JOURNAL OF SOLID STATE CHEMISTRY **91**, 180–185 (1991)

LETTERS TO THE EDITOR

Single Crystals of New Ruddlesden–Popper Phases $(SrLa)_3V_2O_7$ and $Sr_4V_3O_{9.7}$: Preparation, Crystal Structure, and Electrical Resistivity

WENHE GONG, J. S. XUE, AND J. E. GREEDAN

Institute for Materials Research and Department of Chemistry, McMaster University, Hamilton, Canada L8S 4M1

Communicated by J. M. Honig, December 13, 1990

Single crystals of $Sr_{1.5}La_{1.5}V_2O_7$ ($Sr_3Ti_2O_7$-type) and $Sr_4V_3O_{9.7}$ ($Sr_4Ti_3O_{10}$-type) have been grown by a melt method in molybdenum crucibles at high temperatures and from a strontium borate flux. Crystal structures have been refined from single crystal X-ray data. The crystals are large enough for resistivity measurements: $Sr_4V_3O_{9.7}$ is metallic down to 4.2 K, while $Sr_{1.5}La_{1.5}V_2O_7$ is a semiconductor. A possible correlation exists between the observed electrical properties and the degree of distortion in the V–O polyhedra.

I. Introduction

Transition metal oxides with perovskite and related structures have been of interest in our laboratories for several years. In particular, compounds with d^1 configuration ions, especially the series LnTiO$_3$, where Ln is a lanthanide or Y, show remarkable electrical and magnetic properties, such as metal–semiconductor transitions and many varieties of long range and short range magnetic order (*1*). Given the intense interest manifest recently concerning the properties of d^9 compounds, such as the superconducting copper oxides with layered perovskite structures, it seemed reasonable to explore the crystal chemistry and the physical properties of layered perovskite oxides of d^1 ions, i.e., one-electron analogues of the one-hole copper oxides in hopeful anticipation of observing parallel behavior. $SrVO_3$ is a metal with unusual magnetic properties (*2*), but little is known about the existence and properties of the so-called Ruddlesden–Popper, R-P, phases which are reported for the corresponding Sr–Ti–O system (*3*). Sr_2VO_4 (*4, 5*) and $Sr_4V_3O_{9.8}$ (*6*) have been reported recently, but single crystals have not been grown, and a detailed structure is lacking for the latter phase. In addition, no phases with doping on the Sr site, for example by La, have been reported. Here we describe the preparation of single crystals and the crystal structure of a new layered perovskite, $(SrLa)_3V_2O_7$, the detailed structure of $Sr_4V_3O_{10-x}$, and their electrical resistivities.

II. Experimental

Preparation and Crystal Growth

$Sr_{1.5}La_{1.5}V_2O_7$. Single crystals of this material resulted from the melting of the K_2NiF_4-type solid solution $Sr_{1.6}La_{0.4}VO_4$. A mixture of $SrCO_3$ (Ceramic, pure certified chemicals), $LaVO_4$ (made from V_2O_5 and prefired Research Chemicals 99.99% La_2O_3), and V_2O_5 (Fisher, 99.9%) in the molar ratio 1.6 : 0.4 : 1.0 (Sr : La : V) was reduced in hydrogen at 1300°C for 20 hr then

0022-4596/91 $3.00

TABLE I

CRYSTALLOGRAPHIC DATA FOR $Sr_{1.5}La_{1.5}V_2O_7$ AND $Sr_4V_3O_{9.7}$

	$Sr_{1.5}La_{1.5}V_2O_7$	$Sr_4V_3O_{9.7}$
Crystal dimensions (mm)	0.22 × 0.11 × 0.02	0.20 × 0.14 × 0.006
Cell constants (Å)		
a	3.879(1)	3.852(1)
c	20.408(5)	28.00(6)
Cell volume ($Å^3$)	307.07(2)	415.46(2)
μ (cm^{-1})	256.09	267.47
Secondary extinction x	0.0036(4)	0.0006(7)
2θ range (°)	2 ~ 60	2 ~ 60
Total reflections	912	1139
Unique reflection	147	178
R	0.033	0.050
R_w	0.034	0.052

loaded into an open molybdenum crucible and melted by radio frequency induction heating at 1800 ± 50°C under 0.5 atm of prepurified argon. The temperature was measured by a radiation thermometer (300C, IRCON Inc). The sample was then slow cooled over 10 hr to 200°C. Many, black, plate-like crystals were recovered, with dimensions up to $4 \times 2 \times 0.05$ mm^3. EDAX data confirmed the presence of La in the crystals. It has not yet been possible to prepare this phase in the absence of La in either polycrystalline or single crystalline form.

