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► **To cite this version:**

N Thenmozhi, S Sasikumar, R Saravanan, Yen-Pei Fu. Study of Charge Density and Crystal Structure of co-doped LaCrO₃ System . Mechanics, Materials Science & Engineering MMSE Journal. Open Access, 2017, 9, 10.2412/mmse.99.30.568 . hal-01504754

HAL Id: hal-01504754

<https://hal.science/hal-01504754>

Submitted on 10 Apr 2017

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Study of Charge Density and Crystal Structure of co-doped LaCrO₃ System

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DOI 10.2412/mmse.99.30.568 provided by Seo4U.link

Keywords: X-ray diffraction, electron density, co-doping, scanning electron microscopy, magnetic property.

ABSTRACT. The co-doped lanthanum chromite system of (La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O₃ sample has been prepared by high temperature solid state reaction technique. The synthesized sample has been characterized for structural, optical, morphological and magnetic properties by powder XRD, UV-vis, SEM/EDS and VSM. Structural analysis revealed that the prepared sample has orthorhombic structure with space group of *Pnma*. The bonding between the atoms has been analyzed using maximum entropy method (MEM). The bond lengths and mid bond electron densities have been estimated from the 1D electron density profiles. From the optical absorption spectra, the energy band gap of the sample has been calculated as 2.035 eV. From the SEM image, the average particle size of the synthesized sample is 235nm. EDS spectrum of the synthesized sample confirms its purity. Room temperature M-H curves obtained from VSM measurements exhibit predominant antiferromagnetic ordering of the prepared sample. The co-doped LaCrO₃ compounds have been primarily used as cathode as well as inter-connector coating materials in solid oxide fuel cells (SOFC).

Introduction. Lanthanum chromite (LaCrO₃), a perovskite rare-earth oxide material has been investigated for the past five decades due to their rich and interesting properties and essential technological applications. Since lanthanum chromite has high melting point of 2490 °C with high electronic conductivity, it is often used as electrodes in magneto hydrodynamic (MHD) generators [1] and has also been found for use as oxidation catalyst for soot combustion [2], electric heaters [3] and NO_x sensors [4]. Lanthanum chromite is a p-type semiconducting material which exhibits properties like, good physical and chemical stability during the oxidation and reduction process, electro catalytic activity, high thermal expansion coefficient and high mechanical strength [5, 6]. Since the transition metal doped lanthanum chromite has the property of mixed ionic and electronic conductivity, they have been used for electrodes and interconnector materials in solid oxide fuel cell (SOFC) which is a solid electro chemical device, converts chemical energy into electrical energy [7]. Usually, LaCrO₃ crystallizes in orthorhombic structure with *Pnma* space group. The transport properties of lanthanum chromites can be studied by the localized behaviour of the d-electrons [8]. Literature showed various preparation techniques to synthesis lanthanum chromites which include sol-gel method, hydrothermal processing, microwave combustion synthesis, pechini method etc. In the present work, (Co, Cu) doped La-Ca based chromites were prepared through solid state reaction method and we report on structural, optical, morphological and magnetic properties of the synthesized co-doped system.

Experimental. Preovskite sample of (La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O₃ was prepared through solid state reaction method. Appropriate amounts of high purity (99.99%) of La₂O₃, CaCO₃, Cr₂O₃, Co₃O₄ and CuO were mixed with distilled water for 12 h. After dried, these powders were ground and then calcined in air at 1000 °C for 4 h. Thereafter, the calcined samples were pelletized and dry pressed at

100MPa. These pressed pellets were finally sintered out in air at 1500 °C for 6 h with a programmed heating rate of 5°C/min to get the required samples.

To determine the phase purity and sample homogeneity, the sample was characterized by powder X-ray diffraction (XRD) at room temperature by X-ray diffractometer (Bruker AXS D8 advance) with CuK α as the incident beam radiation. Optical band gap measurement was carried out using UV-visible spectrometer Cary 5000 (Varian, Germany). The morphological and elemental analyses were done for the prepared sample using scanning electron microscopy (SEM) (JEOL Model JSM - 6390LV) equipped with an energy dispersive X-ray (EDS) spectrometer (JEOL Model JED – 2300). Magnetic parameters were taken using vibrating sample magnetometer (Lakeshore VSM 7410) at 300K.

Results and discussion.

