ [25]. The $\text{V}_o^{\bullet\bullet}$ 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^{2+} 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 $\text{GaFe}_{0.9}\text{Cr}_{0.1}\text{O}_3$. In terms of the dielectric constant $\epsilon(\omega)$, the electric modulus is given by

$$M^*(\omega) = M'(\omega) + jM''(\omega) = 1/\epsilon^* \quad (2a)$$

$$M'(\omega) = \epsilon'(\omega) / [\epsilon'(\omega)^2 + \epsilon''(\omega)^2] \quad (2b)$$

$$M''(\omega) = \epsilon''(\omega) / [\epsilon'(\omega)^2 + \epsilon''(\omega)^2] \quad (2c)$$

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''_{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''_{max} shifts to lower frequencies as temperature decreased. The frequency region below the peak maximum (M''_{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''_{max} peaks for $\text{GaFe}_{0.9}\text{Cr}_{0.1}\text{O}_3$. The M''/M''_{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 $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ 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 (g_b) 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 $Q(\omega) = B(\omega)^{n-1}$ 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 $3.51 \text{ M}\Omega$, $R_{gb} = 88.81$ and $40.89 \text{ M}\Omega$, $C_g = 8.186 \times 10^{-12}$ and $6.506 \times 10^{-12} \text{ F}$, $C_{gb} = 0.9957 \times 10^{-9}$ and $0.4779 \times 10^{-9} \text{ F}$ for Cr=10 and 15 %, respectively. Thus, the impedance spectroscopy analysis clearly demonstrates that the grain boundaries are more resistive than the grain in $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ 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

$$\sigma(\omega) = \omega \epsilon_0 \epsilon' \tan \delta, \quad (3)$$

where ω is the angular frequency and ϵ_0 is the vacuum permittivity. Figure 9 (a) shows frequency dependence of a.c. conductivity ($\sigma_{\text{a.c.}}$) at various temperatures for $\text{GaFe}_{1.85}\text{Cr}_{0.15}\text{O}_3$. 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 [17]

$$\sigma(\omega) = \sigma_{\text{d.c.}} + A\omega^n, \quad (4)$$

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 ($\sigma_{d.c.}$). The resulting $\sigma_{d.c.}$ is plotted as a function of reciprocal temperature in Figure 9 (b) and it well obeys the Arrhenius law,

$$\sigma = \sigma_0 \exp (E_{cond}/K_B T),$$

where σ_0 is the pre-exponential term, E_{cond} is the conduction activation energy, and K_B is the Boltzmann constant. From the fitting E_{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 $GaFe_{1-x}Cr_xO_3$ ($x=0.05, 0.1$ 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 $Fe^{3+}-O-Fe^{3+}$ superexchange interaction strength when the Cr^{3+} ions replaces some of the Fe ions. The frequency dependent maxima in the imaginary electric modulus at various temperatures are found to obey Arrhenius law with activation energies of ~ 0.22 and 0.27 eV, for $GaFe_{1-x}Cr_xO_3$, $x=0.1$ 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 $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.05, 0.1, 0.15$) ceramic samples. (b) Rietveld analysis results of XRD pattern at RT for the $\text{GaFe}_{0.85}\text{Cr}_{0.15}\text{O}_3$ 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 $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ 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 $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ samples.

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

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

Figure 6. Frequency dependence of (a) ϵ' and (b) $\tan \delta$ of $\text{GaFe}_{0.85}\text{Cr}_{0.15}\text{O}_3$ 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 $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$ 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 $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$, $x=0.1$ and 0.15 .

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

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

Figure 1

Figure 2

Figure 3.

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1. Details of structure refinements with error bar and magnetic properties $\text{GaFe}_{1-x}\text{Cr}_x\text{O}_3$.

x	0.05	0.1	0.15
a ($\text{\AA}$)	8.7348(9)	8.7532(4)	8.7308(7)
b ($\text{\AA}$)	9.3799(1)	9.3776(5)	9.3756(4)
c ($\text{\AA}$)	5.0771(2)	5.0769(9)	5.0765(5)
V ($\text{\AA}^3$)	415.98(1)	415.78(3)	415.55(3)
Reliability factors			
R _p	10.3	9.90	10.1
R _{wp}	9.34	8.30	8.73
R _B	4.84	4.56	5.06
X 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

