ELECTRICAL PROPERTIES OF Cr^{+3} SUBSTITUTED $LaFe_{1-x}Cr_xO_3$

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Single phase $LaFe_{1-x}Cr_xO_3$ (*x*= 0, 0.1, 0.2, 0.3, 0.4, 0.5) compounds were prepared by sol-gel method. The structural phase purity was confirmed by X-ray diffraction pattern. Measurement of dielectric constant (*ε*) and dielectric loss (*tanδ*) as a function of temperature (50-350 ^oC) at different frequencies reveal a magnetic phase transition above room temperature. Transition temperature decreases with increase in Cr^{+3} substitutions. DC electrical resistivity also shows strong dependence upon Cr^{+3} concentration 'x'. Estimation of activation energy has suggested P-type semiconducting behaviour for the compounds.

1. Introduction

The orthoferrite $LaFeO_3$ (LFO) is a very well-known canted antiferromagnetic material with high value of Neel temperature ($T_N \approx 740K$) [1,2]. It is chemically stable in both reducing and oxidizing atmosphere. LFO with substitution on both *A* and *B* sites show many useful properties like high electrical conductivity, thermal stability, high dielectric constant, low dielectric loss, moderate permittivity, polarizability, ferroelectricity, piezoelectricity and high oxygen ion conductivity [3,4]. These properties have made these compounds suitable for application in oxygen permeable membrane, catalytic activity in the complex oxidation of hydrocarbons, catalytic combustion of methane, sensors, microwave dielectrics, hot electrode for magneto hydrodynamic [MHD] power generation and solid electrolytes [5-10]. Undoped LFO under ambient conditions is an insulator and crystallizes in orthorhombic structure Pbnm [11, 12]. Remarkably, the existence of multiferroic properties, magnetocapacitance and high dielectric constant has been observed [13]. Regarding structure stability, it contains only trivalent metal ions which make it interesting system for investigation with isovalent substitutions. In particular, the replacement of Fe^{+3} by Cr^{+3} and its effect on structural, magnetic and other properties have been partially discussed [14, 15]. Particularly, the substitution of Cr^{+3} seems to decrease the dielectric loss and stabilizes the dielectric properties [16], more intensive investigation is needed to fully reveal effect of Cr^{+3} substitution on the electrical properties of LFO.
We report on the capacitance, dielectric loss, P-E hysteresis loops and resistivity for Cr^{+3} substituted LFO compounds at various temperatures. Contrary to usual solid state reaction synthesis route that involves several heating processes involving calcination and sintering at high temperature which results in loss of energy and time [17-19], we prepared the samples by sol-gel method with better homogeneity and small grain size. This low temperature (≈ 950 ^oC) synthesis compared to solid state reaction one (≈ 1500 ^oC) also helped in reducing leakage current and oxygen vacancies due to volatile behaviour of CrO_3.

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2. Experimental details

Polycrystalline $LaFe_{1-x}Cr_xO_3$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) were prepared by sol-gel auto combustion method. Analytical grade metal nitrates $La(NO_3)_3.6H_2O$, $Fe(NO_3)_3.9H_2O$, $C_6H_8O_7.H_2O$ and $Cr(NO_3)_3.9H_2O \geq$ (99 %purity) were dissolved in deionized water in stoichiometric ratio. Citric acid in 1:3 ratio with respect to metal nitrates was added as complexant and stirred continuously. During stirring ammonia solution was added drop wise to maintain the pH value equal to 7. The transparent mixture was stirred at 60 ^{o}C for 10 hours to obtain gel which was then kept at 70 ^{o}C to obtain dried gel. Gel was burnt during auto combustion process and foamy powder was achieved undergoing following chemical reaction;

$$La(NO_3)_3.6H_2O + [Fe(NO_3)_3.9H_2O]_{1-x} + [Cr(NO_3)_3.9H_2O]_x + C_6H_8O_7.H_2O + NH_3.H_2O \rightarrow$$
$$LaFe_{1-x}Cr_xO_3 + \ell CO_2 \uparrow + mN_2 \uparrow + nH_2O \uparrow \qquad (1)$$
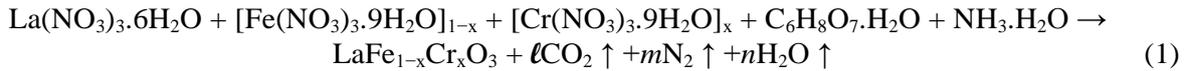
The powder was grinded and sintered at 950 ^{o}C for 3 hours in a box furnace (Heraeus, D-6450 Hanau, Germany). The sintered powder was pressed into pellets at 50 kN pressure and annealed in air at 800 ^{o}C for 1 hour in order to remove defects and oxygen deficiency that may occurred because of heat treatment. The pure phase of these prepared samples was determined by XRD using Cu K_α radiation. Later on, the samples were cut into 2 mm rectangular shape pieces for the measurement of dielectric properties. Ag paste and Ag wire were used to make electrode and connections. Dielectric constant was measured on heating the sample from 50 to 350 ^{o}C temperature in 10-100 kHz frequency range using a LCR meter (Agilent 4984A). Ferroelectric hysteresis loops were measured both at room and liquid nitrogen temperature at a frequency of 1 Hz using an aixACCT EASY CHECK 300 ferroelectric tester and Matsusada high voltage amplifier. DC electrical resistivity was measured by two probe method on heating the samples from room temperature to 150 ^{o}C (423K) using a source meter (Keithley 2400C).

