Preparation of water soluble l-arginine capped CdSe/ZnS QDs and their interaction with synthetic DNA: Picosecond-resolved FRET study

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Studies on the structural, electrical and magnetic properties of LaCrO₃, LaCr₀.₅Cu₀.₅O₃ and LaCr₀.₅Fe₀.₅O₃ by sol–gel method

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A R T I C L E   I N F O

Article history:
Received 18 October 2011
Received in revised form 22 March 2012
Accepted 18 April 2012
Available online 25 April 2012

Keywords:
B. Sol–gel chemistry
C. Impedance spectroscopy
D. Dielectric properties
D. Magnetic properties

A B S T R A C T

The structural, electrical and magnetic properties of LaCr₀.₅M₀.₅O₃ (M = Cr³⁺, Cu²⁺ and Fe³⁺) synthesized by a sol–gel technique were studied. The X-ray diffraction pattern shows the structure to be orthorhombic and the size of the particles is around 100 nm as seen from the TEM images. The effects of Cu²⁺ and Fe³⁺ on the electrical properties of LaCrO₃ were studied using impedance spectroscopy at room temperature (RT). The properties of LaCr₀.₅Cu₀.₅O₃ were studied over a wide range of temperature from RT to 553 K. A maximum conductivity of 1.7 × 10⁻¹ S cm⁻¹ was observed for LaCr₀.₅Cu₀.₅O₃ at a measured temperature of 553 K. The impedance spectra indicate a negative temperature coefficient of resistance (NTCR) and also imply the conduction is through bulk of the material. The magnetic studies performed using a SQUID magnetometer interpret the antiferromagnetically ordered LaCrO₃ to behave ferromagnetically on the addition of Cu²⁺ and Fe³⁺, and the magnetization was found to be enhanced in the LaCr₀.₅Fe₀.₅O₃.

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1. Introduction

The lanthanum chromite, LaCrO₃ is a typical perovskite material with the general formula of ABO₃. The ideal perovskite structure, ABO₃, has a cubic symmetry and can be described as a three-dimensional network of corner-sharing BO₃ octahedra with BOB angles of 180°; most of which bear some extent of distortion. It displays some unique physical properties, such as high mechanical strength, high melting point (2400 °C), good electronic conductivity, a high thermal expansion coefficient, physical and chemical stability in oxidizing and reducing atmospheres, and the ability to withstand higher temperatures and electro-catalytic activity, which makes them useful in high temperature applications such as inter connectors in solid oxide fuel cells [1], sensors [2], catalysis, etc. It has been synthesized by various techniques such as the hydrothermal method [3], the sol–gel method [4], the citrate–gel method [5], the hydrazine method [6], etc.

In this study we report the effects on the structural, electrical and magnetic phenomena caused by the doping of both divalent (Cu²⁺) and trivalent (Fe³⁺) cations on LaCrO₃ synthesized by the sol–gel method. LaCrO₃ doped with various metal ions such as Li- and Sr [7], Mg, Ca- and Sr [8], Ca [9], Co [10], Sm³⁺- and Sr²⁺ [11], Cu-, Ni- and V [12], and Fe [13] were previously studied. It has already been discovered that the substitution of lower valent ions for Cr³⁺ or La³⁺ would enhance the sinterability, magnetization, and conductivity of lanthanum chromite [14]. The reason for considering sol gel as the synthetic method relies on the ability to obtain a homogeneous distribution of cations at the atomic scale and a uniform size in the nanometer range, with a rather simple technique that does not require high temperature and vacuum. To the best of our knowledge, a detailed analysis of electrical and magnetic studies of LaCr₀.₅M₀.₅O₃ (M = Cr³⁺, Cu²⁺ and Fe³⁺) has not been reported on materials synthesized by the sol–gel method. In addition, the conductance spectra were fitted by non-linear square fit method using Jonscher’s Power Law and discussed the detailed conducting mechanism also. The synthesized LaCr₀.₅M₀.₅O₃ were studied using XRD, FTIR, SEM, AC impedance spectroscopy and SQUID magnetometry in order to study the structural, electrical and magnetic properties.

