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RESEARCH ARTICLE

STRUCTURAL AND ELECTRICAL PROPERTIES OF Sr- SUBSTITUTED PEROVSKITES NANO CRYSTALLINE $LaCrO_3$

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ABSTRACT

Nanocrystalline strontium (Sr) doped Lanthanum Chromium oxide ($LaCrO_3$) were prepared by sol-gel techniques. The influence of different concentrations of Sr doped nanocrystalline $La_{1-x}Sr_xCrO_3$ (x= 0,0.1,0.2,0.3) and calcinations temperature were investigated on the structure, morphology, and crystallite size by X-ray diffraction (XRD).The X-ray diffraction studies of $LaCrO_3$. Powder have shown that the as prepared powder was single phase, crystalline and has a cubic perovskite structure. The particle size calculated from FWHM was 50nm. . The electrical properties for all the samples have been studied as a function of frequency in the range 42Hz-50MHz and temperature ranging 30-700^{0}c. The appearance of peak in imaginary part of impedance (Z'') for each concentration and shifting of this peak with temperature towards higher frequency side indicated that the presence of electric relaxation.

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INTRODUCTION

The lanthanum chromite, $LaCrO_3$ is a typical perovskite material with the general formula of ABO_3. The ideal perovskite structure, ABO_3, has a cubic symmetry and can be described as a three-dimensional network of corner-sharing BO_3 octahedra with BOB angles of 180^0. Most of which bear some extent of distortion. It displays some unique physical properties, such as high mechanical strength, high melting point (2400^{0}C), good electronic conductivity, a high thermal expansion coefficient, physical and chemical stability in oxidizing and reducing atmospheres, and the ability to withstand high temperatures and electro-catalytic activity, which makes them useful in high temperature applications such as inter connectors in solid oxide fuel cells (Duran *et al.,* 2004), sensors (Zhao *et al.,* 2000), catalysis, etc. It has been synthesized by various techniques such as the hydrothermal method (Zheng *et al.,* 1999), the sol–gel method (Zhigalkina *et al.,* 1988), the citrate–gel method (Sujatha Devi *et al.,* 1993), the hydrazine method (Azegami *et al.,* 1988), etc. In this study, $La_{1-x}Sr_xCrO_3$ perovskite oxides were prepared by a sol gel method. 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 (Suda *et al.,* 2002; Mori *et al.,* 2002; Sakai *et al.,* 1990). The use of dopants in these materials is extremely useful, and they can also improve their electrical properties, i.e. Sr. Pure $LaCrO_3$ is a p-type conductor (Sharma *et al.,* 2005) with quite low conductivity in either oxidizing or reducing environment ,e.g. 0.33S/cm at 800^{0}C in air and 0.09S/cm at 800^{0}C in reducing atmosphere. In general, doping alkaline earth(AE) elements such as Mg, Ca, Sr and Ba at the A-site in $LaCrO_3$ to improve the conductivity value of perovskites .In addition, doping bivalent A elements may introduce a Cr^{3+} to Cr^{4+} transition (Ranjan *et al.,* 2009). The synthesized $La_{1-x}Sr_xCrO_3$ were studied using XRD, FTIR and AC impedance spectroscopy in order to study the structural and electrical properties.

Experimental method

Polycrystalline $La_{1-x}Sr_xCrO_3$(x=0, 0.1,0.2,0.3) were prepared using sol–gel method. High purity nitrates were used for the preparation. A stoichiometric mixture lanthanum nitrate and Chromium nitrate and Strontium were used as raw materials. A stoichiometric mixture of nitrates was mixed with citric acid and ethylene glycol and stirred magnetically at 800^{0}C for 3 hrs to obtain a homogenous mixture; the solution was further heated in a pressure vessel at about 130^{0}C for 12 hrs and subsequently kept at 350^{0}C for 3 hrs a muffle furnace and then milled to a fine powder. The dried powder was then calcinated in the range of 350°C to 750^{0}C for 6 hrs in order to improve the crystallinity of the powder. The impedance measurement were done on the pellets (the pellets of 13.2 mm diameter and15.45 mm thickness were made by applying a pressure of 8 tons on the powered sample) by using an LCR meter. Impedance measurement were carried out in the frequency range 42Hz - 500 MHz and at temperature range 37 to 700 ^{0}C.

