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BRIEF COMMUNICATION

Evidence for Superconductivity in $SrTa_2S_5$ and Metallic Characteristics of $SrNb_2S_5$

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A strontium niobium sulfide, $SrNb_2S_5$, and a strontium tantalum sulfide, $SrTa_2S_5$, have been successfully synthesized by a sulfurization method using CS_2. $SrNb_2S_5$ and $SrTa_2S_5$ have hexagonal structures with lattice constants of $a = 3.361$, $c = 24.06$ Å and $a = 3.306$, $c = 24.26$ Å, respectively. $SrNb_2S_5$ shows metallic conductivity and temperature-independent susceptibility with an extremely small Curie–Weiss contribution at low temperatures. $SrTa_2S_5$ exhibits a superconducting transition at 2.75 K (midpoint). The superconducting transition temperature of $SrTa_2S_5$ depends on the purity of specimens. We have verified that the high-purity specimen shows the superconducting transition with a much lower T_c than that of low-purity specimen. © 1998 Academic Press

Key Words: **Ternary sulfide; $SrNb_2S_5$; $SrTa_2S_5$; sulfurization method; powder X-ray diffraction; electrical resistivity; magnetic susceptibility; superconductivity.**

INTRODUCTION

A number of ternary sulfides have been reported in Ba–*M*–S (*M* = transition metals) systems, but very few in Sr–*M*–S systems. Six sulfides, SrV_2S_4 (1), SrV_2S_5 (2), $SrNb_2S_5$ (3), $SrTaS_3$ (4), $SrTa_2S_5$ (3, 5), and $Sr_{17}Ta_{10}S_{42}$ (6), have been reported so far in the Sr–*M*–S (*M* = V, Nb, Ta) systems. We have previously reported preparation, and transport and magnetic properties of SrV_2S_5 (2) and superconducting and normal state properties of $SrTa_2S_5$ (5).

AM_2S_5 compounds (A = Sr, Ba; M = V, Nb, Ta) exhibit a large variety of physical properties, which makes them interesting. SrV_2S_5 shows semiconducting temperature dependence in the resistivity and temperature-independent susceptibility with a small Curie–Weiss contribution at low temperatures (2). $BaNb_2S_5$ shows metallic conductivity above 1.9 K and Pauli paramagnetism (7). $SrTa_2S_5$ and $BaTa_2S_5$ show metallic properties and exhibit superconducting transition around 3 K (5, 8). These sulfides have hexagonal symmetries in these crystal structures, while SrV_2S_5 has a rhombohedral symmetry. All sulfides have complicated superstructures and the atomic positions of them have not yet been determined (2, 3, 8). Lattice constants and physical properties of the AM_2S_5 compounds are summarized in Table 1. As far as we know, BaV_2S_5 has not been reported.

A strontium niobium sulfide, $SrNb_2S_5$, has a hexagonal structure with a complicated superstructure (3). However, transport and magnetic properties of $SrNb_2S_5$ have not been reported. We have prepared $SrNb_2S_5$ and $SrTa_2S_5$ by a sulfurization method using CS_2. In this report, we show the temperature dependence of electrical resistivity and magnetic susceptibility for $SrNb_2S_5$ which shows metallic characteristics and does not exhibit any indications of superconductivity above 1.45 K. Furthermore, we present an experimental verification for the superconductivity in high-purity specimen of $SrTa_2S_5$.