2. Experimental method

LaCrO₃ was prepared by using La₂O₃ (Sigma–Aldrich), HNO₃, Cr(NO₃)₃·9H₂O (Himedia) as the starting precursors, citric acid (C₆H₈O₇) (Merck) and polyethylene glycol (M.W:400) were used as the chelating agent. In order to control the particle size and uniformity PEG was used as the carrier that leads to enhanced crystallization during heat treatment. For the typical synthesis of
5 g of LaCrO₃, the stoichiometric amounts of La₂O₃ (3.41 g) were fully dissolved in 2.8 ml of HNO₃, resulting in [La(NO₃)₃] with the liberation of voluminous gases. Then 8.37 g of [Cr(NO₃)₃]·9H₂O dissolved in 30 ml of double-distilled water was then added to the above mixed solution. 0.01 mol of a saturated citric acid solution and 10 ml of polyethylene glycol (M.W-400) were then added to the above solution. This solution was constantly stirred to form a uniform sol, followed by drying at 80 °C to obtain gel precursors. The gel precursor was heated continuously at a constant temperature of 80 °C. After 1½ h the gel was converted into powder form with evolution of dense white fumes that was calcined in a furnace for 4 h at temperatures ranging from 600 °C to 900 °C. For the synthesis of 0.5 mol Cu and Fe doped LaCrO₃, i.e., LaCr₀.₅Cu₀.₅O₃ and LaCr₀.₅Fe₀.₅O₃, the stoichiometric quantities of [Cu(NO₃)₂]·6H₂O (1.92 g) and [Fe(NO₃)₃]·9H₂O (4.13 g) were dissolved in 15 ml of distilled water individually and the above mentioned experimental procedure was repeated.

The phase purity and crystallinity of LaCrO₃, LaCr₀.₅Cu₀.₅O₃, and LaCr₀.₅Fe₀.₅O₃ were identified by powder X-ray diffraction analysis with an XPERT-PRO diffractometer using CuKα radiation with a wavelength of 1.5405 Å. Their corresponding lattice parameters are calculated using CELREF software. The surface morphology and particle size were analyzed by scanning electron microscopy (JEOL-JEM 100SX) at an accelerating voltage of 20 kV. The FTIR spectra of the samples were recorded in the range of 4000–400 cm⁻¹ with a Nicolet Avatar FTIR spectrophotometer. In order to proceed with the electrical studies, the resultant calcined powder was then pressed into pellet form and heat treated again at 200 °C for 1 h. For better ohmic contact, a silver paste was applied on both sides of the pellet before it was sandwiched between the two electrodes of the sample holder. The ac electrical conductivity measurement was done with a computer controlled impedance analyzer, HIOKI 3532 LCR HITESTER, in the frequency of 50 Hz to 10 kHz. The magnetic properties were measured using a Superconducting Quantum Interference Design (SQUID) magnetometer MPMS XL7 in the temperature range of 2–350 K and a 0–5 T field. The temperature-dependent susceptibility was measured using the DC procedure. The sample was cooled to 2 K under a zero magnetic field. A low magnetic field (100.0 mT) was applied and data were collected from 2 K to 350 K (zero-field cooled, ZFC). Field-cooled (FC) measurements were performed from 2 K to 350 K with an applied field during the cooling process.