$Sr_4V_3O_{9.7}$. A mixture of $Sr_{1.6}La_{0.4}VO_4$ and $SrVO_3$ (weight ratio about 1.3 : 1.0) and an equal weight of $Sr_3B_2O_6$ was loaded into a Mo crucible, $\frac{3}{4}$ or 1 in. diameter. The crucible and contents were then evacuated to 10^{-6} mm Hg in an induction heating furnace. The system was back-filled to 0.5 atm of prepurified argon and then heated to 1700 ± 50°C and cooled to room temperature in 10 hr. Deep blue-violet crystals were recovered up to $3 \times 2 \times 0.03$ mm^3. In spite of the presence of La in the melt, its concentration in the crystals was shown by EDAX to be less than 1%. It has not yet been possible to prepare single crystals of this phase without including La in the melt.

Resistivity Measurements

The van der Pauw method was used for all dc resistivity measurements. Samples were provided with four contacts, using silver paint and 0.025 diameter gold wire. The contacts were ohmic. The measurements were performed using a Keithley-181 nanovoltmeter. For both samples, $Sr_{1.5}La_{1.5}V_2O_7$ and $Sr_4V_3O_{9.7}$, the crystals used were about 3×2 mm^2 in area and the resistivities are specified for current flow in the *ab* plane.

X-Ray Diffraction

The single crystal data were obtained on a Nicolet P3 diffractometer with graphite monochromatized Mo$K\alpha$ radiation λ = 0.71069 Å in the θ–2θ scan mode at room temperature. Scan speed varied from 4.9 to 29.3°/min and four octants (*hkl* and *hkl*) were collected. Absorption corrections

TABLE II

POSITIONAL AND THERMAL PARAMETERS FOR $Sr_{1.5}La_{1.5}V_2O_7$

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}
$(Sr/La)_1$	$2b$	0	0	$\frac{1}{2}$	0.0085(6)	0.0085(6)	0.0061(13)
$(Sr/La)_2$	$4e$	0	0	0.3173(1)	0.0079(4)	0.0079(4)	0.0033(9)
V	$4e$	0	0	0.0959(1)	0.0061(7)	0.0061(7)	0.0001(23)
O_1	$2a$	0	0	0	0.0193(45)	0.0193(45)	0.0010(99)
O_2	$8g$	0	$\frac{1}{2}$	0.0962(4)	0.0102(30)	0.0061(28)	0.0153(48)
O_3	$4e$	0	0	0.1989(7)	0.0219(34)	0.0219(34)	0.0074(67)

Note. Occupation factors for Sr_1 and Sr_2 are 0.48(4) and 0.53(2), respectively.

TABLE III

POSITIONAL AND THERMAL PARAMETERS FOR $Sr_4V_3O_{9.7}$

Atom	Position	x	y	z	$B(\text{Å}^2)$	Occupation
Sr_1	$4e$	0	0	0.4309(1)	0.0092(9)	
Sr_2	$4e$	0	0	0.2980(1)	0.0070(5)	
V_1	$2a$	0	0	0	0.0101(18)	
V_2	$4e$	0	0	0.1387(1)	0.0091(13)	
O_1	$4c$	0	$\frac{1}{2}$	0	0.0170(69)	
O_2	$4e$	0	0	0.0690(5)	0.0106(45)	0.85(4)
O_3	$8g$	0	$\frac{1}{2}$	0.1380(3)	0.0106(45)	
O_4	$4e$	0	0	0.2097(5)	0.0121(28)	