- [1] Gajek M, Bibes M, Fusil S, Bouzehouane K, Fontcuberta J, Barthelemy A, and Fert A 2007 *Nature Mater.* **6** 296.
- [2] Wang K F, Liu J M., and Ren Z F 2009 *Adv. Phys.* **58** 321.
- [3] Arima T, Higashiyama D, Kaneko Y, He J.P, Goto T, Miyasaka S, Kimura T, Oikawa K, Kamiyama T, Kuumai R, Tokura Y 2004 *Phys.Rev.B* **70** 064426.
- [4] Mohamed M Bakr, Senyshyn A, Ehrenberg H and Fuess H 2010 *J. Alloys Compd.* **492** L20-L27.
- [5] Taguchi H 1997 *J. Solid State Chem.* **131** 108.
- [6] Belayachi A, Loudghiri E, El Yamani M, Nouges M, Dormann J L and Taibi M 1998 *Ann. Chim. Sci. Mater.* **23** 297.
- [7] Kuznetsov Maxim V, Pankhurst Quentin A, Parkin Ivan P and Morozov Yury G 2001 *J. Mater. Chem.* **11** 854.
- [8] Li J H and Sun Q C 2008 *Rare Metals* **27** 362.
- [9] Yang Z P, Zhang R, Yang L L, and Chang Y F 2007 *Mater. Res. Bull.* **42** 2156.
- [10] Rodriguez-Carvajal J 1993 *Physica B (Amsterdam)* **192** 55.
- [11] Chae Kwang Pyo, Lee Young Bae, Lee Jae Gwang and Lee Sung Ho 2000 *J. Magn. Magn. Martter.* **220** 59.
- [12] Fang H C, Yang Z, Ong C K, Li Y, and Wang C S 1998 *J. Magn. Magn. Mater.* **187** 12.
- [13] Lee S W, An S Y, Ahn G Y, and Kim C S 2000 *J. Appl. Phys.* **87** 6238.
- [14] Kim Kwang Joo, Lee Hee Jung, Lee Jung Han, Lee Seungho, and Kim Chul Sung 2008 *J. Appl. Phys.* **104** 083912.
- [15] Cole MW, Hubbard C, Ngo E, Ervin M and Wood M 2002 *J Appl Phys* **92** 475.
- [20] Hu Mei-feng, Zhuo Yue, Wang Sheng-xiang and Tian Yu 2008 *J Mater. Sci.* **43** 3162.
- [17] Jonscher A.K, *Dielectric Relaxation in Solids*, Chelsea Dielectric Press, London, 1983.
- [18] Singh N K, Choudhary R N P and Panigrahi A 2002 *Matter. Lett.* **57** 36.
- [19] Dutta Alo and Sinha T P 2007 *Phys.Rev.B* **76** 155113.
- [20] Dutta Alo and Sinha T P 2010 *Physica B* **405** 1475.
- [21] Hsiao Yu-Jen, Chang Yee-Shin, Fang Te-Hua, Chai Yin-Lai, Chung Chao-Yu and Chang Yen-Hwei 2007 *J. Phys. D: Appl. Phys.* **40** 863
- [22] Dwivedi R K, Kumar D and Parkash O 2001 *J.Mater.Sci.* **36** 3649.
- [23] Du Yi, Cheng Zhen Xiang, Dou Shi Xue, Shahbazi Mahboobeh and Wang Xiao Lin 2010 *Thin Solid Films*.
- [24] Kroger F A and Vink H 1956 *J.Solid state Phys.* **3** 307.
- [25] Idress M, Nadeem M and Hassan M M 2010 *J.Phys.D:Appl.Phys.* **43** 155401.
- [26] Tanaka M, Siratori K and Kimizuka N 1984 *J. Phys. Soc. Jpn.* **53** 760.
- [27] Khomchenko V A, Kiselev D A, Vieira J M, Jian J.,Kholkin A L, and Lopes A M L , Porelov Y G, Araujo J P and Maglione M 2008, *J.Appl.Phys.* **103** 024105
- [28] Macdonald J R and Barsoukov E, *Impedance spectroscopy: Theory, Experiment, and application*, 2nd ed., Wiley-Interscience, New Jersey, 2005.
- [29] Molak A, Paluch M, Pawlus S, Klimontko J, Ujma Z and Gruszka I 2005 *J.Phys. D: Appl. Phys.* **38** 1450.
- [30] Bharti Chandrahas and Sinha T P 2010 *Solid State Sci.* **12** 498
- [31] A.R. James, S. Priya, K. Uchino and K. Srinivas J. *Appl. Phys.* **90** (2001), p. 3504
- [32] Macdonald J R, *Impedance spectroscopy*, Wiley, New York, 1987.
- [33] Behera Banarji, Nayak P and Vhoudhary R.N.P/ 2007 *J. Alloy Comp.* **436** 226.