3. Results and discussion
3.1. Structural properties

In order to find the optimized compound formation temperature, LaCrO₃ is calcined at different temperatures from 600 to 900 °C. The XRD patterns for LaCrO₃ calcined at different temperatures (600–900 °C) for 4 h are shown in Fig. 1. The LaCrO₃ calcined at 600 °C for 4 h shows a crystalline nature with too many short and blunt peaks corresponding to the majority impurity phases of LaCrO₄ and minor peaks of Cr₂O₃. LaCrO₄ decomposes into LaCrO₃ and 0.5Cr₂O₃ as the temperature is raised to 700 °C. It is well known [15] that LaCrO₄ is an inevitable intermediate phase before it transforms into LaCrO₃ single phase. On the other hand LaCrO₃ calcined at 800 and 900 °C shows a sharp and well-defined peak, indicating that the prepared sample possesses a single phase and a highly crystalline nature. The calculated XRD parameters such as lattice constant, cell volume, crystallite size and surface area for the three different calcinations temperatures (700, 800 and 900 °C) are given in Table 1. The crystallite sizes calculated using the Debye–Scherer formula are in the range of nm, which increases with increasing calcination temperature due to the particle agglomerations. The specific surface area of the sample has been calculated using the following formula, \(d = 6/\rho s^{2/3}\) g/cm³, where \(d\) is the average particle size, \(\rho\) is the density and \(s\) is the specific surface area. It can be seen that the surface area decreases with the increase in temperature. It is well known that the surface area is indirectly proportional to the size of the particles.

Fig. 2 shows the XRD pattern of LaCrO₃, LaCr₀.₅Cu₀.₅O₃, and LaCr₀.₅Fe₀.₅O₃ particles calcined at 900 °C. The observed peaks are sharp and with a high intensity, which indicates that the prepared sample possesses a high crystalline nature with a single-phase formation of LaCrO₃. In addition to that, some CuO peaks were observed in the LaCr₀.₅Cu₀.₅O₃ samples. The calculated lattice parameter values of LaCrO₃ are \(a = 5.49\) Å, \(b = 7.75\) Å and \(c = 5.51\) Å, which are in good agreement with the standard pattern [JCPDS file No. 89-8770] and are attributed to the Pnma space group with orthorhombic structure [16]. The lattice parameter values of LaCr₀.₅Cu₀.₅O₃ are \(a = 5.49\) Å, \(b = 7.78\) Å and \(c = 5.50\) Å, and the corresponding lattice parameter values of LaCr₀.₅Fe₀.₅O₃ are

![Fig. 1. XRD pattern of LaCrO₃ calcined at (a) 600 °C, (b) 700 °C, (c) 800 °C and (d) 900 °C.](image-url)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice constants</th>
<th>Cell volume (Å³)</th>
<th>Crystallite size (nm)</th>
<th>Surface area (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO₃—700 °C</td>
<td>(a = 5.48) Å</td>
<td>234.716</td>
<td>33</td>
<td>104</td>
</tr>
<tr>
<td>LaCrO₃—800 °C</td>
<td>(a = 5.48) Å</td>
<td>234.543</td>
<td>37</td>
<td>95</td>
</tr>
<tr>
<td>LaCrO₃—900 °C</td>
<td>(a = 5.49) Å</td>
<td>234.904</td>
<td>43</td>
<td>82</td>
</tr>
</tbody>
</table>

Table 1: XRD parameters.
compared to Cr–O and hence the packing density is lower for Fe doped sample leading to higher cell volume. The difference in cell volume indirectly enumerates the substitution effect of Cu$^{2+}$ and Fe$^{3+}$ in the Cr$^{3+}$ position. In fact, the cell volume of LaCr$_{0.5}$Cu$_{0.5}$O$_3$ should be high due to the larger ionic size of Cu$^{2+}$ (0.73 Å) when compared with Fe$^{3+}$ (0.64 Å) and Cr$^{3+}$ (0.63 Å) cations. The observed low cell volume of LaCr$_{0.5}$Cu$_{0.5}$O$_3$ may be due to the segregation of CuO as a secondary phase. The calculated X-ray density values are 6.753 g/cm$^3$, 6.894 g/cm$^3$, 6.735 g/cm$^3$ for LaCrO$_3$, LaCr$_{0.5}$Cu$_{0.5}$O$_3$, and LaCr$_{0.5}$Fe$_{0.5}$O$_3$, respectively. These lattice density values are in good agreement with the reported value of 6.772 g/cm$^3$ for LaCrO$_3$ (JCPDS file No. 89-8770).