Powder XRD and Rietveld refinement. Figure 1 shows the X-ray diffractogram of the synthesized polycrystalline sample $(La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O_3$. Sharp XRD peaks with narrow full width at half maximum shows that the crystals are well crystallized. All the XRD peaks in figure 1 could be indexed to orthorhombic crystal lattice of $LaCrO_3$ with JCPDS card number 33-0701. To investigate the structural properties in detail the XRD data is subjected to Rietveld refinement [9] technique using the software JANA 2006 [10]. During the refinement process, the cell parameters, background profile shape, peak shift and preferred orientation were refined and hence the difference between the observed XRD profile and theoretically generated profile is minimized. Refinement of the synthesized sample $(La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O_3$ was carried out in the orthorhombic setting of space group $Pnma$ (space group number: 62) with four molecules per unit cell and the refined profile is presented in figure 2. For the orthorhombic structure, the Wyckoff position for La and Ca atoms is 4C (0.0267, 0.25, -0.004); for Cr, Co and Cu is 4b (0, 0, 0.25); for O1 apex atom is 4C (0.4905, 0.25, 0.0684); for O2 planar atom is 8d (0.2193, 0.5361, 0.2195) [11]. The orthorhombic unit cell of $(La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O_3$ obtained through VESTA is shown in figure 3. It consists of corner linked octahedra CrO_6 in which the central Cr atom is surrounded by six oxygen atoms. The La atom is at the space between the octahedra. The refined structural parameters are given in table 1. With the substitution of Ca at La site and (Co, Cu) at Cr site, the volume of the unit cell is decreased when it is compared with the volume of the undoped lanthanum chromite (234.52\AA^3 from JCPDS # 33-0701). The reason is that the doped Ca^{2+} (1.34\AA) ions having smaller ionic radii replacing La^{3+} (1.36\AA) ions and also the doped Cu^{3+} (0.54\AA) [12] having smaller ionic radii replacing the Cr^{3+} (0.615\AA) [12] ions.

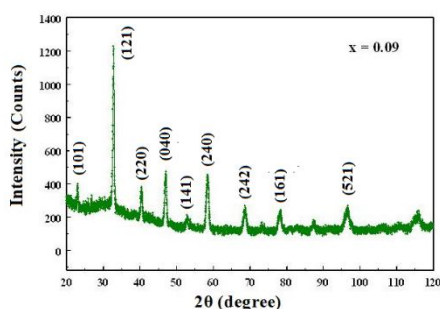


Fig. 1. Raw profile of $(La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O_3$.

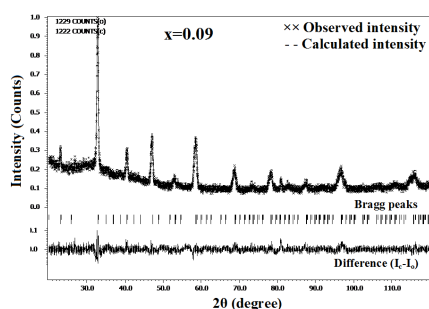


Fig. 2. Fitted profile.

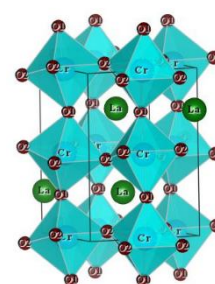


Fig. 3. The unit cell of obtained from VESTA.

Table 1. Structural parameters.

| Parameters | Values |
|---------------------------|-----------|
| a (Å) | 5.4426(5) |
| b (Å) | 7.6831(2) |
| c (Å) | 5.4631(4) |
| $\alpha=\beta=\gamma$ (°) | 90 |
| Volume (Å ³) | 228.45(5) |
| Density (gm/cc) | 6.41(8) |
| R_p (%) | 7.03 |
| R_{obs} (%) | 4.90 |
| GOF | 1.20 |
| $F_{(000)}$ | 393 |

Table 2. EDS elemental composition.

| Atomic (At %) | | | | | |
|---------------|------|-------|------|------|-------|
| La | Ca | Cr | Co | Cu | O |
| 26.64 | 6.71 | 23.47 | 2.61 | 2.38 | 31.47 |

Band gap determination. The optical energy band gap of the prepared compound $(La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O_3$ was determined from UV-visible absorption spectra. Tauc's equation [13] relates the absorption coefficient (α) and the energy band gap of the material (E_g) as $\alpha hv = A (hv - E_g)^n$, where hv is the photon energy, A is the proportionality constant, $n = 1/2$ for direct band gap materials and $n = 2$ for indirect band gap materials. A graph is drawn by taking (hv) along the X-axis and $(\alpha hv)^2$ along the Y-axis as shown in figure 4. From this Tauc plot, the extrapolation of the linear portion of the curve to X-axis, gives the energy band gap. The energy band gap obtained for the synthesized sample from Tauc plot is 2.035 eV.