EXPERIMENTAL

Sample Preparations

$SrNb_2S_5$ and $SrTa_2S_5$ were prepared by the sulfurization method using CS_2. Stoichiometoric mixtures of $SrCO_3$ (purity 99.99%, −300mesh) and Nb_2O_5 (99.9%, −300mesh) or $SrCO_3$ and Ta_2O_5 (99.9%, −300mesh) were thoroughly mixed in an agate mortar. An alumina boat containing these mixtures was placed inside a quartz tube with an inner diameter of 3.5 cm in an electric furnace and heated to 800°C (30°C/min) under Ar atmosphere. Then CS_2 gas was carried by flowing Ar gas into the quartz tube. The flowing rate of Ar gas was 50 cm^3/min, which related the flowing rate of CS_2 gas. The CS_2 gas was supplied by evaporating liquid CS_2 in a bottle and the flowing rate of CS_2 gas empirically determined. The optimum condition of these processes required fairly high skill and experience. The

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TABLE 1
Lattice Constants and Physical Properties of AM_2S_5 (A = Sr, Ba; M = V, Nb, Ta)

		Lattice constants			
Compound	Crystal system	a (Å)	c (Å)	Physical property	References
SrV_2S_5	Rhombohedral	3.314	35.023	Semiconductive	(2)
BaV_2S_5	Unknown				
$SrNb_2S_5$	Hexagonal	3.361	24.06	Metallic ($T > 1.45$ K)	Present work
		3.359	24.00		(3)
$BaNb_2S_5$	Hexagonal	3.32	24.88	Metallic ($T > 1.9$ K)	(7)
		3.331	24.72		(3)
$SrTa_2S_5$	Hexagonal	3.306	24.26	Superconductive ($T_c = 2.75$ K)	Present work
		3.32	24.1	Superconductive ($T_c = 3.16$ K)	(5)
		3.306	24.28		(3)
$BaTa_2S_5$	Hexagonal	3.3258	25.208	Superconductive ($T_c = 2.88$ K)	(8)
		3.3204	25.005	Superconductive ($T_c = 3.14$ K)	(8)

sulfurization was made through gradual chemical reactions by the substitution of sulfur for oxygen in the starting materials at 800°C for 5 h. Excess CS_2 gas without being used for the reaction was safely trapped in a cold trap and a NaOH aqueous solution outside the furnace. After cooling to room temperature (5°C/min), resultant powders, which stuck fast to each other, were ground and pressed into rectangular bars of about 2.0 × 2.0 × 10.0 mm. Subsequently, these bars of $SrNb_2S_5$ were sealed in an evacuated quartz tube with an extra 5 wt% of sulfur for the total weight of $SrNb_2S_5$ and heated to 700°C for a period of 3 days in another electric furnace. The bars of $SrTa_2S_5$ were also sealed in an evacuated quartz tube without extra sulfur and heated to 900°C for a period of 3 days. The sulfur contents of specimens were determined from the difference in weight between the starting materials and product, assuming Sr, Nb, and Ta elements do not sublimate from the specimen in sample preparations.

We could not obtain a single phase specimen of $SrNb_2S_5$ when the initial cation ratio was Sr : Nb = 1 : 2 in the sample preparation. A well-crystallized specimen was obtained with the initial cation ratio of Sr : Nb = 1 : 1 in which the specimen might be composed of two phases, $SrNb_2S_5$ and SrS. This tendency in the sample preparation is similar to the results by Saeki *et al.* (3).

Measurements

Lattice constants were determined by powder X-ray diffraction method using Cu$K\alpha$ radiation. The lattice constants were determined by extrapolation to Bragg angle $2\theta = 180°$, using the extrapolation function $\cos^2\theta/\sin\theta$. Electrical resistivity, ρ, was measured by a standard dc four-probe method with a current density of about 0.3 A/cm^2 over the temperature range 1.45 to 300 K. The sintered rectangular bar samples with dimensions of about 2.0 × 2.0 × 10.0 mm were used for measurements of ρ. Silver paste (Du Pont No. 4922 thinned with *n*-butyl acetate) was used to fabricate the contacts. The dc current was applied in both directions alternately and taking the average values of the observed voltage to compensate for the thermal emf. Magnetic susceptibility, χ, which refers to a magnetization divided by a constant field, M/H, was measured in constant fields of 10 Oe and 10 kOe with a SQUID magnetometer (Quantum Design) over the temperature range 1.8 to 300 K. The powder samples solidified with cyanoacrylate adhesives were used for the measurements of χ. Background contribution due to the cyanoacrylate adhesives was subtracted from the experimental results.