The FT-IR spectrum for LaCrO$_3$ calcined at 900 °C and scanned in the range of 400–4000 cm$^{-1}$ (figure not given) showed two main absorption peaks. The higher frequency band extends from 800 to 475 cm$^{-1}$ with a center of 540 cm$^{-1}$ due to a stretching vibration and the low frequency band extends from 475 to 300 cm$^{-1}$ with a center of 400 cm$^{-1}$ due to a bending vibration [17] of metal oxygen bonds. The high frequency band of 582.23 cm$^{-1}$ corresponds to the Cr–O stretching vibration of LaCrO$_3$. For LaCr$_{0.5}$Cu$_{0.5}$O$_3$ and LaCr$_{0.5}$Fe$_{0.5}$O$_3$, the high frequency bands of 596.05 cm$^{-1}$ and 576.02 correspond to the Cu–O stretching vibration and Fe–O stretching vibration, respectively.

### 3.2. Morphological analysis

Fig. 3(a–c) represents the SEM image of LaCrO$_3$, LaCr$_{0.5}$Cu$_{0.5}$O$_3$, and LaCr$_{0.5}$Fe$_{0.5}$O$_3$. It can be seen that the LaCrO$_3$ and LaCr$_{0.5}$Cu$_{0.5}$O$_3$ particles are finely distributed without much agglomeration with a slightly distorted shape and sizes were in the sub micrometer range. On the other hand, LaCr$_{0.5}$Fe$_{0.5}$O$_3$ exhibits an agglomerated morphology and has both smaller and larger particles. The TEM image of LaCrO$_3$ is given in Fig. 3(d) and the inset is its corresponding SAED pattern. These images show a dot pattern, confirming the single crystalline nature of the material. To examine the actual size of the particles produced by the sol–gel
method, the TEM image was recorded. The particles were irregular in shape. The micrographs show the agglomerates of the particles, which were found to be highly dense.

3.3. Electrical properties

3.3.1. Impedance spectral analysis

The complex impedance spectroscopy is a powerful technique for studying the electrical behavior of the sample. The ac impedance response of a material is due to the number of R–C parallel cells, and the impedance associated with a single R–C cell is given by the following:

\[ Z' = Z - jZ'' = R_a - \frac{j}{ωC_a} \]

(1)

where \( Z' \) and \( Z'' \) are the real and imaginary parts of \( Z \).

Fig. 4 represents the Cole–Cole plot of LaCrO\(_3\), LaCr\(_{0.5}\)Cu\(_{0.5}\)O\(_3\), and LaCr\(_{0.5}\)Fe\(_{0.5}\)O\(_3\) collected at room temperature. The inset (a) is an enlarged view of LaCrO\(_3\) and LaCr\(_{0.5}\)CuO\(_3\). A single semicircle has been observed for all the three samples that correspond to the parallel combination of bulk resistance, \( R_b \), and bulk capacitance, \( C_b \), which infers that the conduction is through the bulk of the material, i.e., grain interior [18]. The value of \( R_b \) can be obtained by intercepting the semicircle on the X-axis, and the capacitance value can be calculated using \( 2πfR_bC_b = 1 \). The capacitance value thus obtained is in the order of \( 10^{-12} \) F. From this figure it can be seen that the center of the semicircle is depressed below the real axis, which indicates that the relaxation of ions are non-Debye in nature [19]. The ionic conductivity of the sample is calculated using the \( σ = (\ln R/\ln A) S \ cm^{-1} \) equation, where \( R \) is the bulk resistance of the sample, \( A \) is the thickness of the sample, and \( \ln \) is the area of the sample. The calculated conductivity values for all three samples are given in Table 2. LaCr\(_{0.5}\)CuO\(_3\) possesses a higher value of conductivity than LaCr\(_{0.5}\)FeO\(_3\) and LaCrO\(_3\). The conductivity is enhanced since the Cu\(^{2+}\) substitution creates cation vacancies according to the equation Cr\(^{3+}\) = Cu\(^{2+}\) + e\(^-\). Similar observations have already been reported by Berger et al. for LaCr\(_{1-x}\)M\(_{x}\)O\(_3\) (M = Ni, Cu; \( x = 0–0.2 \)) materials [20]. The inset (b) of Fig. 4 shows the Cole–Cole plot of Cu-doped LaCrO\(_3\) that is measured in a temperature range of 300–533 K, since the maximum value of conductivity is obtained for the copper-doped sample. From the figure, it is seen that the value of bulk resistance decreases with the increase in temperature, i.e., a negative temperature co-efficient of resistance (NTCR), which indicates that the material is semi-conducting. In addition, the value of ionic conductivity increases with the increase in temperature, which is due to the increase in the thermally activated mobility of the charge carriers according to the hopping conduction mechanism [21]. The detailed conductivity mechanism is given in the conductance spectral analysis.

