

## RAPID COMMUNICATION

Structural Characterization of the Perovskite Series  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$ 

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The perovskite-type compounds  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$ ,  $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ , have been synthesized by alkoxide methods, and the room temperature structures characterized using X-ray synchrotron powder diffraction. The  $x = 0$  endmember,  $\text{LaCrO}_3$ , and the  $x = 0.1$  compound are orthorhombic in space group  $Pbnm$ , the compounds with  $x = 0.2$  to  $x = 0.7$  inclusive are rhombohedral in  $R\bar{3}c$ , and the  $x = 0.8$  and  $x = 0.9$  compounds are, like the  $x = 1$  endmember  $\text{SrTiO}_3$ , cubic in  $Pm\bar{3}m$ . This sequence differs from that reported recently in this journal (R. H. Mitchell and A. R. Chakhmouradian, *J. Solid State Chem.* 144, 81–85, 1999), but is as expected by comparison with the high-temperature behavior of the end member  $\text{LaCrO}_3$ .

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## INTRODUCTION

Recently, Mitchell and Chakhmouradian (1) reported on the synthesis by conventional ceramic methods of the doubly substituted perovskite series  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$ . The room temperature structures of the endmember perovskites are known,  $\text{LaCrO}_3$  being orthorhombic in  $Pbnm$  (2), and  $\text{SrTiO}_3$  being the aristotype cubic perovskite, space group  $Pm\bar{3}m$  (3). Mitchell and Chakhmouradian reported that the sequence of structures upon increasing  $x$  was orthorhombic ( $Pbnm$ ), tetragonal ( $I4/mcm$ ), and finally cubic. This sequence of transitions is similar to that observed in other doped perovskites including  $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3$  and  $\text{SrTi}_{1-x}\text{Zr}_x\text{O}_3$  (4, 5). But heating the  $\text{LaCrO}_3$  endmember is known (6) to induce a transition at around 550 K to a rhombohedral structure, in  $R\bar{3}c$ , and near 1300 K this transforms to cubic. Similar transitions are observed upon heating  $\text{BaCeO}_3$  (7) or by Zr doping in  $\text{BaCe}_{1-x}\text{Zr}_x\text{O}_3$  (8). The difference between the composition- and temperature-de-

pendent sequence of phases for the chromates is unusual, and for this reason we decided to undertake a further investigation.

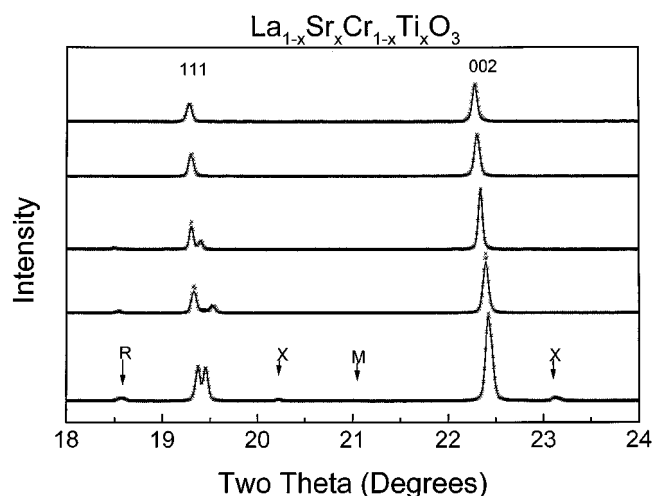
## EXPERIMENTAL

The compounds  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$ ,  $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ , were prepared as follows. An aqueous solution containing the appropriate stoichiometric amounts of lanthanum, strontium and chromium nitrates was added to an ethanolic solution of titanium (IV) isopropoxide. After hydrolysis the resulting solutions were shear mixed and dried at 90°C on a hot plate. The salts were decomposed at 700°C for 1 h and then calcined in air at 750°C for 1 h. The resulting powders were wet ball milled for 16 h using Y-stabilized zirconia balls. The milled powders were redried at 90°C and then pressed into 12-mm pellets at 5000 psi. The oxides were finally sintered in air at 1500°C for 48 h.

X-ray diffraction patterns were recorded using the Australian National Beamline Facility's powder diffractometer on beamline 20B (9), located at the Photon Factory, KEK, Tsukuba, Japan. The wavelength was set at  $\lambda = 0.75094 \text{ \AA}$  (determined by calibration using NIST silicon Standard Reference Material 640b). The samples were housed in 0.3-mm dia. capillaries that were rotated during the measurements. Patterns were recorded on image plates, from 5° to 85°  $2\theta$ , at a step interval of 0.01°. The Rietveld method (10) was used in the final stages of the data analysis.

## RESULTS

The structures were identified first from the splitting of the main peaks, and from the presence or otherwise of the



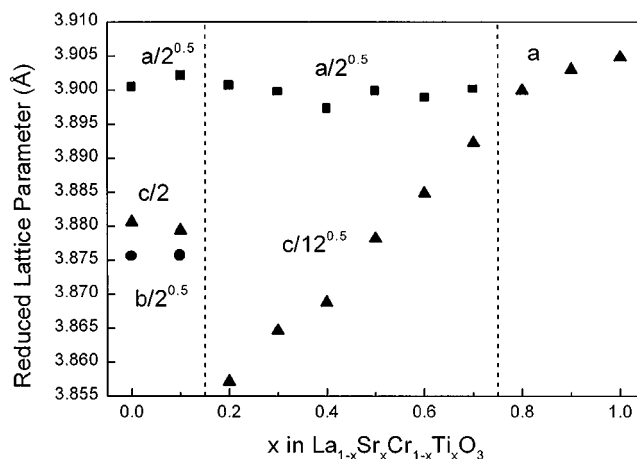
**FIG. 1.** Portion of the observed and calculated diffraction profiles for  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$ , from the bottom  $x = 0, 0.2, 0.5, 0.8,$  and  $1.0$ . The splitting of the 111 reflection in both the orthorhombic and rhombohedral structures is obvious, as is the presence of the  $R$ -point superlattice reflections in the rhombohedral phase. Additional  $M$ -point and  $X$ -point reflections are observed in the orthorhombic phase.