SEM/EDS analysis. The surface morphology of the synthesized sample was analyzed through its SEM image which is shown in figure 5. It shows the presence of the particles of different sizes which are heterogeneously distributed. The particle sizes were in the range of 230nm-240nm. Figure 6 represents the EDS spectra of the prepared co-doped sample. Peaks in EDS spectrum indicate the different elements (La, Ca, Cr, Co, Cu and O) present in the sample. The elemental composition in at% is given in table 2 and it confirms the purity of the sample.

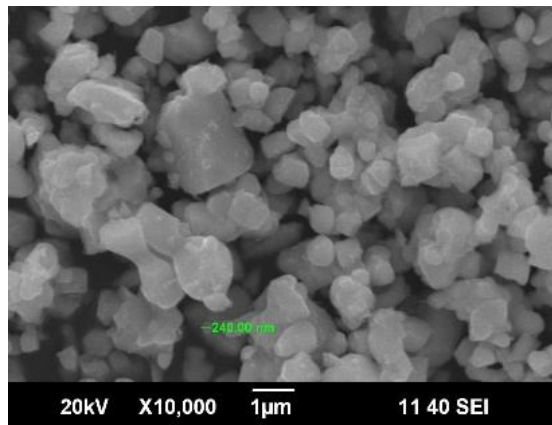


Fig. 4. UV-Visible plot.

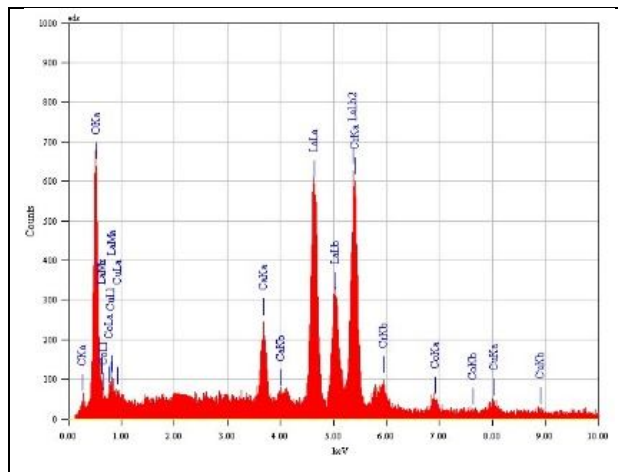


Fig. 5. SEM image.

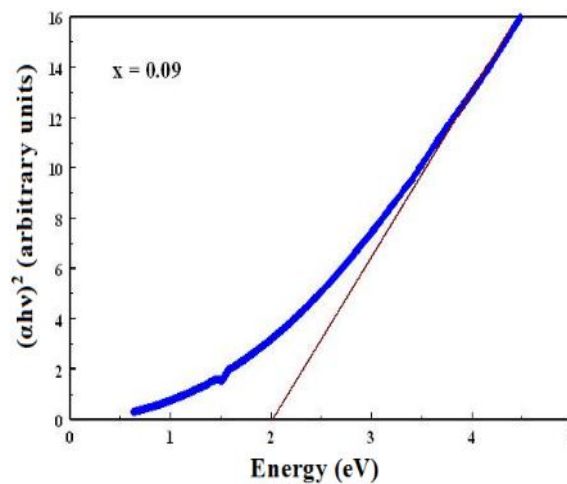


Fig. 6. EDS spectra.

Magnetic property. Lanthanum chromite is G-type antiferromagnetic material with Neel temperature $T_N = 282K$ and at room temperature, it behaves as a poor electrical conductor [14]. The synthesized sample $(La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O_3$ was analyzed for magnetic studies using VSM. The M-H loop recorded at room temperature is shown in figure 7 and the magnetic parameters are

given in table 3. The M-H loop does not show any hysteresis and the observed low value of magnetization indicates that the sample is attributed to antiferromagnetism due to Cr³⁺ spins.

Table 3. Magnetic parameters from VSM measurements.

| Parameters | values |
|---|--------|
| Ms ×10 ⁻³ (emu g ⁻¹) | 2.52 |
| Hc (G) | 473.36 |
| Mr ×10 ⁻³ (emu g ⁻¹) | 42.543 |

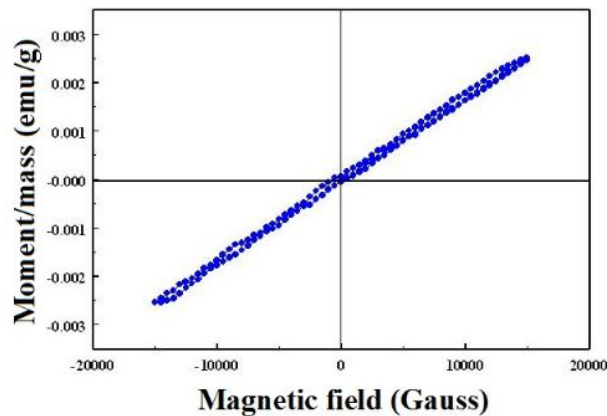


Fig. 7. M-H curve.

