Structural characterization of layered perovskite oxides $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ and $LaSr_2TiCrO_7$

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ABSTRACT

In the present work, we report structural characterization of the $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ and $LaSr_2TiCrO_7$ phases by Rietveld analysis using GSAS program. Both the phases crystallize with tetragonal unit cell in the space group I4/mmm. The selected bond distances, as determined from structural refinements, suggests that the octahedra in both the phases are distorted.

Keywords: Ruddlesden-Popper phases; X-ray diffraction; Rietveld analysis

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INTRODUCTION

A rich variety of oxides classified as Ruddlesden-Popper (RP) phases are described as intergrowth structures having the general formula $(AO)(ABO_3)_n$, where A is usually a rare-earth, alkaline-earth, or alkali ion and B can be a 3d or 4d transition-metal ion. The crystal structure of RP phases can be described by the stacking of finite n layers of perovskite ABO_3 between rock salt AO layers along the crystallographic c direction [1, 2]. The corner-sharing BO_6 octahedra form infinite sheets in the *ab* plane where strong electronic interactions can occur. With increasing n, anisotropic properties and an increase in dimensionality may be expected in RP phases. While the $n = 1$ member of this series (A_2BO_4) exhibits a quasi-two-dimensional K_2NiF_4-type structure, with only one layer of corner sharing BO_6 octahedra along the c direction, the compound ABO_3, which corresponds to the $n = \infty$ member of this series, assumes the three-dimensional distorted perovskite structure. In the second member of the RP family, $A_3B_2O_7$, two infinite BO_6 sheets are connected in the c direction between the rock-salt layers. The physical properties of various members within a given series are governed primarily by the identity and valence of the transition-metal ion, the width n of the ABO_3 perovskite slabs, the B-O-B bond angle and the oxygen content.

In our earlier work [3], we have reported the synthesis, electric transport and magnetic properties of Ruddlesden-Popper (RP) phases $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ ($n = 1$) and $LaSr_2TiCrO_7$ ($n = 2$). In this reported work, much has been left about the structural characterization of the phases. In the present work, we report structural characterization of the $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ and $LaSr_2TiCrO_7$ phases by Rietveld analysis using *GSAS* program. The selected bond distances have been determined on the basis of structural parameters derived from structural refinements.

EXPERIMENTAL SECTION

$La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ and $LaSr_2TiCrO_7$ phases have been synthesized by standard ceramic method from La_2O_3, $SrCO_3$, TiO_2 and Cr_2O_3 (purity 99.9%), the details have been described elsewhere [3].

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Formation of single-phase products and their crystal structures were studied by powder X-ray diffraction (PXRD) with Bruker AXS diffractometer type D 76181 Karlsruhe, Germany using CuK$_\alpha$ radiations. For Rietveld refinements, the data were collected in the 2θ range 10–100° with a step size of 0.02^o. The refinements were carried out by means of the program *GSAS* [4]. The selected bond distances have been determined on the basis of structural parameters derived from structural refinements.

RESULTS AND DISCUSSION

The Rietveld refinements of $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ were carried out in the space group *I4/mmm* starting with atomic positions taken from Sr_2TiO_4 [1] with La/Sr and O(2) atoms situated at special positions 4e and 4e with coordinates (0, 0, z). The Ti/Cr atoms are located at (0, 0, 0) in sites 2a, and the O(1) atoms at (0, 0.5, 0) in sites 4c. In case of $LaSr_2TiCrO_7$, refinements were carried out in the space group *I4/mmm* starting with atomic positions taken from $Sr_3Ti_2O_7$ [2] with La/Sr(2), Ti/Cr and O(2) atoms situated at special positions 4e with coordinates (0, 0, z) and O(3) at 8g with coordinates (0, 0.5, z). The La/Sr(1) and O(1) atoms are located (0, 0, 0.5) in sites 2b and O(1) atoms at (0, 0, 0) in sites 2a. A sixth-order Chebychev polynomial for the background, zero, pseudo-Voigt profile function (*U*, *V*, *W* and *X*), lattice parameters, atomic coordinates and isothermal temperature factors U_{iso} were used in the refinement. Thermal parameters were constrained to be the same for atoms occupying the same site. The occupation factors for the metals were fixed by taking sample stoichiometry into account, assuming that the La/Sr and Ti/Cr cations were randomly distributed over the sites, while those of oxygen atoms were refined. No evidence of oxygen non-stoichiometry could be obtained from the XRD structural refinements and the oxide ion sites were therefore fixed at full occupancy. We noticed that calculated diffraction patterns match well with measured ones. The difference observed between the intensities of the measured and calculated diffraction lines can be attributed by the existence of preferential orientation of the crystallites in the samples. The results of refinements are listed in Tables 1 and 2 along with the residuals for the weighted pattern R_{wp}, the pattern R_p, and the goodness of fit χ^2. The reliable parameters R_{wp}, R_p and χ^2 are reasonable for assigning the structure to the phases on the basis of the Rietveld analysis. The observed, calculated, and difference profiles for the Rietveld refinements of samples $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ and $LaSr_2TiCrO_7$ are shown in Fig.1.