3. Results and discussion

Fig. 1 shows the XRD pattern obtained at room temperature for $LaFe_{1-x}Cr_xO_3$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5). All peaks are indexed according to JCPDS card no. 37-1493. The absence of un-indexed peak confirms the single phase of the prepared samples. $LaFe_{1-x}Cr_xO_3$ crystallizes in orthorhombic structure with space group *Pbnm* (62). Peaks clearly shift towards higher 2θ degree with the increase in Cr doping; for example, the (121) peak at $2\theta = 32.14$ for x = 0 shifts to 32.40 for x = 0.5, which may suggest decrease in cell size. It is in accordance to the previous reports [20] because Cr^{+3} has smaller ionic radii (0.615 ^{o}A) as compared to Fe^{+3} ion (0.645 ^{o}A) in high spin state with a coordination number of 6 [21]. These results also confirm the gradual replacement of Cr^{+3} ions with Fe^{+3} ions.
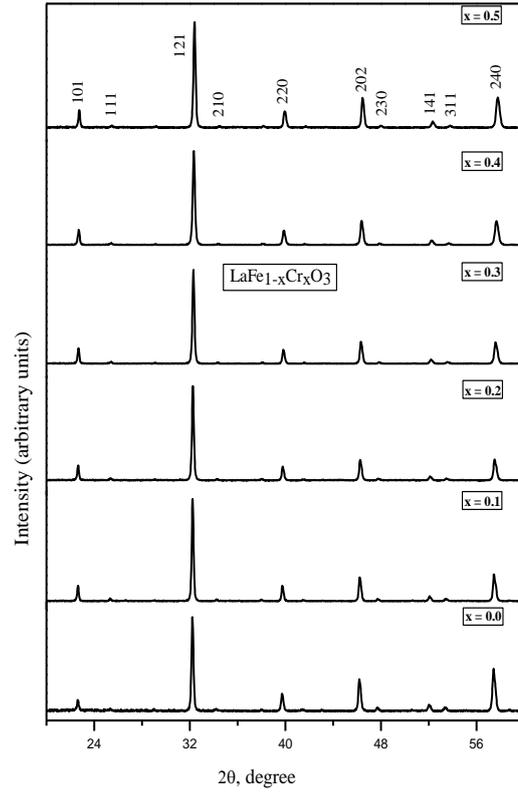
Fig. 1. Powder XRD patterns for LaFe$_{1-x}$Cr$_x$O$_3$ (0.0 ≤ x ≤ 0.5).