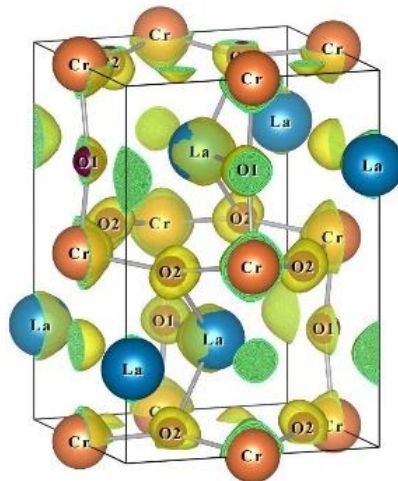


Fig. 8. Three dimensional electron density isosurface.

Charge density analysis by MEM. The charge density distribution around La-O and Cr-O bonds of the synthesized sample (La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O₃ was analyzed using maximum entropy method (MEM) [15], which uses the cell parameters and structure factors extracted from Rietveld method [9]. MEM method is used to study about the bonding behaviour of any crystalline material. MEM computations were implemented by the software PRIMA [16]. For our calculation, the unit

cell was divided into $48 \times 64 \times 48$ pixels. The resultant electron density distribution in the orthorhombic unit cell was visualized using VESTA [17], the visualization software.

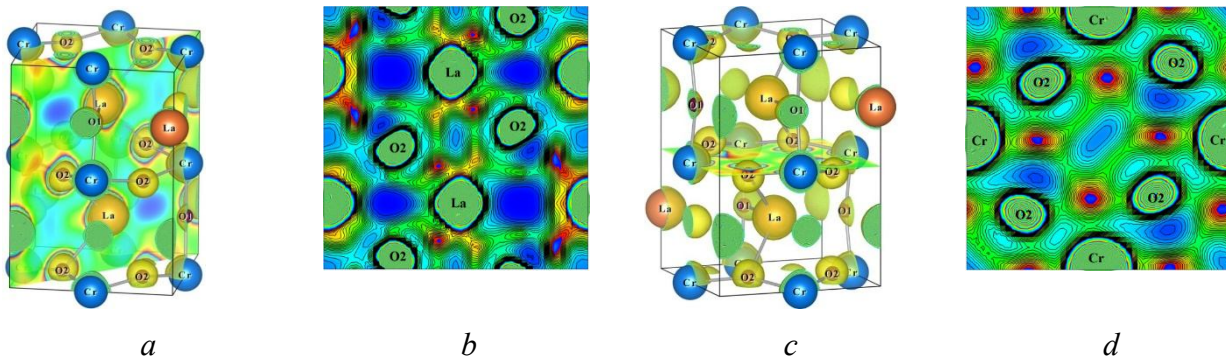


Fig. 9. 3D unit cells of $(La_{0.8}Ca_{0.2})(Cr_{0.87}Co_{0.1}Cu_{0.03})O_3$ with a) (101) and c) (020) planes shaded. Two dimensional electron density distribution on b) (101) and d) (020) planes for $(La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O_3$.

Figure 8 illustrates the three dimensional electron density distributions in the unit cell of the prepared sample with the iso-surface level $3.0 \text{ e}/\text{\AA}^3$. In the 3D unit cell, the La, Cr and O atoms are clearly seen and the picture confirms the orthorhombic phase of the synthesized sample. Figures 9a and 9c denote the 3-dimensional orthorhombic unit cell with (101) and (020) planes shaded. To analyze the bonding behaviour, the 2D electron density contour maps for these two significant crystallographic planes (101) and (020) were displayed as figures 9b and 9d. These maps are drawn in the range $0-1.0 \text{ e}/\text{\AA}^3$ with the contour interval of $0.04 \text{ e}/\text{\AA}^3$. From figure 9b, it can be observed that there is no charge sharing taking place between La and O2 atoms which means that the bond La-O2 has ionic nature. Figure 9d indicates that, there is a presence of bond charges along the path between Cr and O2 atoms which shows the bond Cr-O2 has covalent nature. To estimate the mid bond electron densities for the bonds, the 1D electron density profiles were drawn. Figures 10a and 10b are the 1D line profiles for La-O2 and Cr-O2 bonds respectively. The bond length and mid bond electron density values are given in table 4. The mid bond electron density for La-O2 bond is $0.4801 \text{ e}/\text{\AA}^3$ and the bond length is 2.4462 \AA . The mid bond electron density value for La-O2 bond confirms that the bond is less ionic in nature. The bond length for Cr-O2 bond is 1.9618 \AA . The mid bond electron density value for Cr-O2 is $0.2786 \text{ e}/\text{\AA}^3$ which confirms that the bond is less covalent in nature. Hence, for the prepared sample, the bond La-O2 is less ionic and the bond Cr-O2 is less covalent. The bond length values agree well with the reported values [18, 19]. The decrease in covalent character of Cr-O2 bond may attribute to the antiferromagnetic nature of the synthesized sample. Figure 10c shows the 1D map for O1-O2 bond. The mid bond density value for O1-O2 bond confirms that the bond has the ionic nature with partly covalent character.