The unit cell parameters obtained from the Rietveld refinements (Tables 1 and 2) are slightly different from those reported in our earlier work [3]. The data in Tables 1 and 2 suggests that the values of both parameters *a* and *c* are smaller than those of Sr_2TiO_4 (*a*=3.88 Å and *c*=12.60 Å) [1] and $Sr_3Ti_2O_7$ (*a*=3.90 Å and *c*=20.38 Å) [2] which could be due to the difference in ionic radii of Ti^{4+} and Cr^{3+} and La^{3+} and Sr^{2+} ions. It has been observed that the lattice constant *c* of $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ and of $LaSr_2TiCrO_7$ phases showed a dramatic variation compared to *a*. The systematic increase in *c* with increasing *n* is attributed to the addition of perovskite layers between the rock salt-like (La,Sr)O layers along the *c* direction where the layers are stacked.

The selected bond distances, obtained from structural refinements, are tabulated in the Table 3. The data in Table 3 suggests that (Ti/Fe)O$_6$ octahedra in both the phases are not perfectly regular consisting, typically, of four short in-plane Ti/Fe–O(1) equatorial distances (1.93123 Å) and two Ti/Fe–O(2) slightly longer apical distances (2.04999 Å) in case of $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ while there are four in-plane Ti/Fe–O(3) distances (1.94233 Å), two apical Ti/Fe–O(1) (1.94888 Å) and Ti/Fe–O(2) distances (1.88804 Å) distances in case of $LaSr_2TiCrO_7$. The mean values of Ti/Fe–O bond distances (1.97Å for $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ and 1.93 Å for $LaSr_2TiCrO_7$ Å) are in good agreement with those obtained from the sum of Shannon's ionic radii (1.96 Å) [5].

The distortion of (Ti/Cr)O$_6$ octahedra may be parameterized by the bond-length distortion of the octahedral, Δ, calculated using the equation:

$$\Delta = (1/6)\sum_{n=1}^{6}[d_n - \langle d \rangle / \langle d \rangle]^2$$

The values of Δ (Table 3), obtained by using the above equation, show that the (Ti/Cr)O$_6$ octahedra in the phase $LaSr_2TiCrO_7$ are slightly distorted, while the distortion is much higher in $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ phase.

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Table 1 Structural parameters of La$_{0.5}$Sr$_{1.5}$Ti$_{0.5}$Cr$_{0.5}$O$_4$

Atom	x	y	z	$Uiso$ (Å^2)	Occupancy
La/Sr	0	0	0.3556(2)	0.0147	0.25/0.75
Ti/Cr	0	0	0	0.0192	0.5/0.5
O(1)	0	0.5	0	0.0532	1
O(2)	0	0	0.1635(14)	0.0286	1

$a = 3.8624(1)$, $c = 12.5437(8)$, $R_{WP} = 0.1643$, $R_P = 0.1196$, $\chi^2 = 4$

Table 2 Structural parameters of LaSr$_2$TiCrO$_7$

Atom	x	y	z	$Uiso$ (Å^2)	Occupancy
La/Sr(1)	0	0	0.5	0.0186	0.333/0.667
La/Sr(2)	0	0	0.3129(2)	0.0223	0.333/0.667
Ti/Cr	0	0	0.0961(5)	0.0249	0.5/0.5
O(1)	0	0	0	0.0695	1
O(2)	0	0	0.1895(12)	0.0396	1
O(3)	0	0.5	0.0924(10)	0.0297	1