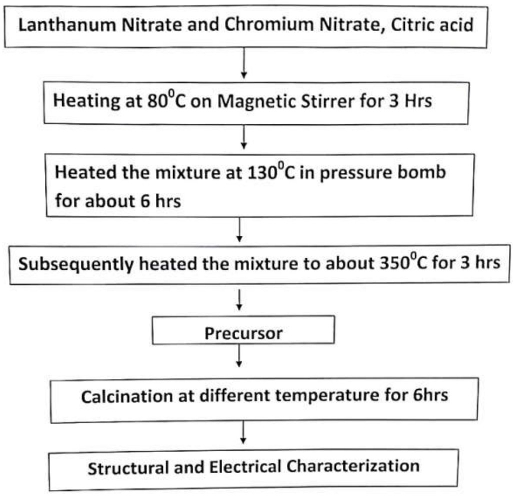

Fig. 1. Flow chart for the preparation of $LaCrO_3$ nanomaterial

RESULTS AND DISCUSSION

X-Ray Diffraction Study: Figure 1(a& b) shows the XRD patterns of nanocystalline $LaCrO_3$ and La $_{0.8}$ Sr $_{0.2}$CrO$_3$ calcined at 550^{O}C calcined at 6 hrs respectively. The diffraction peaks for nanocystalline $LaCrO_3$ at 2θ values of about 22.9 ,32.67, 40.27, 46.89, 58.22 ,68.63 corresponds to (110), (112), (022), (004), (114), (224) planes shows orthorhombic phase of $LaCrO_3$. The diffraction data is good agreement with JCPDS card of $LaCrO_3$ (JCPDS No.24-1016) as shown in fig. 1(a) No additional peaks are seen due to addition of Sr in $LaCrO_3$ because Sr is substituted in the lanthanum site forming a homogeneous mixture shown in Fig.1(b) XRD pattern of $La_{0.8}Sr_{0.2}CrO_3$, indicates that ions Sr^{2+} partially substitute for ions La^{3+} in the $LaCrO_3$ crystal lattice. The ionic radii of Sr^{2+} (1.21 Å) are very close to that of La^{3+} and Sr is incorporated into the $LaCrO_3$ lattice at the La site. The particle size was calculated using the Scherrer's formula [12]. The Scherrer formula is given by:

$$D= 0.9 \lambda / \beta \cos \theta \quad (1)$$

where D is the average particle size perpendicular to the reflecting planes, λ is the X-ray wavelength, β is the full width at half maximum (FWHM), and θ is the diffraction angle. The average particle size was found to be about 50 nm.

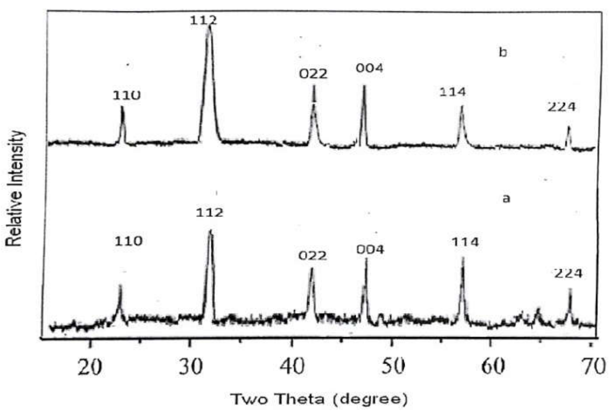

Figure 1(a&b). XRD patterns of nanocystalline $LaCrO_3$ and La $_{0.8}$ Sr $_{0.2}$CrO$_3$ calcined at 550^{O}C calcined at 6 hrs