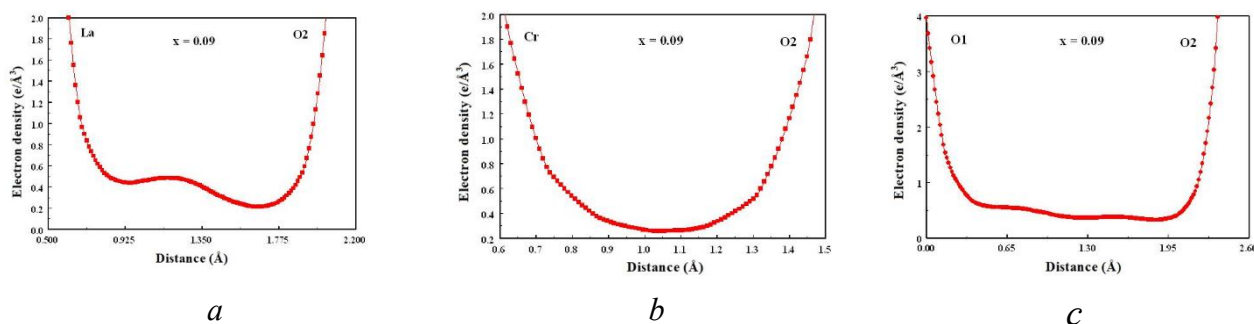


Fig. 10. One dimensional electron density profiles along a) La and O2 b) Cr and O2 c) O1 and O2 atoms in $(La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O_3$.

Table 4. Bond lengths and mid bond electron densities for La-O2, Cr-O2 and O1-O2 bonds for $(La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O_3$.

| Bonding | | | | | |
|-----------------|--|-----------------|--|-----------------|--|
| La-O2 | | Cr-O2 | | O1-O2 | |
| Bond length (Å) | Mid bond electron density ($e/\text{Å}^3$) | Bond length (Å) | Mid bond electron density ($e/\text{Å}^3$) | Bond length (Å) | Mid bond electron density ($e/\text{Å}^3$) |
| 2.4462 | 0.4801 | 1.9618 | 0.2786 | 2.7500 | 0.3661 |

Summary. Single phased $(La_{0.8}Ca_{0.2})(Cr_{0.81}Co_{0.1}Cu_{0.09})O_3$ ceramic sample was synthesized by conventional solid state reaction technique at 1500 °C for 6 h. The powder X-ray diffraction pattern showed that the prepared sample has orthorhombic perovskite structure with space group $Pnma$. MEM charge density analysis reveals that the bond La-O2 is less ionic and the bond Cr-O2 is less covalent in nature. The optical energy band gap of the sample using UV-visible absorption spectrum is found to be 2.035 eV. Particles of different sizes are visualized through SEM image. Stoichiometry of the synthesized sample was confirmed by EDS spectral analysis. Room temperature VSM measurements confirm the antiferromagnetic behavior of the grown sample.

Acknowledgements. We acknowledge SAIF, Cochin University, India for their help in the collection of X-ray diffraction data, UV-Visible spectra and SEM/EDS spectra. We acknowledge SAIF, IIT Madras, Chennai, for the VSM measurements.

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Cite the paper

N. Thenmozhi, S.Sasikumar, R. Saravanan, Yen-Pei Fu (2017) [Study of Charge Density and Crystal Structure of co-doped \$LaCrO_3\$ System](#). *Mechanics, Materials Science & Engineering*, Vol 9. DOI [10.2412/mmse.99.30.568](https://doi.org/10.2412/mmse.99.30.568)