$a = 3.8803(1)$, $c = 20.2397(16)$, $R_{WP} = 0.1286$, $R_P = 0.1014$, $\chi^2 = 2.39$
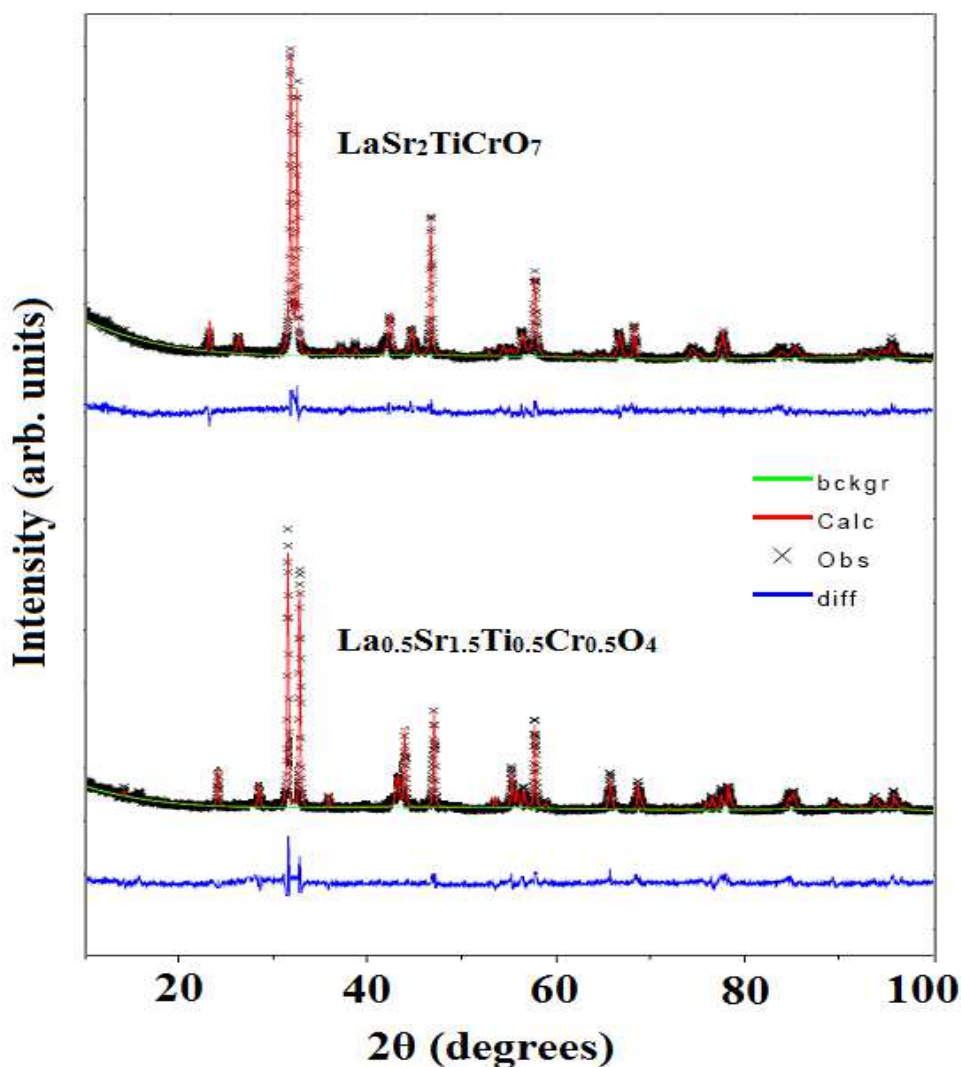
Fig.1 Rietveld refinement profiles for the fit to the XRD patterns of La$_{0.5}$Sr$_{1.5}$Ti$_{0.5}$Cr$_{0.5}$O$_4$ and LaSr$_2$TiCrO$_7$

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Table 3 Selected bond lengths of $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ and of $LaSr_2TiCrO_7$

$La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$		$LaSr_2TiCrO_7$	
Ti/Cr – O(1)×4	1.93123(5)	Ti/Cr – O(1)	1.94888(15)
Ti/Cr – O(2)×2	2.04999(13)	Ti/Cr – O(2)	1.88804(15)
		Ti/Cr – O(3)×4	1.94233(4)
<Ti/Cr – O>	1.97082	<Ti/Cr – O>	1.93437
Δ(Ti/Cr – O)×10^{-4}	8.069	Δ(Ti/Cr – O)×10^{-4}	1.163

CONCLUSION

Rietveld analysis suggests that the phases $La_{0.5}Sr_{1.5}Ti_{0.5}Cr_{0.5}O_4$ and $LaSr_2TiCrO_7$ crystallize with tetragonal unit cell in the space group *I4/mmm*. The refinement parameters show that the octahedra in both the phases are distorted.

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