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Synthesis and Properties of a New d^1 Compound $Sr_4V_3O_{9.8}$ with Layered Structure

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A new layered compound $Sr_4V_3O_{9.8}$ with the $Sr_4Ti_3O_{10}$ structure was successfully synthesized and electrical resistivity and magnetic susceptibility measurements were carried out. The unit cell dimensions of $Sr_4V_3O_{9.8}$ were found to be $a = 0.38428(3)$ nm and $c = 2.7902(2)$ nm. The slope of the resistivity vs temperature curve changed from slightly negative to positive at a temperature of ~70 K as the temperature was increased. The magnetic susceptibility of the sample could be fitted by the Curie–Weiss law, $\chi = \chi_0 + C/(T - \Theta)$, with $\chi_0 = 1.06 \times 10^{-3}$ emu·mole^{-1}, $\Theta = -66$ K, and $C = 5.88 \times 10^{-2}$ emu·K·mole^{-1}.

Introduction

Cubic perovskite-type $SrVO_3$ is known to be a metallic conductor (*1–4*) whose conductivity has been interpreted in terms of an overlapping band model corresponding to two pseudoparticle states with $1\pi^*$ and $2\pi^*$ electrons per V^{4+} ions (*4*). Recently, Cyrot *et al.* (*5, 6*) have reported the semiconductive and antiferromagnetic $3d^1$ compound Sr_2VO_4 with the K_2NiF_4 structure. Usually Sr_2VO_4 is prepared in an H_2 atmosphere at high temperatures; it is recognized to be difficult to obtain in a single phase (*7*).

Recent research on the high-T_c oxide superconductors containing copper with the layered structure have aroused our interest concerning whether or not layered compounds composed of MO_6 octahedra containing metal ions other than copper show a superconductivity. In this letter, we report the synthesis and the properties of a new layered d^1 compound $Sr_4V_3O_{9.8}$.

Experimental

The sample was synthesized by a solid state reaction of a stoichiometric mixture of powders of $SrCO_3$ (99.9% purity) and V_2O_5 (99.99% purity). The powders were thoroughly mixed in an agate mortar with ethanol and pressed into a pellet of 20 mm diameter and 3 mm thickness at a pressure of 60 MPa. The pressed powder was calcined at 1273 K for 12 hr in H_2 with one intermediate pulverization and pelletization. The calcined powder was pulverized, pressed into a pellet of 15 mm diameter and 2 mm thickness at a pressure of 80 MPa and heated at 1573 K in an H_2 atmosphere for 12 hr with

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one intermediate pulverization and pelletization. After the final heating, the sample was furnace-cooled in H_2.

The powder was characterized at room temperature by powder X-ray diffraction, using a Rigaku horizontal Θ–Θ diffractometer with a curved graphite monochromator for $2\Theta = 5$–$120°$, employing a Cu target X-ray tube ($\lambda = 0.15402$ nm) at 40 kV and 25 mA. To avoid possible overlap errors, nonoverlapping peaks higher than $2\Theta = 80°$ were used to determine the unit cell dimensions. Silicon powder was used as an internal standard. The electrical resistivity of the sample was measured using the dc four-probe method with a current density of 160 A/m^2. The magnetic susceptibility of the sample above 77 K was measured by a Shimazu MB-2 Faraday-type magnetic balance.

The oxygen content of the sample was determined from the mass increase in the sample after heating at 1173 K for 12 hr in air.

Results and Discussion

The oxygen content of the sample was found to be 9.8, as determined by oxidation of vanadium ions to the 5+ valence state.

Figure 1 shows the X-ray diffraction pattern for the sample $Sr_4V_3O_{9.8}$. Almost all peaks were indexed by a body centered tetragonal cell (space group *I4/mmm*) with dimensions $a = 0.38428(3)$ nm and $c = 2.7902(2)$ nm. The diffraction data are presented in Table I. The diffraction pattern implies that $Sr_4V_3O_{9.8}$ has the $Sr_4Ti_3O_{10}$ structure which is composed of three alternate layers of perovskite and rock salt (SrO) along the c-direction.

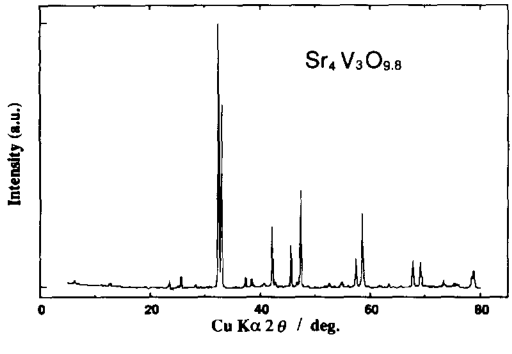

FIG. 1. X-ray diffraction pattern for $Sr_4V_3O_{9.8}$.

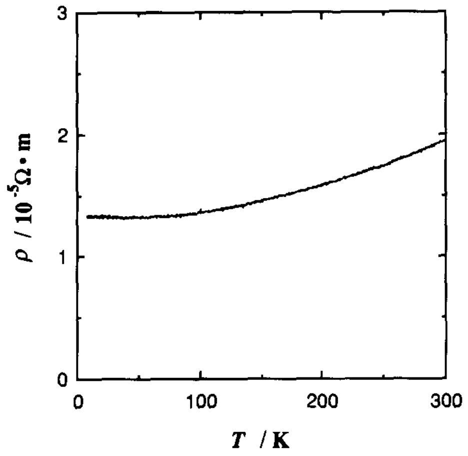

FIG. 2. Temperature dependence of the electrical resistivity for $Sr_4V_3O_{9.8}$.