Electrical properties: Electrical impedance or simply impedance, describes a measure of opposition to alternating current (a.c.). Electrical impedance extends the concept of resistance to a.c. circuits, describing not only the relative amplitudes of the voltage and current, but also the relative phases. When the circuit is driven with direct current (d.c), there is no distinction between impedance and resistance; the latter can be thought of as impedance with zero phase angles. The symbol for impedance is usually *z* and it may be represented by writing its magnitude and phase in the form $z\angle\theta$. However, complex number representation is more powerful for circuit analysis purposes. The term impedance was coined by Oliver Heaviside *et al.* (2000) and Kennelly *et al.* (2002) was the first to represent impedance with complex numbers in 1893. Impedance is defined as the frequency domain ratio of voltage to current. The magnitude of the complex impedance is the ratio of voltage to current amplitude. Complex impedance spectrum (CIS) is a non-destructive and powerful experimental technique for the characterization of micro structural and electrical properties of some electronic materials over a wide range of frequency and temperature (Berger *et al.,* 2007). There are many ways by which CIS data may be plotted. In CIS field, where capacitive rather than inductive effects dominate, conventionally one plots log*(Z)'* ≅ −*Z*'' on the *y*-axis vs. Re*(Z)* ≅*Z*' on the *x*-axis to give a complex-plane impedance plot. But it has the disadvantage of not indicating frequency response directly, but may nevertheless be very helpful in identifying conduction processes that all present. The complex impedance equations (Zheng *et al.,* 2000) can be written as

$$Z^* = Z' - J Z'', \quad (1)$$
$$Z' = R/1 + (\omega RC)2 \quad (2)$$
$$Z'' = R(\omega RC)/(1 + \omega RC)2 \quad (3)$$

where *Z*' and *Z*'' are the real and imaginary components of impedance, *ω* the angular frequency, *R* and *C* are resistance and capacitance, respectively. $j^2 = -1$, this relation offers wide scope for a graphical analysis of the various parameters under different conditions of temperature or frequency. The systematic procedure for the analysis of a.c. measurements is to plot the results in the complex impedance plane; *Z*' Vs *Z*''. These plots are useful for determining the dominant resistance of the sample. However, these are insensitive to smaller resistances. A separation of the grain and grain boundary properties has been achieved using an equivalent circuit model in impedance analysis. It is understood that at the peaks of semicircles, (Chaisan *et al.,* 2005) the equation can be written as

$$2\pi f\max \tau = 1, \quad (4)$$

here, τ is the mean relaxation time

Fig. 3(a-d) shows the variation of *Z*' with frequency at different measuring temperatures $LaCrO_3$ and $La_{1-x}Sr_xCrO_3$ at different temperature. The value of Z′ is higher at lower frequency region and as the frequency increases, the value of Z′ decreases monotonically and attains a constant value at high frequency region at all temperatures. The decrease in the Z′ value at low frequency region in all the compounds indicate that the conductivity of these compounds increases with the increase of frequency due to the increase of hopping of charge carriers between the localized ions. At low frequency, the value of Z′ for these compounds decreases with the increase of temperature and these values merge at high frequency region