Dielectric response as a function of temperature for different samples is shown in Fig. 2. On increasing Cr-content in LFO, two features clearly observed are; one upward shift of dielectric constant (ϵ_r) which exhibits a peak centered at around 250 ^{o}C for x = 0 and second its shift to low temperature; i.e. around 60 ^{o}C for x = 0.4. The observed trend is found similar to the ones reported also for Mn^{+3} doped transition metal oxide systems [22, 23].
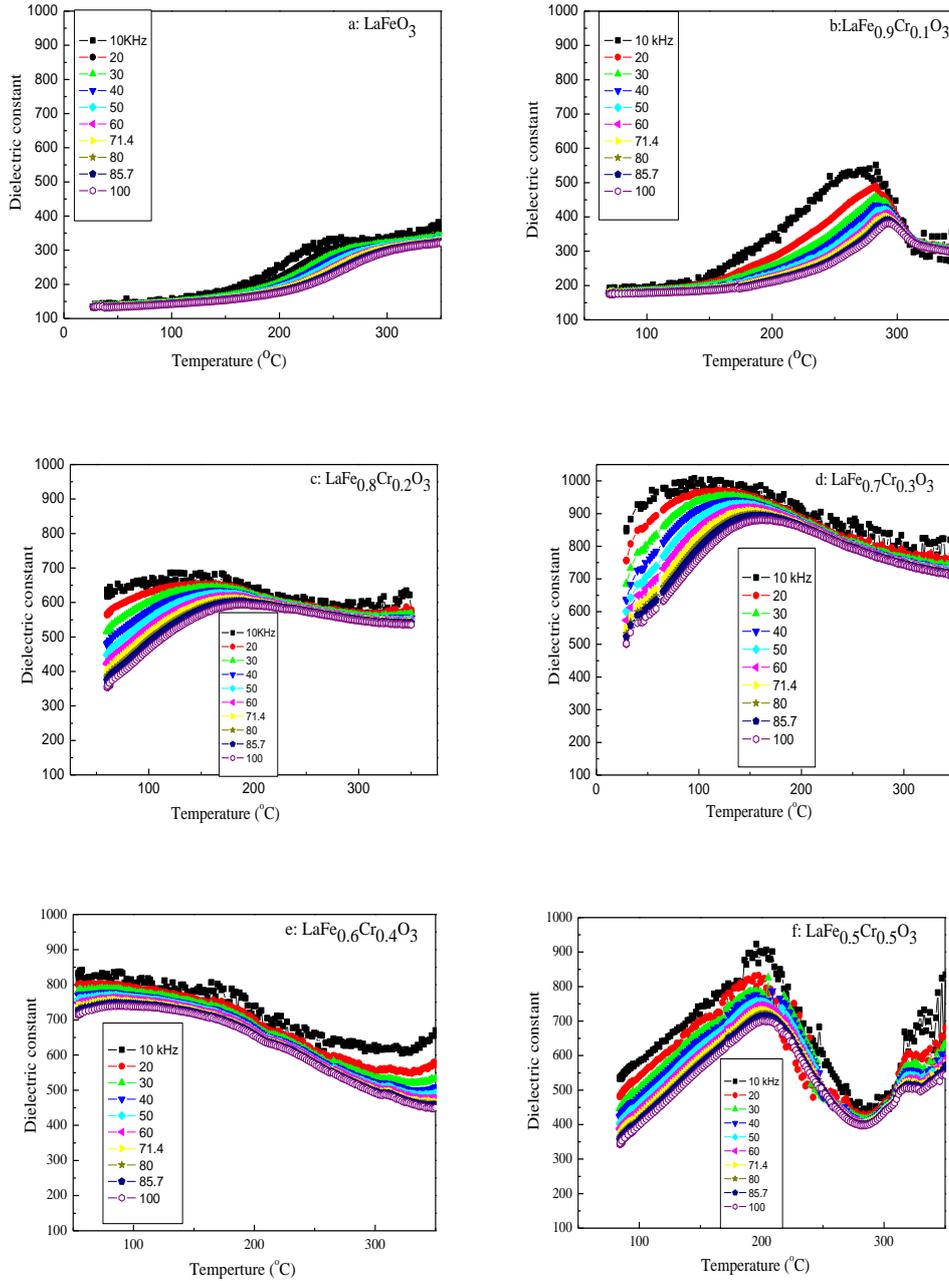
Fig. 2. Dielectric constant as a function of temperature
at different frequencies for LaFe$_{1-x}$Cr$_x$O$_3$.

Monotonic increase in dielectric constant at 10 kHz is observed on increasing temperature up to 230 ^{o}C, i.e. a temperature close to the Curie temperature (202 ^{o}C) for LFO. On substitution of Cr^{+3}, considerable decrease in Neel temperature from 467 ^{o}C (740 K) in LFO to 7 ^{o}C (280 K) in *LaCrO$_3$* has been reported [24]. So transition in Cr^{+3} substituted samples can be ascribed due to antiferromagnetic to paramagnetic phase transition. Dielectric constant in ferrites is also strongly dependant on magnetic ordering [25]. At temperature lower than transition temperature, it is difficult for domain walls to move and therefore, less extrinsic contribution to the dielectric constant is expected. At around transition temperature domain walls become very active as thermal energy is nearly equal to the potential barrier for domain movement. It results in high dielectric response near

transition temperature. At temperature well above transition temperature, domain walls disappear which results in small dielectric response again. Dielectric loss (*tanδ*) as a function of temperature shows that it increases on increasing the Cr-content in LFO, which may be associated to a change in dc conductivity at higher temperature.
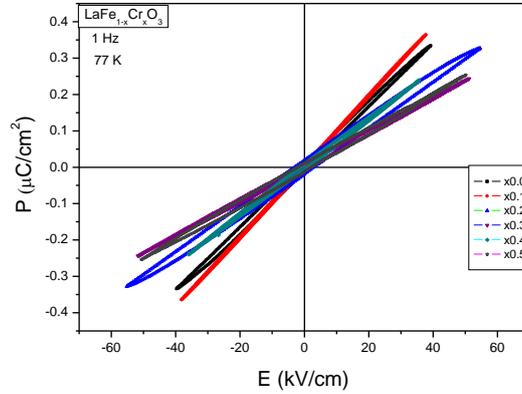
Fig. 3. P-E hysteresis loops for LaFe$_{1-x}$Cr$_x$O$_3$ at 77 K