were applied using the ψ-scan method, and a secondary extinction correction was applied according to $F^* = F(1 - 0.0001F^2x/\sin\theta)$, where F^* is the calculated structure factor and x is the extinction coefficient. Refinement was carried by the program SHELX 76 in space group $I4/mmm$ (No. 139) in both cases. Cell constants were determined by least-squares refinement of 15 well-centered reflections in the range $20° \leq 2\theta \leq 30°$. At the end of refinement the difference Fourier maps showed only 1.1 and 1.5 residual electrons/cm^3 for $Sr_{1.5}La_{1.5}V_2O_7$ and $Sr_4V_3O_{9.7}$, respectively. For both samples the occupation number of the oxygen sites was refined. In the case of $Sr_4V_3O_{10-x}$ one site was found to be 85(4)% occupied giving $x = 0.3(1)$, while no significant oxygen deficiency was detected in $Sr_{1.5}La_{1.5}V_2O_7$. It was not possible to check this by thermogravimetric analysis as the individual crystals are too small for TGA. Table I lists other parameters relevant to the particular compounds examined.

TABLE IV

BOND DISTANCES (Å) FOR $Sr_{1.5}La_{1.5}V_2O_7$ AND $Sr_4V_3O_{9.7}$

$Sr_{1.5}La_{1.5}V_2O_7$			$Sr_4V_3O_{9.7}$		
$(Sr/La)_1–O_1$	(×4)	2.743(2)	$Sr_1–O_1$	(×4)	2.730(5)
$(Sr/La)_1–O_2$	(×8)	2.760(2)	$Sr_1–O_2$	(×4)	2.724(4)
$(Sr/La)_2–O_2$	(×4)	2.623(5)	$Sr_1–O_3$	(×4)	2.726(5)
$(Sr/La)_2–O_3$	(×4)	2.763(5)	$Sr_2–O_3$	(×4)	2.630(3)
$(Sr/La)_2–O_3$	(×1)	2.418(16)	$Sr_2–O_4$	(×4)	2.732(3)
$V–O_1$	(×1)	1.959(3)	$Sr_2–O_4$	(×1)	2.477(15)
$V–O_2$	(×1)	1.940(1)	$Sr_1–O_1$	(×4)	1.926(1)
$V–O_3$	(×4)	2.101(15)	$Sr_1–O_2$	(×2)	1.931(14)
			$V_2–O_2$	(×1)	1.951(14)
			$V_2–O_3$	(×4)	1.926(1)
			$V_2–O_4$	(×1)	1.988(14)

III. Results and Discussion

Two new Ruddlesden–Popper phases, $(SrLa)_3V_2O_7$ and $Sr_4V_3O_{10-x}$, have been prepared in single crystal form. While this work was in process polycrystalline $Sr_4V_3O_{9.8}$ was reported, but detailed structural information is lacking (*6*). $(SrLa)_3V_2O_7$ is reported here for the first time in any form. That these compounds are Ruddlesden–Popper phases is suggested by the cell constants, Table I, which are very similar to those of $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ (*3*). The structure refinement for both compounds is confirmatory; the results are listed in Tables II and III. Assuming possible compositions for both phases to be $Sr_{3-x}La_xV_2O_{7-y}$ and $Sr_{4-x}La_xV_3O_{10-y}$, refinement yields $x = 1.46$, $y = 0.0$ for the former and $x = 0.0$, $y = 0.30$ for the latter. These values are in reasonable accord with the Sr/La ratio estimated from EDAX data. Selected bond distances are shown in Table IV.

The data of Figs. 1 and 2 indicate that

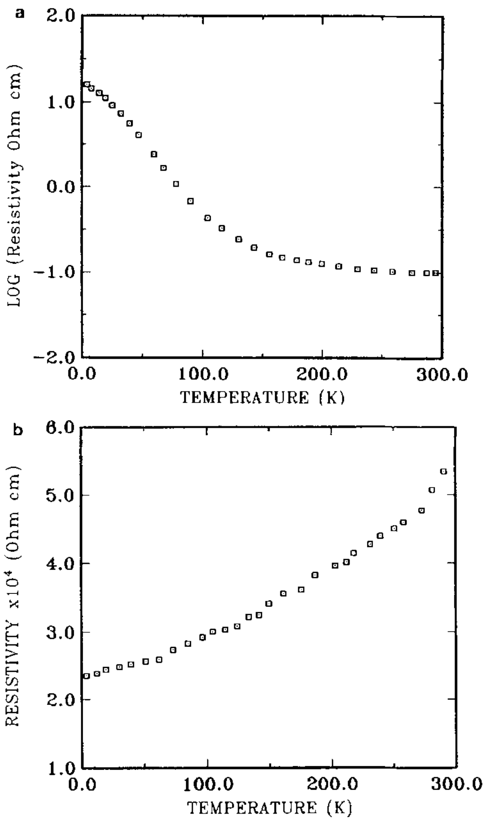

FIG. 1. Temperature dependence of the resistivity (*ab* plane) for (a) $Sr_{1.5}La_{1.5}V_2O_7$ crystal and (b) $Sr_4V_3O_{9.7}$ crystal.