RESULTS AND DISCUSSION

Powder X-ray diffraction patterns are shown in Fig. 1. The diffraction patterns have been indexed on the basis of the hexagonal cell with lattice constants of $a = 3.361$ and

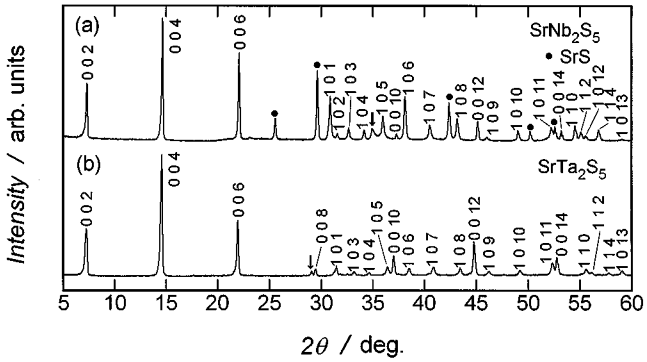

FIG. 1. Powder X-ray diffraction patterns of (a) $SrNb_2S_5$ and (b) $SrTa_2S_5$ at room temperature. Peaks with a solid circle are those of SrS and peaks with an arrow are unindexed.

$c = 24.06$ Å for $SrNb_2S_5$ and $a = 3.306$ and $c = 24.26$ Å for $SrTa_2S_5$, respectively. These assigned indices are given in Fig. 1. Peaks due to SrS are also shown in Fig. 1a and weak peaks indicated by an arrow in Fig. 1 remain unindexed. These peaks also have been observed by Saeki *et al.* (3) and they indicate that they come from superstructures of $SrNb_2S_5$ and $SrTa_2S_5$. It can be seen in Fig. 1 that the intensities of the (00*l*) peaks are fairly strong in comparison with the others. This fact suggests that these crystallites of $SrNb_2S_5$ and $SrTa_2S_5$ are preferentially oriented. The detailed crystal structures of $SrNb_2S_5$ and $SrTa_2S_5$ have not been determined because of complicated structures with the superstructures (3).

Figure 2 shows the temperature dependence of the electrical resistivity for a sintered specimen of $SrNb_2S_5$ between 4.2 and 300 K. The magnitude of the resistivity of $SrNb_2S_5$ is on the order of $10^{-3}\,\Omega$ cm at room temperature and the temperature dependence is metallic, $d\rho/dT > 0$. The resistivity ratio, $\rho(280\text{ K})/\rho(4.2\text{ K})$, of our specimen containing SrS has been estimated to be about 5.4. It was reported by Matsuura *et al.* (7) that $R(300\text{ K})/R(4.2\text{ K})$ of single phase of $BaNb_2S_5$ is about 4.7.

In the temperature range between 20 and 50 K, the electrical resistivity $\rho(T)$ can be expressed as a power law,

$$\rho(T) = \rho_0 + AT^n, \qquad [1]$$

where ρ_0 is the temperature-independent resistivity, and A and n are constants. From the slope of the straight line in a plot of $\log[\rho(T) - \rho_0]$ vs $\log T$, which is not given here, the value of n has been determined to be 2.5. At high temperatures, ρ tends toward a linear function of T.

Figure 3 shows the temperature dependences of the electrical resistivity for sintered specimens of $SrNb_2S_5$ and $SrTa_2S_5$ between 1.45 and 5 K. $SrTa_2S_5$ exhibits an abrupt superconducting transition at 2.75 K (midpoint), while $SrNb_2S_5$ does not indicate superconducting transition down to 1.45 K.

