

Structure and electric transport properties of $\text{LnSr}_2\text{FeTiO}_7$ ($\text{Ln} = \text{La}, \text{Nd}$ and Gd)

SURESH GUPTA, V SINGH, B L SHARMA[†] and INDU BHUSHAN SHARMA*

ISCAS Institute of Solid State & Materials Science, Jammu University Campus, Jammu 180 006, India

[†]Department of Chemistry, University of Jammu, Jammu 180 006, India

MS received 24 June 2010

Abstract. Three new phases with compositions, $\text{LaSr}_2\text{FeTiO}_7$, $\text{NdSr}_2\text{FeTiO}_7$ and $\text{GdSr}_2\text{FeTiO}_7$, were prepared by the traditional ceramic method. Lazy–Pulverix analysis of the X-ray diffraction data suggests that the phases crystallize in the RP-type ($n = 2$) structure in the space group, $I4/mmm$. The cell dimensions along the c -axis decrease with decrease in size of the rare earth ions. Electrical resistivity, as a function of temperature, shows that the materials are insulators and the resistivity decreases with decrease in the size of the rare earth ion, which is attributed to increase in the three-dimensional character.

Keywords. RP-type phases; XRD studies; electrical resistance.

1. Introduction

Ruddlesden–Popper type phases with composition, $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ (where A is an alkaline earth/rare earth ion and B is a transition metal ion), are known to exhibit interesting structural, electric transport and magnetic properties in the literature (Zhang *et al* 1994; Briceno *et al* 1995; Battle *et al* 2004; Shrivastava *et al* 2005a, b). These phases usually crystallize with tetragonal or orthorhombic unit cell in the space group, $I4/mmm$ or $Fmmm$. The $n = 1$ phases are two-dimensional in character, while $n = 3$ phases are three-dimensional. The phases in between these two possess characters between 2 and 3 dimensions. The physical properties of these phases, especially the electric transport and magnetic properties, are known to depend upon the nature and balance state of the ions at A and B sites, B–O–B bond angle, oxygen content and so on. It has been observed that large variation in properties is observed in many cases with partial substitution at the sites A and B (Mahesh *et al* 1996; Morimoto *et al* 1996; Sharma and Magotra 1999; Shilovo *et al* 2002; Sharma *et al* 2005).

In the present study, three new RP-type phases ($n = 2$) with compositions, $\text{LaSr}_2\text{FeTiO}_7$, $\text{NdSr}_2\text{FeTiO}_7$ and $\text{GdSr}_2\text{FeTiO}_7$, have been prepared and their crystal structure determined by Lazy–Pulverix analysis of the XRD data (Yvon *et al* 1977). The electrical resistivity as a function temperature has also been studied.

2. Experimental

2.1 Synthesis

The phases with compositions, $\text{LaSr}_2\text{FeTiO}_7$, $\text{NdSr}_2\text{FeTiO}_7$ and $\text{GdSr}_2\text{FeTiO}_7$, were synthesized by the traditional ceramic method by heat treatment of the constituent oxides, Gd_2O_3 , Nd_2O_3 , La_2O_3 , Fe_2O_3 and TiO_2 (purity, 99.9%). The constituent oxides in the stoichiometric ratio corresponding to the composition of these phases were weighed, pulverized and homogenized by grinding in cyclohexane. The dry homogenized mixtures of the oxides were pressed into pellets in a hydraulic press and heat treated at 1560 K (with 10° variation) in a tube furnace in static air atmosphere for about 60 h with a number of intermediate grindings and pelletizing. The products were pulverized to fine powder for further investigation.

2.2 X-ray diffraction study

The product phases were subjected to room temperature X-ray diffraction studies on a Rigaku Multiflex X-ray diffractometer at a scanning speed of 1°/min in the 2 θ range 10–70°. A representative X-ray diffraction pattern is given in figure 1.