$Sr_{1.5}La_{1.5}V_2O_7$ is a semiconductor while $Sr_4V_3O_{9.7}$ is a metal over the temperature range 4.2 to 300 K. The resistivity curve of Fig. 1 plotted as log ρ versus T is a sigmoidal with temperature. Only a portion of the data produces a linear log ρ versus T^{-1} law, yielding an activation energy of ~0.03 eV within the range 75 to 155 K. The metallic behavior of $Sr_4V_3O_{9.7}$ can be compared with the polycrystalline results of Ref. (*5*). The 300 K resistivity value for the crystals of 5 × 10^{-4} ohm cm^{-1} is lower by an order of magnitude than that for the polycrystal, 2 × 10^{-3} ohm cm^{-1}, which is the expected trend. The temperature dependence of the resistivity cannot be fitted to a power law in this range. More detailed studies of the electrical and the magnetic properties of these materials are in progress.

It is useful to compare the structural details and the electrical properties of these new phases with related compounds such as $SrVO_3$ and Sr_2VO_4 in the case of $Sr_4V_3O_{9.7}$, which contains predominantly V^{4+}, $3d^1$, and $LaVO_3$ and $SrLaVO_4$ for $Sr_{1.5}La_{1.5}V_2O_7$, which contains predominantly V^{3+}, $3d^2$. In previous studies of a related $3d^1$ system, the LnTiO$_3$ series, where Ln is a lanthanide, a correlation was noted between the degree of distortion in the Ti–O octahedron and the electrical properties, namely that the activation energy for conduction increased monotonically with the degree of distortion (*7*). In this case the distortion is of tetragonal symmetry; the four V–O distances in the plane normal to the fourfold axis are necessarily equal. Thus, a convenient distortion index (DI) is given by $[(V–O)_{c\text{-axis}} - (V–O)_{\text{plane}}]/(V–O)_{\text{plane}}$. Both $SrVO_3$ and Sr_2VO_4 contain only one type of octahedron while for $Sr_4V_3O_{9.7}$ there are two distinct octahedra, as can be seen in Fig. 2b, comprising a block of three octahedra stacked along the c-axis, one central and two terminal. For cubic $SrVO_3$, which is metallic, the DI is, of course, exactly zero, while for semiconducting Sr_2VO_4, DI = 0.036. Metallic $Sr_4V_3O_{9.7}$ is interesting, as the DI for the terminal octahedra is 0.021, similar to Sr_2VO_4, while for the central octahedron it is 0.004, an order of magnitude smaller. A DI of similar magnitude can be computed for metallic $LaTiO_3$, 0.006 (*8*). This suggests that the metallic properties of $Sr_4V_3O_{9.7}$ may be associated with the central VO_6 octahedron, raising the possibility that the d electrons associated with the terminal octahedra may not be delocalized. In fact, the magnetic susceptibility of polycrystalline $Sr_4V_3O_{9.8}$ can be analyzed in terms of Curie–Weiss law plus temperature-independent contributions (*6*). Of course, metallic