Figure 2 shows the resistivity of the sample measured by the dc four-probe method. As shown in this figure, the slope of the resistivity changes from slightly negative to positive near ~70 K.

Figure 3 shows the magnetic susceptibility of the sample above 77 K. The data showed a paramagnetic $\chi(T)$ dependence and were analyzed according to the expression

$$\chi = \chi_0 + C/(T - \Theta),$$

where χ_0 is the temperature-independent paramagnetism, and the second term represents the usual paramagnetic temperature variation with the Curie constant C and the characteristic temperature Θ. The $\chi(T)$ value was corrected by subtracting the orbital diamagnetism of the relevant ions $\chi_{dia} = -0.20 \times 10^{-3}$ emu per one mole of

TABLE I

X-RAY DIFFRACTION DATA OF $Sr_4V_3O_{9.8}$

h	*k*	*l*	$d_{obs.}$ (nm)	$d_{cal.}$ (nm)	*I*
0	0	2	1.41	1.3951	1
0	0	4	0.70	0.6976	2
0	0	6	0.467	0.4650	1
1	0	1	0.382	0.3807	4
1	0	3	0.356	0.3551	1
0	0	8	0.3492	0.3488	5
1	0	5	0.3170	0.3165	20
1	0	7	0.2768	0.2767	100
1	1	0	0.2720	0.2717	65
1	1	2	0.2666	0.2667	1
1	1	4	0.2534	0.2532	1
1	0	9	0.2414	0.2413	5
1	1	6	0.2348	0.2346	5
0	0	12	0.2328	0.2325	1
1	1	8	0.2145	0.2144	28
1	0	11	0.2120	0.2117	2
0	0	14	0.1993	0.1993	21
1	1	10	0.1946	0.1947	3
2	0	0	0.1921	0.1921	49
1	0	13	0.1874	0.1874	1
2	0	6	0.1775	0.1776	<1
1	1	12	0.1767	0.1767	2
0	0	16	0.1743	0.1744	4
2	1	1	0.1715	0.1715	2
2	1	3	0.1691	0.1690	7
2	0	8	0.1683	0.1683	
1	0	15	0.1674	0.1674	
2	1	5	0.1643	0.1642	1
1	1	14	0.1607	0.1607	1
2	0	10	0.1583	0.1583	46
2	1	7	0.1578	0.1578	
0	0	18	0.1550	0.1550	1
1	0	17	0.1510	0.1509	<1
2	1	9	0.1503	0.1503	3
2	0	12	0.1482	0.1481	1
1	1	16	0.1467	0.1468	3
2	1	11	0.1422	0.1423	1
0	0	20	0.1394	0.1395	<1
2	0	14	0.1383	0.1383	16
1	0	19	0.1376	0.1372	2
2	2	0	0.1359	0.1359	15
2	2	2		0.1352	
1	1	18	0.1346	0.1346	<1
2	1	13	0.1343	0.1342	<1
2	0	16	0.1291	0.1291	4

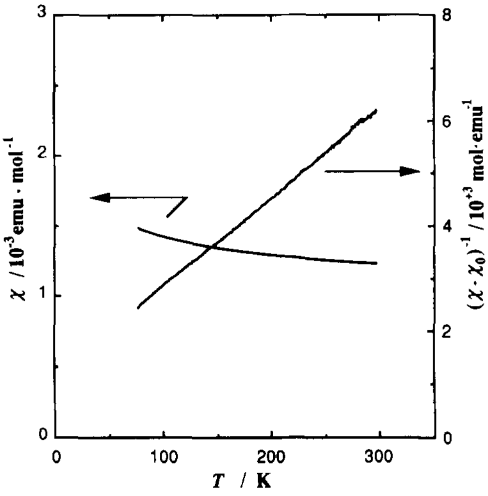

FIG. 3. Temperature dependences of the magnetic susceptibility χ (left ordinate) and $(\chi - \chi_0)^{-1}$ (right ordinate) of $Sr_4V_3O_{9.8}$.

$Sr_4V_3O_{9.8}$ The parameters χ_0, C, and Θ were estimated by the least-mean squares technique to yield $\chi_0 = 1.06 \times 10^{-3}$ emu·mole^{-1}, $C = 5.88 \times 10^{-2}$ emu·K·mole^{-1}, and $\Theta = -66$ K. We note the following characteristics: (1) χ_0 reflects the metallic conductivity shown in Fig. 2. (2) Θ indicates a characteristic temperature corresponding to the antiferromagnetic interaction between vanadium ions. (3) The Curie constant reflects the effective magnetic moment of vanadium ions as expressed by

$$C = 3(P_{\text{eff}}^2\mu_B^2/k_B) \cdot N_0,$$

where P_{eff} is the effective Bohr magneton number as an index of the magnetic moment strength of the vanadium ions. Using this equation, the number P_{eff} was obtained as 0.396 per one mole of vanadium ions. Since the "ideal" ionic composition $Sr_4V_3O_{10-x}$ is represented by $Sr_4^{2+}V_{3-2x}^{4+}V_{2x}^{3+}O_{10-x}^{2-}$, the $Sr_4V_3O_{9.8}$ compound is representable as $Sr_4^{2+}V_{2.6}^{4+}V_{0.4}^{3+}O_{9.8}^{2-}$. The weak paramagnetism for the sample may be attributed to a contribution from localized V^{3+} ions ($3d^2$).

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