2.3 Electrical resistivity measurement

The electrical resistivity of the pellets of phases, sintered at 1400 K for 6 h before use, was studied by four-probe method in the temperature range 10–300 K using a Leybold

*Author for correspondence (indubsharma@rediffmail.com)

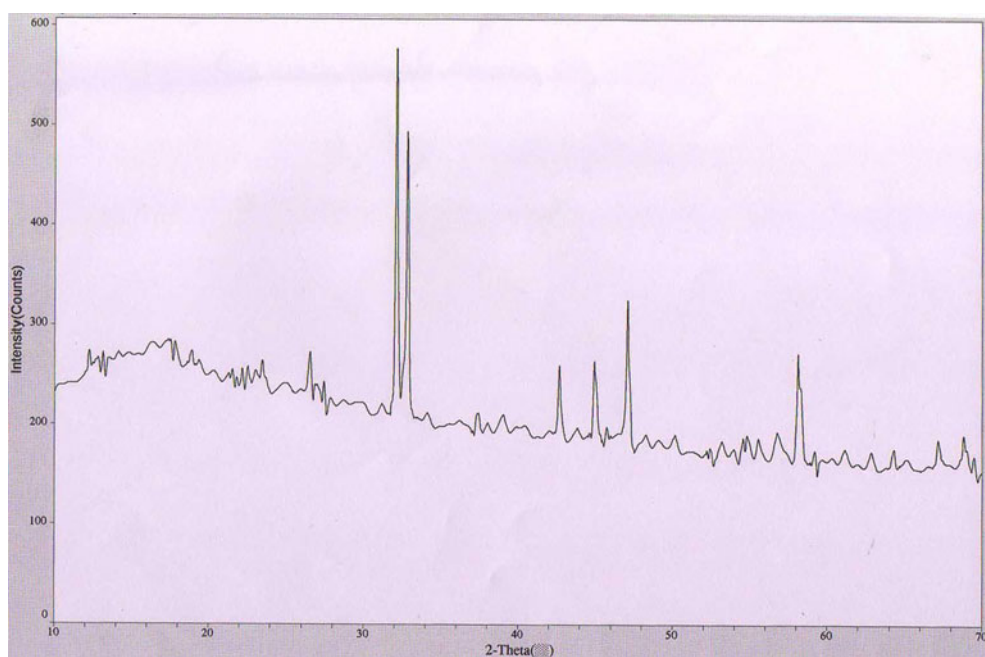


Figure 1. X-ray diffraction pattern of $\text{LaSr}_2\text{FeTiO}_7$.

Closed cycle helium cryostat, using Keithley 6517 A electrometer/high resistance meter. Thin wires were attached to the surface of the pellets with silver epoxy for the purpose of electrodes.

3. Results and discussion

3.1 Crystal structure

The X-ray diffraction results have been indexed on a tetragonal unit cell and the cell parameters were refined with the programme 'Cell' and the same are given in table 1. The

estimated standard deviations in the unit cell have been calculated by the least squares method giving the value of the factor, R better than 0.0007. Applying the Lazy-Pulverix programme, theoretical X-ray diffraction intensities for the phases have been generated using the unit cell dimensions as given in tables 1–3 and the structural parameters (position coordinates and the space group, $I4/mmm$) of the well known RP-type phase, $\text{Sr}_3\text{Ti}_2\text{O}_7$ (Ruddlesden and Popper 1958). The values of the positional coordinate z (x and y coordinates remaining constant), which result in good agreement between experimental and theoretical intensities, are given in table 4. The calculated d -values along with their intensities are given along with the experimental data in tables 1–3. The results show fair agreement between the experimental and the theoretical data, especially when no preferred ori-

Table 1. Powder X-ray diffraction data of $\text{LaSr}_2\text{FeTiO}_7$ (space group : $I4/mmm$, $a = 3.895 \text{ \AA}$; $c = 20.211 \text{ \AA}$).

| h | k | l | $d_{\text{obs}} (\text{\AA})$ | $d_{\text{cal}} (\text{\AA})$ | I_{obs} | I_{cal} |
|-----|-----|-----|-------------------------------|-------------------------------|------------------|------------------|
| 0 | 0 | 6 | 3.362 | 3.356 | 8 | 13 |
| 1 | 0 | 5 | 2.786 | 2.785 | 100 | 100 |
| 1 | 1 | 0 | 2.725 | 2.727 | 70 | 61 |
| 1 | 1 | 6 | 2.124 | 2.128 | 20 | 17 |
| 1 | 1 | 10 | 2.019 | 2.011 | 21 | 16 |
| 2 | 0 | 0 | 1.942 | 1.947 | 38 | 37 |
| 2 | 0 | 6 | 1.678 | 1.683 | 5 | 6 |
| 0 | 0 | 12 | 1.764 | 1.676 | 3 | 2 |
| 2 | 1 | 5 | 1.592 | 1.598 | 33 | 37 |
| 2 | 0 | 10 | 1.391 | 1.399 | 4 | 17 |
| 2 | 2 | 0 | 1.372 | 1.377 | 5 | 11 |