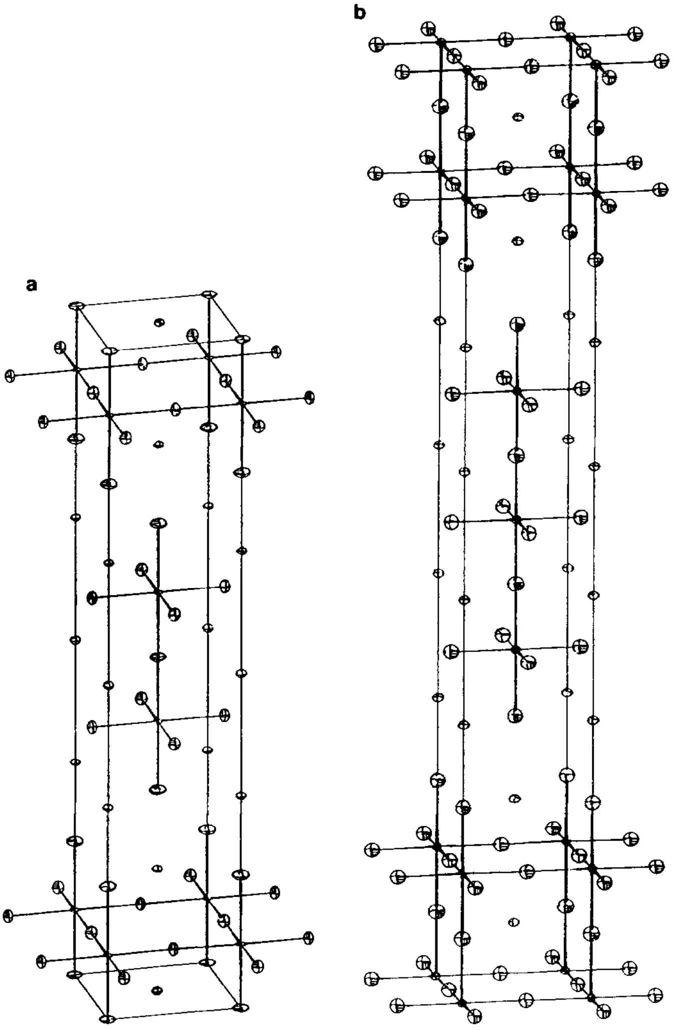

FIG. 2. Unit cells for (a) $Sr_{1.5}La_{1.5}V_2O_7$ and (b) $Sr_4V_3O_{9.7}$.

conductivity could result from the small amount of electron doping due to the oxygen nonstoichiometry; $Sr_4V_3O_{9.7}$ contains formally 20% V^{3+}. It should be noted that similar and even larger doping levels in the $Sr_{2-x}La_xVO_4$ system are not sufficient to produce metallic behavior (*9*).

For the predominantly V^{3+}, $3d^2$ systems all of the known oxides are semiconductors, $LaVO_3$, $SrLaVO_4$, and $Sr_{1.5}La_{1.5}V_2O_7$. Correlation effects are expected to be more important here but the DIs are all similar, 0.036 for $LaVO_3$ (*10*), 0.090 for $SrLaVO_4$ (*11*), and 0.047 for $Sr_{1.5}La_{1.5}V_3O_7$.

Acknowledgments

We thank the Natural Science and Engineering Research Council of Canada and the Ontario Centre for Materials Research for financial support.

References

1. J. E. GREEDAN, *J. Less-Common Metals* **111,** 335 (1985).

2. P. Dougier, J. C. C. Fan, and J. B. Goodenough, *J. Solid State Chem.* **14,** 247 (1975).
3. S. N. Ruddlesden and P. Popper, *Acta Crystallogr.* **11,** 54 (1958).
4. M. Cyrot, B. Lambert-Andron, J. L. Soubeyroux, M. J. Rey, Ph. Dehauht, F. Cyrot-Lackmann, G. Fourcaudot, J. Beille, and J. L. Tholence, *J. Solid State Chem.* **85,** 321 (1990).
5. M. J. Rey, Ph. Dehaught, J. C. Joubert, B. Lambert-Andron, M. Cyrot, and F. Cyrot-Lackmann, *J. Solid State Chem.* **86,** 101 (1990).
6. M. Itoh, M. Shikano, R. Liang, H. Kawaji, and T. Nakamura, *J. Solid State Chem.* **88,** 597 (1990).
7. J. E. Greedan, *in* "The Rare Earths in Modern Science and Technology" (G. J. McCarthy, H. B. Silber, and J. J. Rhyne, Eds.), Vol. 3, p. 431, Plenum, New York (1982).
8. M. Eitel and J. E. Greedan, *J. Less-Common Metals* **116,** 95 (1986).
9. W. Gong and J. E. Greedan, unpublished.
10. V. G. Zubkov, I. F. Berger, Z. M. Pesina, G. V. Bazuev, and G. P. Shveikin, *Dokl Akad. Nauk SSSR* **288,** 881 (1986).
11. Wenhe Gong, M. Sc. thesis, McMaster University (1990).