weak superlattice peaks associated with the different octahedral tilt patterns. Indexing the main peaks on the basis of the aristotype cubic structure, tetragonal distortion would be indicated by splitting of the  $h00$  peaks, without splitting of the  $hhh$  peaks, and rhombohedral splitting by the reverse. The peak splitting in orthorhombic  $Pbnm$  is more complex, and includes splitting of the  $hhh$  peaks (but with an intensity ratio differing from that in rhombohedral) as well as of the  $h00$  (5).

The  $\text{SrTiO}_3$  endmember was cubic as expected. Patterns from the  $x = 0.8$  and  $x = 0.9$  compounds showed no evidence of splitting in the  $h00$ ,  $hhh$  (see Fig. 1) or any other peak, nor was there any sign of superlattice reflections.<sup>1</sup> In particular, even at synchrotron resolution, we saw no sign of the splitting of the 332 peak reported by Mitchell and Chakhmouradian—in any case the splitting of this peak would tend to indicate a rhombohedral rather than tetragonal distortion. We conclude that for  $x = 0.8$  to  $x = 1$  inclusive the structures are cubic,  $Pm\bar{3}m$ .

At compositions from  $x = 0.7$  down to  $x = 0.2$ , the  $hhh$  peaks were split but there was no splitting of the  $h00$  peaks (Fig. 1). Superlattice reflections due to  $R$ -point distortions could be seen throughout this composition range, but none attributable to  $M$ -point distortions (see Reference 11, 12 for further discussion of these). This is consistent with a rhombohedral structure in space group  $R\bar{3}c$ . At  $x = 0.2$  there was evidence of the main peaks from a second perovskite phase, but the quantity was so small as to prevent its identification.

<sup>1</sup> We note that in using a laboratory diffractometer such weak superlattice reflections may not be observed even when they are present.



**FIG. 2.** Variation of the lattice parameters with composition in  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$ . For  $x < 0.2$  the structures are in  $Pbnm$ , for  $x = 0.2$  to  $0.7$  inclusive the structures are in  $R\bar{3}c$ , and for  $x > 0.7$  the structures are in  $Pm\bar{3}m$ .

The  $x = 0.1$  compound was, like the  $\text{LaCrO}_3$  endmember, clearly orthorhombic. The main peaks showed more complex splitting (see Fig. 1), and superlattice reflections from  $R$ -point,  $M$ -point, and  $X$ -point distortions could all be seen. The previously established space group (1, 2) was confirmed.

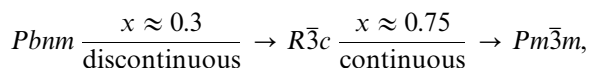
The patterns were then analyzed by the Rietveld method, using program LHPM (10), assuming the structures indicated above. Atomic coordinates obtained for  $\text{LaCrO}_3$  were in satisfactory agreement with those from Khattak and Cox (2), and coordinates obtained in the other refinements were typical for the structures assumed.<sup>2</sup> The lattice parameters obtained from the Rietveld refinements are shown in Fig. 2. It is instructive to compare this figure with the similar figure shown by Mitchell and Chakhmouradian (1), their Fig. 4. In general terms, we show only one lattice parameter (cubic), whereas Mitchell and Chakhmouradian show two (from their assumption of tetragonal) that are equal within the experimental error, and we show only two lattice parameters (rhombohedral), whereas two of the three orthorhombic parameters of Mitchell and Chakhmouradian are similarly equal. Where Mitchell and Chakhmouradian show three distinct lattice parameters we agree the structure is orthorhombic, except at  $x = 0.2$ , where it may be that, in the proximity of the phase boundary, we have produced the rhombohedral rather than the orthorhombic phase.

Additionally to our room temperature study, we have recorded patterns from  $\text{LaCrO}_3$  and the  $x = 0.1$  compound,

<sup>2</sup> In  $Pbnm$  the  $A$ -type cations are on the  $4c$  site at  $x y \frac{1}{2}$ , the  $B$  cations on the  $4a$  sites at  $0 0 0$ , O1 on the  $4c$  sites at  $x y \frac{1}{2}$ , and O2 on the  $8d$  sites at  $x y z$ . In  $R\bar{3}c$  the  $A$  cations are on  $6a$  sites at  $0 0 \frac{1}{2}$ , the  $B$  cations on the  $6b$  sites at  $0 0 0$ , and the O on the  $18e$  sites  $x 0 \frac{1}{2}$ ; and in  $Pm\bar{3}m$  the  $A$  cations are at  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ , the  $B$  cation at  $0 0 0$ , and O at  $\frac{1}{2} 0 0$ .

each as a function of temperature. We have confirmed both these compounds undergo a first-order transition from orthorhombic to the rhombohedral  $R\bar{3}c$ , the transition temperatures being 300 and 150°C for the  $x = 0$  and  $x = 0.1$  compounds, respectively. Likewise we observed at 200°C the  $x = 0.2$  compound had the rhombohedral structure and there was no evidence for a second perovskite phase.

In summary, we have investigated the structural sequence in the series  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-x}\text{Ti}_x\text{O}_3$  in view of a report that this differed from the sequence found on heating  $\text{LaCrO}_3$  (6). We have found, contrary to the previous report, that the sequence is



which is in accord with the behavior of  $\text{LaCrO}_3$  on heating.

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