The variations of the real part of impedance (\( Z' \)) with a frequency of LaCrO\(_3\), LaCr\(_{0.5}\)CuO\(_3\), and LaCr\(_{0.5}\)FeO\(_3\) are given in Fig. 5. The value of \( Z' \) is found to be higher for Fe-doped LaCrO\(_3\) than for the parent and undoped sample. This is due to the lattice distortion caused by the addition of Fe in LaCrO\(_3\), resulting in a decrease in the conduction pathway of the mobility charge carriers [22]. Hence, the impedance increases, which causes the conductivity to be decreased well below the parent one. The variation in the real part of impedance \( Z' \) with a frequency of Cu-doped LaCrO\(_3\) at various ranges of temperatures is given as an inset (a) in Fig. 5. It is seen that the value of \( Z' \) decreases with the increase in temperature and frequency, indicating that the sample might increase in conductivity with the increase in temperature and frequency, which can be confirmed from the conductance spectral analysis. For the entire range of temperature, the curve merges together at higher frequencies, which is due to the release of space charge that is built up at the grain boundaries [23]. The decrease in the \( Z' \) value with the increase in temperature clearly indicates that the material possesses temperature-dependent electrical relaxation phenomena.

Fig. 6 shows the variation of \( Z'' \) with a frequency for LaCrO\(_3\), LaCr\(_{0.5}\)CuO\(_3\), and LaCr\(_{0.5}\)FeO\(_3\) at room temperature. The enlarged view of LaCrO\(_3\), LaCr\(_{0.5}\)CuO\(_3\), and LaCr\(_{0.5}\)FeO\(_3\) are shown in Fig. 6 (inset (a)). Among the three samples, the Fe-doped LaCrO\(_3\) has a maximum value of \( Z'' \). The doping of Fe increases the net impedance of the sample, since the addition of iron causes a net