P-E hysteresis loops measured at liquid nitrogen temperature (77 K) are shown in Fig. 3. At room temperature (not shown), only *LaFe$_{1-x}$Cr$_x$O$_3$* for x = 0 shows anti-ferroelectric behaviour with value of coercive field (E$_c$), maximum polarization (P$_{max}$) and remnant polarization (P$_r$) is 0.698 *kV/cm*, 0.467 *μC/cm^2* and 0.084 *μC/cm^2* respectively. At 77 K, it can be seen that P$_{max}$ and E$_c$ values decrease with increasing 'x' which is consistent with the previous reports [19, 26] in which *LaCrO$_3$* was found to have paraelectric/non-hysteric behaviour at all temperatures. However, we have observed a ferroelectric behaviour for x = 0.2, at a temperature of 77 K. This shift from non hysteric to hysteric behaviour may be attributed to the reorientation of dipoles which is related to the motion of domain walls. This unique behaviour of Cr doped *LaFeO$_3$* opens up new horizon to look further for multiferroicity below 77 K.
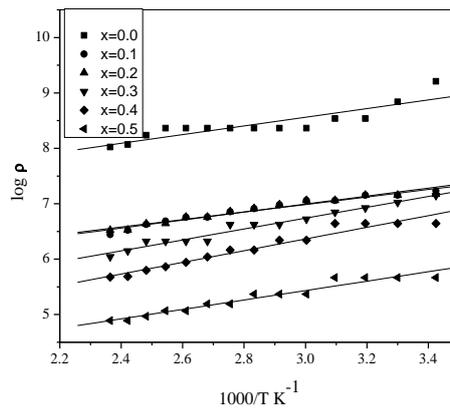
Fig. 4. Variation of Resistivity (ρ) with temperature for LaFe$_{1-x}$Cr$_x$O$_3$.

Table I: Activation energy Vs Cr^{+3} concentration for $LaFe_{1-x}Cr_xO_3$.

Cr^{+3} concentration	Activation Energy (eV)
0.0	0.477
0.1	0.456
0.2	0.436
0.3	0.403
0.4	0.368
0.5	0.348

Temperature dependent electrical resistivity has been measured for $LaFe_{1-x}Cr_xO_3$ (x = 0.1, 0.2, 0.3, 0.4, 0.5) in the temperature range 293-423 K in order to study the conduction process in these compounds as shown in Fig.4. The ρ decreases exponentially with increase in temperature suggesting a typical semiconducting behaviour. This temperature induced change in the ρ may be due to thermally activated drift mobility of charge carriers which suggests a hopping conduction mechanism. The electrical resistivity of the material is decreased significantly because of the low resistivity of the material phase [27]. The Arrhenius relation $\rho/T = \rho_o exp(Ea/k_BT)$, where ρ is the resistivity, ρ_o the constant, E_a activation energy and k_B is the Boltzmann constant, gives a linear $\log\rho$ versus 1000/T plot for small polaron conduction as shown in the Fig.4. Activation energy calculated from slope of $\log\rho$ versus 1000/T is tabulated in Table 1. For pure LFO activation energy value is comparable with those reported in literature [28]. ABO_3 oxides are generally considered as electronic conductors because close packed nature of perovskite structure restricts ionic conduction and activation energy for oxide ion conductors is mostly >0.9 eV. For n-type polaronic conduction their value is less than 0.2 eV and greater than 0.2 eV for p-type polaronic conduction of holes [29]. So the calculated activation energy suggests a p-type polaronic conduction in the Cr^{+3} substituted LFO system above room temperature.

4. Conclusion

Single phase Cr substituted $LaFe_{1-x}Cr_xO_3$ compound has been successfully prepared by sol-gel method and found that gradual substitution of Cr has no effect on the structure. On Cr substitution, the drastic change observed in dielectric behaviour is attributed to a phase transition from antiferromagnetic to paramagnetic above room temperature. The Cr substitution results in decrease of Neel temperature which may be caused by the intrinsic contribution by the activation of domain walls. Ferroelectric P-E curves show paraelectric behaviour in doped samples with small ferroelectric response at 77 K. Activation energy values calculated from DC electrical resistivity data reflects a p-type polaronic conduction in the system above room temperature.

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