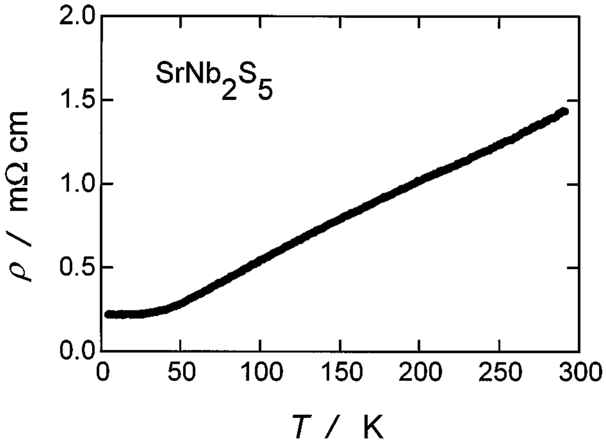

FIG. 2. Temperature dependence of the electrical resistivity for sintered specimen of $SrNb_2S_5$ over the temperature range 4.2 to 300 K.

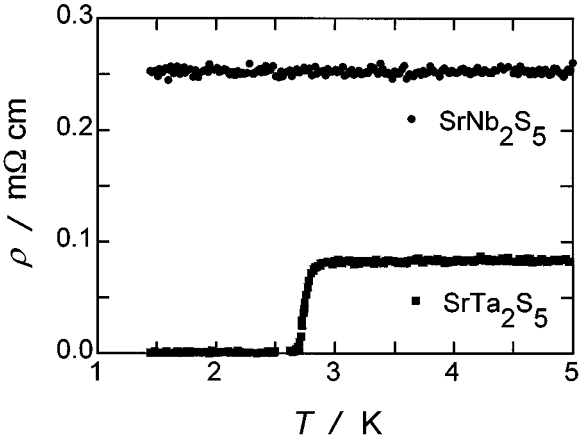

FIG. 3. Electrical resistivity versus temperature for the sintered specimens of $SrNb_2S_5$ and $SrTa_2S_5$ between 1.45 and 5.0 K.

We have previously reported that the superconducting transition temperature of $SrTa_2S_5$ is 3.16 K (5). The specimen used for these measurements has been prepared by a solid state reaction of SrS, Ta, and S in an evacuated quartz tube, which shows broad diffraction peaks and has some unindexed peaks (5). In the present work, a new specimen of $SrTa_2S_5$ exhibits the superconducting transition at 2.75 K (midpoint), which has been prepared by the sulfurization method using CS_2. It is indicated by Nozaki *et al.* (7) that the superconducting transition temperature of $BaTa_2S_5$ depends on specimens which have been prepared by different heat treatments. They have reported the superconducting properties of two types of compound in $BaTa_2S_5$ and discussed the relationship between their physical properties and the fine superlattice formation in the crystal structure (7).

Figure 4 shows the temperature dependence of magnetic susceptibility of $SrNb_2S_5$ between 10 and 300 K in an applied magnetic field of 10 kOe. This specimen used for the measurements contains a small amount of SrS which is a nonmagnetic insulator. The magnitude of the diamagnetic susceptibility due to the atomic core electrons for $SrNb_2S_5$ has been subtracted. The following values are used for the subtraction: $\chi_{\text{dia}} = -15(\text{Sr}^{2+})$, $-16(\text{Nb}^{4+})$, $-38(\text{S}^{2-}) \times 10^{-6}$ emu/mol (9). The magnetic susceptibility can be expressed as

$$\chi = \chi_0 + C/(T - \theta), \qquad [2]$$

where χ_0 is the temperature-independent term, C is the Curie constant, and θ is the asymptotic Curie temperature. The effective magnetic moment per niobium ion from the