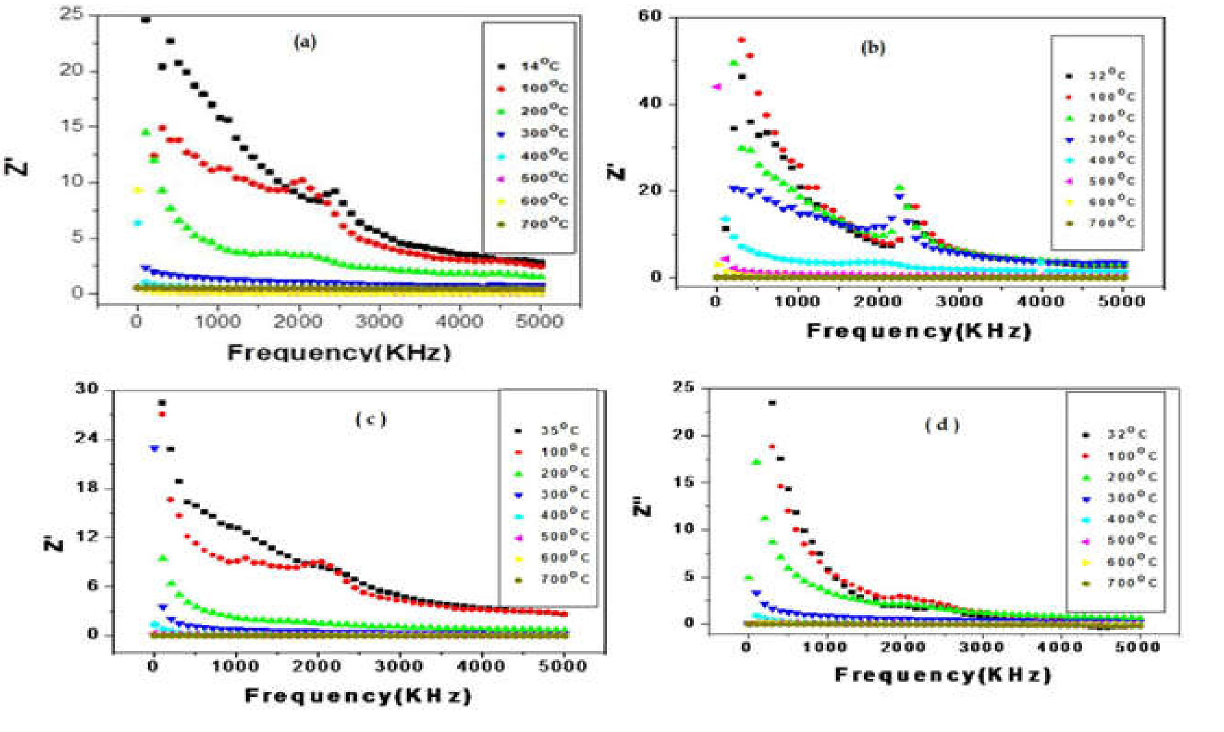

Fig. 3(a, b, & C) : Frequency dependence of real and imaginary parts of impedance Z' (a) $LaCrO_3$, (b) $La_{0.9}Sr_{0.1}CrO_3$ and (c) $La_{0.8}Sr_{0.2}CrO_3$ (d) $La_{0.7}Sr_{0.3}CrO_3$