Table 2. Powder X-ray diffraction data of $\text{NdSr}_2\text{FeTiO}_7$ (space group : $I4/mmm$, $a = 3.895 \text{ \AA}$; $c = 20.162 \text{ \AA}$).

| h | k | l | $d_{\text{obs}} (\text{\AA})$ | $d_{\text{cal}} (\text{\AA})$ | I_{obs} | I_{cal} |
|-----|-----|-----|-------------------------------|-------------------------------|------------------|------------------|
| 1 | 0 | 3 | 3.358 | 3.369 | 6 | 4 |
| 0 | 0 | 6 | 3.352 | 3.360 | 2 | 3 |
| 1 | 0 | 5 | 2.280 | 2.801 | 100 | 100 |
| 1 | 1 | 0 | 2.759 | 2.754 | 65 | 61 |
| 1 | 1 | 6 | 2.126 | 2.130 | 18 | 20 |
| 2 | 0 | 0 | 1.940 | 1.948 | 39 | 37 |
| 2 | 1 | 5 | 1.591 | 1.599 | 31 | 36 |
| 2 | 2 | 0 | 1.372 | 1.377 | 8 | 11 |

Table 3. Powder X-ray diffraction data of $\text{GdSr}_2\text{FeTiO}_7$ (space group: $I4/mmm$, $a = 3.897 \text{ \AA}$; $c = 19.992 \text{ \AA}$).

| h | k | l | $d_{\text{obs}}(\text{\AA})$ | $d_{\text{cal}}(\text{\AA})$ | I_{obs} | I_{cal} |
|-----|-----|-----|------------------------------|------------------------------|------------------|------------------|
| 1 | 0 | 3 | 3.354 | 3.364 | 5 | 7 |
| 1 | 0 | 5 | 2.784 | 2.791 | 100 | 100 |
| 1 | 1 | 0 | 2.751 | 2.756 | 65 | 68 |
| 1 | 1 | 6 | 2.120 | 2.124 | 22 | 25 |
| 2 | 0 | 0 | 1.952 | 1.949 | 40 | 42 |
| 2 | 1 | 3 | 1.682 | 1.686 | 2 | 3 |
| 2 | 1 | 5 | 1.588 | 1.598 | 33 | 37 |
| 2 | 0 | 10 | 1.391 | 1.395 | 8 | 14 |
| 2 | 2 | 0 | 1.372 | 1.378 | 6 | 12 |

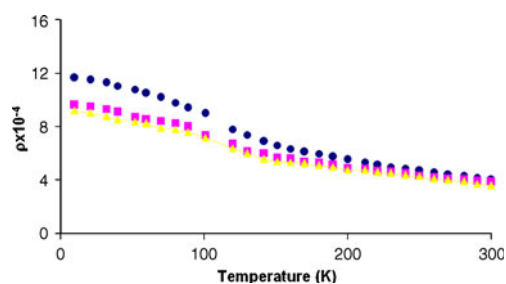
Table 4. Positional coordinate (z) in $\text{LaSr}_2\text{FeTiO}_7$, $\text{NdSr}_2\text{FeTiO}_7$ and $\text{GdSr}_2\text{FeTiO}_7$ (x and y coordinates remain fixed).