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. (K)</th>
<th>( R_b (Ω) ) (± 0.0001)</th>
<th>( σ_b ) (S cm(^{-1}))</th>
<th>( σ_d ) (Ω cm) (± 0.0001)</th>
<th>( n ) (± 0.0001)</th>
<th>( μ ) cm(^2)/V-s</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO(_3)</td>
<td>300</td>
<td>5367</td>
<td>1.60 × 10(^{-3})</td>
<td>1.70 × 10(^{-5})</td>
<td>0.571</td>
<td>2.013</td>
</tr>
<tr>
<td>LaCr(_{0.5})FeO(_3)</td>
<td>300</td>
<td>142,099.2</td>
<td>2.76 × 10(^{-6})</td>
<td>2.80 × 10(^{-6})</td>
<td>7.185</td>
<td>0.911</td>
</tr>
<tr>
<td>LaCr(_{0.5})CuO(_3)</td>
<td>300</td>
<td>14446.6</td>
<td>1.261 × 10(^{-4})</td>
<td>1.27 × 10(^{-4})</td>
<td>2.018</td>
<td>1.872</td>
</tr>
<tr>
<td>333</td>
<td>1295.3</td>
<td>651.55</td>
<td>2.796 × 10(^{-9})</td>
<td>2.80 × 10(^{-9})</td>
<td>4.508</td>
<td>1.626</td>
</tr>
<tr>
<td>413</td>
<td>470.93</td>
<td>368.68 × 10(^{-9})</td>
<td>3.87 × 10(^{-9})</td>
<td>5.774</td>
<td>1.476</td>
<td>8.7 × 10(^{2})</td>
</tr>
<tr>
<td>453</td>
<td>264.65</td>
<td>6884 × 10(^{-9})</td>
<td>6.88 × 10(^{-9})</td>
<td>8.385</td>
<td>1.359</td>
<td>11 × 10(^{2})</td>
</tr>
<tr>
<td>493</td>
<td>174.03</td>
<td>1047 × 10(^{-4})</td>
<td>10 × 10(^{-4})</td>
<td>13.141</td>
<td>1.042</td>
<td>16.7 × 10(^{2})</td>
</tr>
<tr>
<td>533</td>
<td>106.01</td>
<td>1718 × 10(^{-3})</td>
<td>1.70 × 10(^{-3})</td>
<td>15.204</td>
<td>1.902</td>
<td>17.8 × 10(^{2})</td>
</tr>
</tbody>
</table>
LaCr$_{0.5}$Fe$_{0.5}$O$_3$, frequency increases due to broadening of the peak and relaxation process in the material. As the temperature increases, there is a shift in the peak toward the high frequency side that arises due to the presence of a space charge in the material [25].

LaCrO$_3$ and LaCr$_{0.5}$Cu$_{0.5}$O$_3$ possess a lower value of the impedance at room temperature (inset shows the real part of impedance vs frequency of LaCr$_{0.5}$Cu$_{0.5}$O$_3$ at different temperatures). The inset (b) of Fig. 6 represents the variation of the imaginary part of impedance ($Z''$) with frequency at different temperatures of Cu doped LaCrO$_3$. The spectra show a single peak at all temperatures whose center does not lie at the same frequency indicating the non-Debye type of relaxation [24]. The broadening of the peak increases with increase in temperature which indicates the electrical relaxation process in the material to be temperature dependent that is due to the localized electrons responsible for conduction mechanism. As the temperature is increased, there is a shift in the peak toward the high frequency side that arises due to the presence of a space charge in the material [25].

The dc conductivity ($\sigma_{dc}$), frequency exponent (n), hopping frequency ($\omega_0$), mobility ($\mu$), and carrier concentration (N), could be found on the basis of Jonscher’s power law by a non-linear fitting for all the conductivity graphs. The non-linear curve fitting of LaCr$_{0.5}$Cu$_{0.5}$O$_3$ at 300 K is shown in Fig. 8, and the derived conductivity parameters are tabulated in Table 2. The dc conductivity value obtained from the conductance spectra agree well with that from the Cole–Cole plot. According to the power law, $\sigma(\omega)$ is directly proportional to $\omega^n$. The physical meaning of n is, if $n \leq 1$, then the hopping of charge carriers is translational motion.
with a sudden hopping and if \( n \geq 1 \) then it involves a localized hopping [27]. It can be seen from Table 2 that the value, \( n \), is greater than 1 for \( \text{LaCrO}_3 \) and \( \text{LaCr}_{0.5}\text{Cu}_{0.5}\text{O}_3 \), which indicates that the hopping motion is localized and is less than 1 for \( \text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3 \). This infers the translation motion involved in the iron-doped sample. From the figure, it is seen that the copper-doped lanthanum chromite shows a higher conductivity at all the applied frequencies and has a value of \( 1.7 \times 10^{-4} \text{ S cm}^{-1} \). The doping of divalent ion, \( \text{Cu}^{2+} \), causes \( \text{Cr}^{3+} \) transition to \( \text{Cr}^{4+} \), producing more holes in the valence band. This results in the reduction of the energy band gap, thereby increasing the conductivity [28]. It has already been deduced from impedance spectral analysis for the enhancement in the conductivity of the copper-doped sample that the addition of \( \text{Cu}^{2+} \) creates cation vacancies. It can also be seen that there is a decrease in the conductivity of Fe-doped \( \text{LaCrO}_3 \) which is due to the grain boundary effect. The donor cations play an important role in the conduction process. During the motion of charge carriers through the material, several mobile carriers get trapped in the potential well. These donors create a donor level near the conduction band as the temperature is increased.