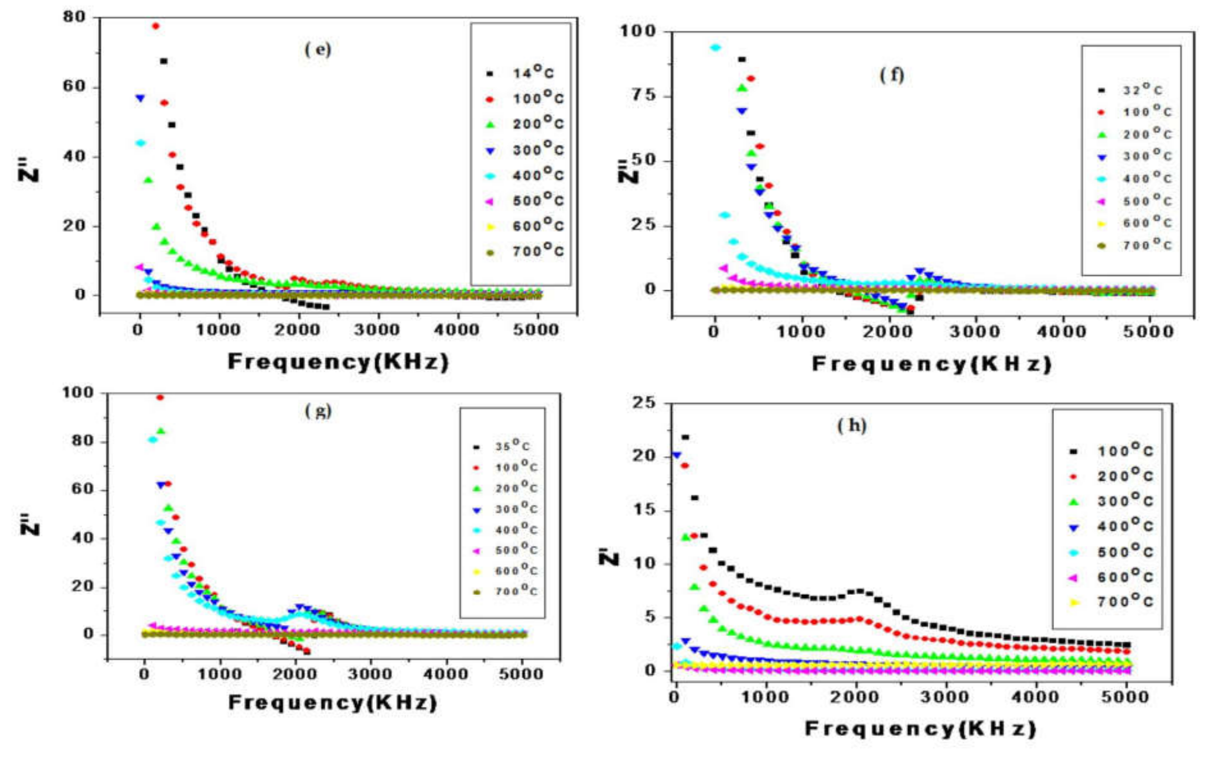

Fig. 3 Frequency dependence of imaginary part of impedance Z″ (e) $LaCrO_3$, (f) $La_{0.9}Sr_{0.1}CrO_3$, (g) $La_{0.8}Sr_{0.2}CrO_3$ (h) $La_{0.7}Sr_{0.3}CrO_3$

Fig. 3 (E-H) shows the frequency dependence of imaginary part of impedance (Z″) of $LaCrO_3$ and $La_{1-x}Sr_xCrO_3$. The shift in the peak frequency is because of the presence of electrical relaxations in the material and increase in the rate of hopping of charge carriers. This relaxation is a temperature dependent relaxation. Asymmetric broadening of peaks indicates distribution of spread of relaxation time (Tiwari Balgovind and Chuadhari, 2008). The magnitude of Z″ at *f* max decreases with the temperature indicating the presence of space charge polarization at low frequency which disappears at high frequency (Suman *et al.,* 2005; Sen *et al.,* 2008). The magnitude of Z″ at *f* max increases with the increase of Sr content. The peak in the Z″ data shifted in the low frequency side with the increase of Sr. This may be attributed to a phenomenon with maximum capacitive effects on Sr substitution due to the increase of ac conductivity i.e. existence of negative temperature coefficient of resistance (NTCR) in the compounds. Decrement of Z′ with the increase of temperature and frequency suggests a possible release of space charge and consequently lowering of barrier properties in these materials (Adamczyk *et al.,* 2007). For a given temperature, with the increase of Sr concentration in $LaCrO_3$, Z′ increases [see Fig3(.a-d)] which indicates an enhancement of the bulk resistance of the compounds with the substitution provides an insight into the electrical processes having the largest resistance in accordance with equations (2) and (3) (Kumar *et al.,* 2006). The plots show that *Z*" values attain a peak (*Z*" max*)* at all measuring temperatures. The magnitude of *Z*" max decreases with temperature indicating decrease in the resistive property of the sample. With the increase of temperature, the peak position of Z″ shifts towards higher frequency side.

Conclusion

A series of polycrystalline $La_{1-x}Sr_xCrO_3$(x=0.1, 0.2,0.3) samples have been synthesized by sol–gel method . X-ray diffraction analysis revealed the nanocrystalline nature in the prepared sample. The XRD pattern of $La_{0.8}Sr_{0.2}CrO_3$ shows perovskite p-type with orthorhombic structure. The electrical conductivity studies showed the NTCR character of $LaCrO_3$ and $La_{1-x}Sr_xCrO_3$ (x = 0.1, 0.2, 0.3). The frequency variation of ac conductivity at different temperatures indicates that the conduction process is thermally activated.

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