| Atoms | $\text{LaSr}_2\text{FeTiO}_7$ | $\text{NdSr}_2\text{FeTiO}_7$ | $\text{GdSr}_2\text{FeTiO}_7$ |
|----------|-------------------------------|-------------------------------|-------------------------------|
| La/Sr(1) | 0.5 | 0.5 | 0.5 |
| La/Sr(2) | 0.3075 | 0.3102 | 0.3140 |
| Fe/Ti | 0.089 | 0.094 | 0.085 |
| O(1) | 0.093 | 0.086 | 0.091 |
| O(1) | 0.1842 | 0.1921 | 0.1881 |
| O(3) | 0.0 | 0.0 | 0.0 |

entation effects have been taken into consideration in generation of the theoretical intensities. This confirms formation of new RP-type ($n = 2$) phases with the composition, $\text{LaSr}_2\text{FeTiO}_7$, $\text{NdSr}_2\text{FeTiO}_7$ and $\text{GdSr}_2\text{FeTiO}_7$. It was also observed that in case of $\text{LaSr}_2\text{FeTiO}_7$, when heated in oxygen atmosphere, the tetragonal structure transforms into the orthorhombic form.

3.2 Electrical resistivity

The specific electrical resistance (ρ) vs temperature (K) plot for these phases is given in figure 2. There is continuous increase in specific resistance with decrease in temperature. The temperature coefficient of resistivity is negative, which is the typical behaviour of insulators. The plot, however, shows that with substitution of rare earth ions, the resistivity decreases with decrease in the ionic size. It is highest in case of the phase containing Ln^{3+} ion and decreases in the phases with Nd^{3+} and Gd^{3+} ions, the least being in the case of the Gd^{3+} containing phase. This may be attributed to increase in the 3D character because of coming closer of the $(\text{Fe/Ti})_2\text{-O}$ and the $(\text{Ln/Sr})\text{-O}$ layers along the c -axis as a result of decrease in the ionic size. The X-ray diffraction studies confirm that there is decrease in c -axis with decrease in the ionic size of the Ln ion in $\text{LaSr}_2\text{FeTiO}_7$, $\text{NdSr}_2\text{FeTiO}_7$ and $\text{GdSr}_2\text{FeTiO}_7$. However, for precise understanding of

**Figure 2.** Log ρ vs temperature (K) of \bullet , $\text{LaSr}_2\text{FeTiO}_7$; \blacksquare , $\text{NdSr}_2\text{FeTiO}_7$ and \blacktriangle , $\text{GdSr}_2\text{FeTiO}_7$.

the variation in the electrical resistance, studies on single crystals may be required.

4. Conclusions

Three new phases with compositions, $\text{LaSr}_2\text{FeTiO}_7$, $\text{NdSr}_2\text{FeTiO}_7$ and $\text{GdSr}_2\text{FeTiO}_7$, have been prepared by the ceramic method. X-ray diffraction studies show that the phases crystallize in the RP-type ($n = 2$) structure. Electric transport studies suggest that the materials are insulators in the temperature range 10–300 K. The specific resistance values decrease with decrease in the rare earth ion.

Acknowledgement

The authors are thankful to DST, New Delhi, for financial support.

References

- Battle P D, Burley J C, Gallon D J and Grey C P 2004 *J. Solid State Chem.* **177** 119
- Briceno G, Chang H, Sun X, Schultz P G and Xiang X D 1995 *Science* **270** 273
- Mahesh R, Mahendiran R, Raychaudhuri A K and Rao C N R 1996 *J. Solid State Chem.* **122** 448
- Morimoto Y, Asamitsu A, Kuwahara H and Tokura Y 1996 *Nature* **380** 141
- Ruddlesden S N and Popper P 1958 *Acta Crystallogr.* **11** 54
- Sharma I B and Magotra S K 1999 *J. Alloys Compd.* **284** 18
- Sharma I B, Kumari S and Gupta S 2005 *J. Alloys Compd.* **402** 12
- Shilovo Y A, Patrakeev M V, Metberg E B, Leonidor I A, Kozhenikov V L and Poeppleneier K R 2002 *J. Solid State Chem.* **168** 275
- Shrivastava O P, Kumar N and Sharma I B 2005a *Mater. Res. Bull.* **40** 731
- Shrivastava O P, Kumar N and Sharma I B 2005b *J. Mater. Sci.* **40** 2945
- Yvon K, Jeitschko W and Parthe E 1977 *Lazy Pulverix, Laboratoire De Crystallographie Aux Rayons-X* (Genève, Switzerland: Université de Genève)
- Zhang Z, Greenblat M and Goodenough J B 1994 *J. Solid State Chem.* **108** 402