Synthesis, structural and electrical conductivity of half-metallic perovskite oxide La$_2$CrNiO$_6$

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Abstract. The half-metallic double perovskite oxide La$_2$CrNiO$_6$ (LCNO) has been synthesised by the sol-gel method. The sample characterisation has been performed using the room temperature X-ray diffraction, Raman spectroscopy and scanning electron microscopy. Rietveld refinement of the room temperature XRD data shows that LCNO crystallises in the orthorhombic phase with space group Pbnm. Impedance spectroscopy has been studied in the wide range of temperature from 30$^\circ$C to 560$^\circ$C and in the frequency range from 42 Hz to 4.8 MHz. In the experimental temperature range the conductivity of LCNO decreases with frequency, which confirms the metallic nature of LCNO.

INTRODUCTION

Half-metallic materials have drawn a large research interest both theoretically and experimentally due to its spintronics applications [1-3]. Half-metals are the ferromagnetic or ferrimagnetic materials that behaves as a conductor for the charge carriers of one spin orientation, but insulator or semiconductor to the charges of other spin orientation. Liu et al. have suggested the half-metallic ferromagnetic behaviour in La$_2$CrNiO$_6$ (LCNO) using first principle calculations method [4]. They suggested conducting behaviour of LCNO in the up-spin channel and semiconducting behaviour in the down spin channel [4]. But there is no experimental study on LCNO to check its conducting property in detail. Here, we have synthesized LCNO by sol-gel citrate method and studied its conductivity property using impedance spectroscopy in a wide range of temperature (30$^\circ$C to 570$^\circ$C) and frequency (42 Hz to 4.8 MHz). Impedance spectroscopy is a very useful tool to study the conducting, dielectric and other physical properties of a material.

EXPERIMENTAL DETAILS

Sample Preparation

The LCNO powder was synthesized by using the sol-gel citrate method. First the reagent grade metal nitrates, La(NO$_3$)$_3$.6H$_2$O, Cr(NO$_3$)$_3$.9H$_2$O and Ni(NO$_3$)$_2$.6H$_2$O were dissolved in distilled water separately by stirring using a magnetic stirrer for 30 minutes. After that these stoichiometric solutions were mixed together and stirred for 30 minutes. Then ethylene glycol (EG) and citric acid (CA) were added drop wise to this solution according to the molar ratio of \{La\}:\{CA\}:\{EG\}=1:1:4 and stirred for 4 hours to obtain a homogeneous mixture. Next, the obtained solution was dried at 120$^\circ$C until the auto-combustion occurs and fluffy precursor LCNO powder is prepared. The precursor was then grinded to get the fine precursor powder and calcined at 850$^\circ$C in the air medium for 8 hours to
get the LCNO powder. The calcined sample was then pelletized into discs using polyvinyl alcohol as a binder and then sintered at 950°C for 5 hours.

**Characterization**

X-ray powder diffractometer (Rigaku Miniflex II) having Cu-Kα (λ=1.54 Å) radiation was used to obtain the room temperature X-ray diffraction (XRD) pattern of LCNO. The Rietveld refinement of the XRD pattern was performed using the Fullprof program [5]. Room temperature Raman spectrum of the synthesized sample was obtained at an excitation wavelength of 488 nm using a Lab-RAM HR 800 (JobinYvon) Raman spectrometer. The surface morphology of the prepared pellet was studied using field emission scanning electron microscopy (FESEM) (FEI Quanta FEG 250). The conductivity of the prepared pellet was measured using a LCR meter (HIOKI-3552) in the wide range of temperature from 30°C to 560°C and in the frequency range from 42 Hz to 4.8 MHz.

![XRD pattern and Rietveld refinement of LCNO](image1.png)

**FIGURE 1(a).** Room temperature XRD pattern and Rietveld refinement of LCNO. (b) The octahedral crystal structure of LCNO, where Cr and Ni form the octahedra.