The conductance spectra of Cu-doped \( \text{LaCrO}_3 \) measured at different temperatures are given in Fig. 9. It can be seen that the conductivity increases with increasing temperature, and there is an onset of relaxation from the dc conductivity region to the dispersive region on increasing frequency that shifts toward the higher frequencies. The hopping frequency \( \omega_0 \) and the carrier mobility \( \mu \) increased with the increase in temperature. Thus, it can be concluded that the applied temperature enhances the mobility of the charge carriers, which leads to higher conductivity. The calculated dc conductivity is found to obey the Arrhenius relation, i.e.:

\[
\sigma_{dc} = \sigma_0 \exp \left(-\frac{E_a}{kT}\right)
\]

where \( \sigma_0 \) is the pre-exponential factor and \( E_a \) is the activation energy. The value of \( E_a \) is found to be 0.1508 eV for the \( \text{LaCr}_{0.5}\text{Cu}_{0.5}\text{O}_3 \), which suggests that a small amount of energy is required for the charge carrier for electrical conduction. The value of the activation energy is found to be lower for \( \text{LaCr}_{0.5}\text{Cu}_{0.5}\text{O}_3 \) than for \( \text{LaCrO}_3 \) (0.1945 eV), which indicates that \( \text{LaCr}_{0.5}\text{Cu}_{0.5}\text{O}_3 \) should possess a maximum conductivity.

3.5. Dielectric spectral analysis

The complex permittivity \( \varepsilon^* \) of a system is defined by

\[
\varepsilon^* = \varepsilon' - j\varepsilon'' \quad \varepsilon^* = \varepsilon' - j \left(\frac{\sigma}{\omega_0\varepsilon_0}\right)
\]

where \( \varepsilon' \) is the real or relative permittivity or dielectric constant, \( \varepsilon'' \) is the imaginary or dielectric loss, \( \sigma \) is the real part of the conductivity, and \( \varepsilon_0 \) is the permittivity of free space [20].

Fig. 10 represents the variation of \( \varepsilon' \) of all the three samples with a frequency at room temperature. The value of the dielectric constant is high at lower frequencies and decreases at higher frequencies. The Cu-doped sample possesses a high value of \( \varepsilon' \) since Cu is an acceptor-doped material that enhances the number of charge carriers, thereby increasing the mobility of the charge carriers. The exchange interaction between \( \text{Cu}^{2+} \) & \( \text{Cu}^{3+} \) and \( \text{Cr}^{4+} \) & \( \text{Cr}^{3+} \) charge carriers enhances the generation of more numbers of electrons/holes, which increase the value of \( \varepsilon' \) than that of the undoped material. The Fe-doped sample possesses a low value of \( \varepsilon' \) compared to that of the parent sample. The hopping exchange of the charges between the localized states is dependent on the displacement of charges with respect to the external field. The
addition of Fe$^{3+}$ ions to LaCrO$_3$ would cause a reduction in the number of Cr$^{3+}$ ions on the B site, which may be mainly responsible for space-charge polarization and the hopping exchange of the charges. This causes a decrease in the dielectric constant due to a decrease in polarization [23]. The inset of Fig. 10 represents the variation of $\varepsilon'$ of Cu-doped samples with a frequency at various temperature ranges. The value of the dielectric constant is high at lower frequencies and it decreases at higher frequencies. The dielectric behavior is due to the Maxwell–Wagner interfacial polarization given by Koop's theory [29]. At a lower frequency, $\varepsilon'$ is proportional to $\omega^{-(s-k)}$, where $s$ ranges from 0.1 to 0.2. At a higher frequency, the dielectric constant value, $\varepsilon'$, is proportional to $\omega^{-(s-k)}$, where $k$ ranges from 0.6 to 0.8 [30]. The $\varepsilon'$ at a lower frequency is due to the formation of a space charge region at the solid–electrode interface [23]. The value of $\varepsilon'$ is low at higher frequencies since the exchange between the charge carriers, Cr$^{4+}$ and Cr$^{3+}$ ions, cannot be oriented by the externally applied electric field.