**RESULTS AND DISCUSSIONS**

**Crystal structure**

The room temperature XRD pattern and the corresponding Rietveld refinement of the synthesized LCNO powder is shown in Fig. 1(a), where the symbols represent the experimental data and the solid line represents the best fit to the XRD data. The bottom blue curve represents the difference between experimental pattern and the calculated one. The Rietveld refinement of the room temperature XRD data shows that LCNO crystallizes in the disorder orthorhombic phase with space group Pbnm. The refined lattice parameters, important bond lengths and angles, atomic positions and the reliability factors of the refinement are shown in Table 1. Fig. 1(b) shows a unit cell presentation of LCNO crystal lattice. Here, Cr/Ni atoms with six O-atoms create (Cr/Ni)O₆ octahedra. In the disorder double perovskite oxide lattice the B and B' atoms are not distributed in a regular alternate fashion. Rather it can be considered as the solid solution of two different perovskite oxides ABO₃ and AB'O₃, where A and B (B and B') atoms represent the cations. Here the B- site cations belong to the 3d transition elements group. The ionic radius is nearly same for two ions Cr³⁺ and Ni³⁺. The B- site ordering is hardly possible for this structure. This type of disorder orientation of atoms in double perovskite crystal structure generates broad and asymmetric peak in the Raman spectra [6, 7].
Hence, for a clear understanding about the LCNO crystal structure Raman spectroscopy of the LCNO was carried out. Fig. 2(a) shows that the room temperature Raman spectra of LCNO in the experimental range is dominated by a broad and asymmetric peak at 683 nm, which may originate due to the symmetric stretching (S) mode vibrations of B/BO₆ octahedral [8]. The broad and asymmetric nature of the peak also reflect that Cr and Ni ions are completely disordered in the LCNO crystal. Hence, both the XRD and Raman spectra suggest the disorder nature of LCNO crystal lattice.

### Table 1: Refined lattice parameters of LCNO crystal.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Wyckoff site and atomic position(x, y, z)</th>
<th>Bond lengths (Å)</th>
<th>Bond angles</th>
<th>Quality parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>4c (0.498, 0.016, 0.250)</td>
<td>La-O₁= 2.254</td>
<td>&lt;Cr/Ni-O₁-Cr/Ni&gt;= 170.1°</td>
<td>χ²=1.24</td>
</tr>
<tr>
<td>Cr</td>
<td>4a (0, 0, 0)</td>
<td>La-O₂= 2.593</td>
<td>&lt;Cr/Ni-O₂-Cr/Ni&gt;= 64.7°</td>
<td>Rₛ=6.76</td>
</tr>
<tr>
<td>Ni</td>
<td>4a (0, 0, 0)</td>
<td>Cr/Ni-O₁= 1.983</td>
<td></td>
<td>Rₕ=8.68</td>
</tr>
<tr>
<td>O₁</td>
<td>4c (0.556, 0.499, 0.250)</td>
<td>Cr/Ni-O₂= 1.763</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>8d (0.213, 0.253, 0.044)</td>
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</table>

### Morphology

SEM image of the LCNO pellet surface is shown in Fig. 2(b). SEM image indicates the compactness of the grains and high density of the prepared LCNO pellet. As well as the distribution of the grain size and the shape are also almost uniform. The calculated average grain size is found to be 61 nm.
Impedance spectroscopy

Figure 3(a) shows the conductivity spectra of LCNO in the temperature range from 30°C to 530°C. For a clear understanding of the conductivity spectra we have indexed the experimental temperature range 280°C to 480°C. It is observed that in the low frequency region the conductivity is almost constant which is equal to the dc conductivity of LCNO. But in the high frequency region conductivity is found to decrease with the frequency, which suggests the metallic nature of LCNO in the temperature range from 30°C to 530°C. In the plateau region, the dc conductivity value is firstly increasing with temperature and then it saturates and around 470°C it decreases with temperature. This type of conductivity clearly indicates that there is semiconducting to metallic transition at that temperature. To know the exact conduction mechanism, we have fitted the ac conductivity data with Drude model (fig. (c)) [9]. This model is described by $\sigma_{AC} = \frac{\sigma_{dc}}{1 + \omega^2 \tau^2}$, where $\tau$ represents the relaxation time of electron-phonon scattering. According to this model, the conduction process is mainly due to the high density of free carriers, which suggests the metallic nature of the sample. In the semiconducting region we have calculated the activation energy according to the Arrhenius law (in fig. 3(b)) and the value is 0.131 eV, which suggests the conduction mechanism of LCNO is due to the electron hopping.

CONCLUSIONS

LCNO has been synthesized by sol-gel citrate method. Rietveld refinement of the room temperature XRD pattern and Raman spectroscopy suggest the disorder orientation of Cr and Ni ions in the Pbnm LCNO crystal lattice. Impedance spectroscopy reveals the metallic nature in Pbnm LCNO in the temperature range from 30°C to 570°C.

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REFERENCES

6. C.L. Bull, P.F. McMillan, Raman scattering study and electrical properties characterization of elpasolite perovskites Ln2(BB’)O6 (Ln = La, Sm...Gd and B, B’ = Ni, Co, Mn), J. Solid State Chem. 2004, 177, 2323-2328.
9. A. Ben Jazia Kharrat, N. Moutia, K. Khirouni, W. Boujelben, Investigation of electrical behavior and dielectric properties in polycristalline Pr0.8Sr0.2MnO3 manganite perovskite, Material Research Bulletin, 2018, 105, 75-83.