3.6. Magnetic properties

The magnetic measurements were carried out with a Superconducting Quantum Interference Device (SQUID) magnetometer. The zero field–cooled (ZFC) and the field-cooled (FC) magnetization curve for the undoped and doped samples at an applied field of 100.00 mT in the temperature range of 5–350 K are given in Fig. 11. The original LaCrO$_3$ presents antiferromagnetic ordering below its Neel temperature of 293 K, which corresponds to the transition observed at around 290 K on the ZFC/FC curve. Doping the samples usually results in lowering the Neel temperature, as already observed for Ca and Sr-doped LaCrO$_3$ [31]. The same behavior is observed for LaCr$_{0.5}$Fe$_{0.5}$O$_3$ with a Neel temperature of 220 ± 5 K, while LaCr$_{0.5}$Cu$_{0.5}$O$_3$ displays two less-defined transitions at 270 and 110 K. The behavior below the Neel temperature is more complex to analyze due to the small particle size that induces spin canting and superparamagnetism. Therefore, the major result lies in the analysis of the Neel temperature discrepancies. Such a trend has been observed for strontium doping with the occurrence of two magnetic transitions, as confirmed by neutron diffraction analysis and heat capacity thermal behavior. The same tendency is also observed for Nd and Ca doping to a greater extent with a Neel temperature as low at 110 K for LaCr$_{0.5}$Ca$_{0.5}$O$_3$ [32].

Fig. 12. Hysteresis curve of LaCrO$_3$ (a), LaCr$_{0.5}$Cu$_{0.5}$O$_3$ (b), and LaCr$_{0.5}$Fe$_{0.5}$O$_3$ (c) at room temperature.

Fig. 12 shows the magnetic hysteresis loop of all the doped and undoped samples. For all the samples, the loops do not reach saturation at 5 T due to the slight non-compensated paramagnetic contribution. The remanent magnetization ($M_r$) for Fe-doped LaCrO$_3$ reaches 0.3 emu g$^{-1}$ with a large coercive field of 0.52 T and a shape typical of antiferromagnetic material. In the case of LaCr$_{0.5}$Cu$_{0.5}$O$_3$, remanent magnetization and the coercive field are only slightly increased, as compared to the undoped sample. From the observed magnetic behavior, one can conclude that the doping results in a single magnetic phase with a decrease of the Neel temperature. The decrease of the antiferromagnetic interactions can be rationalized from the lattice parameter evolution with an increase in cell volume upon doping.

4. Conclusions

LaCr$_{0.5}$M$_{0.5}$O$_3$ (M = Cr$^{3+}$, Cu$^{2+}$ and Fe$^{3+}$) has been synthesized successfully by the sol–gel technique. The synthesized LaCrO$_3$ was identified as an orthorhombic structure and confirmed the compound formation. The grain size was found to increase with the increase in calcination temperature. The impedance spectral analysis shows that the material behaves as a semi-conductor, and the conductivity measurements showed that the mobility of the charge carrier is thermally activated. The doping of Cu on LaCrO$_3$ causes a reduction in the bulk resistance, leading to maximum conductivity. There is an enhancement in the barrier properties on the mobility for the charge carriers of the Fe-doped sample that results in the suppression of the lattice conduction path. It can thus be concluded that the addition of either divalent or trivalent ions in the perovskite LaCrO$_3$ causes a considerable modifications in the structural, electrical and magnetic properties.

References