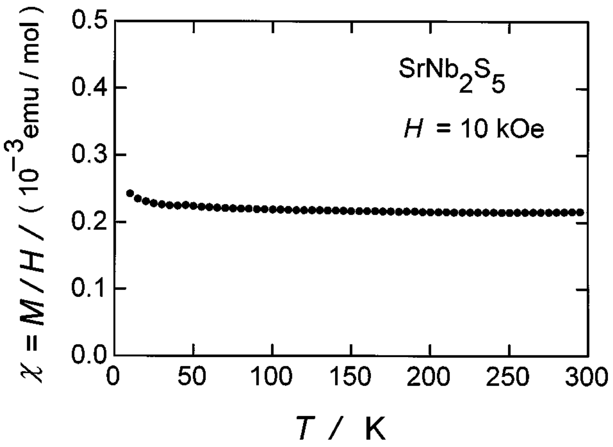

FIG. 4. Temperature dependence of the magnetic susceptibility for $SrNb_2S_5$. Specimen used for the measurement contains SrS.

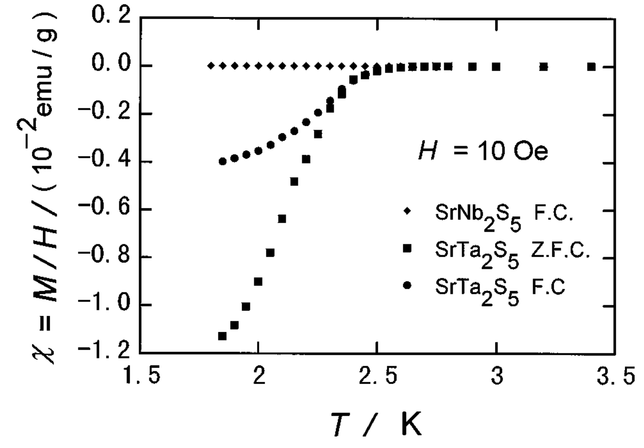

FIG. 5. Magnetic susceptibility versus temperature for $SrNb_2S_5$ and $SrTa_2S_5$ between 1.8 and 3.5 K.

Curie–Weiss term is about 0.04 μ_B which is much less than the spin-only moment (1.73 μ_B) expected for an isolated Nb^{4+} ion. This Curie–Weiss term may originate from magnetic impurities. The temperature-independent term χ_0 comes mainly from the Pauli paramagnetism of $SrNb_2S_5$.

Figure 5 shows the temperature dependences of magnetic susceptibility of $SrNb_2S_5$ and $SrTa_2S_5$ between 1.8 and 3.5 K in an applied magnetic field of 10 Oe. $SrTa_2S_5$ indicates a diamagnetic susceptibility and $SrNb_2S_5$ shows temperature-independent susceptibility above 1.8 K. The superconducting onset transition temperature of $SrTa_2S_5$ is 2.65 K which is slightly less than the value of the midpoint of the electrical resistivity. The absolute value of the diamagnetic susceptibility for zero-field cooling is about 3 times larger than that for field cooling at the lowest temperature.

In summary, we have prepared samples of $SrNb_2S_5$ and $SrTa_2S_5$ by the sulfurization method using CS_2 and investigated transport and magnetic properties of $SrNb_2S_5$ and superconductivity in $SrTa_2S_5$. $SrNb_2S_5$ with small amount of SrS shows metallic conductivity and temperature-independent susceptibility. The single phase of $SrTa_2S_5$ exhibits a superconducting transition at 2.75 K (midpoint).

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REFERENCES

1. W. P. F. A. M. Omloo, J. C. Bommerson, H. H. Heikens, H. Risselada, M. B. Vellinga, C. F. van Bruggen, C. Haas, and F. Jellinek, *Phys. Status Solidi A* **5,** 349 (1971).
2. N. Kijima, S. Ikeda, I. Shimono, T. Matsumoto, S. Tsuji, K. Kumagai, and S. Nagata, *J. Solid State Chem.* **126,** 189 (1996).
3. M. Saeki, M. Onoda, and M. Ohta, *Mater. Res. Bull.* **28,** 279 (1993).
4. A. V. Novoselova and L. A. Aslanov, *Dokl. Akad. Nauk. SSSR* **172,** 357 (1967).
5. N. Kijima, K. Morie, S. Nagata, and I. Shimono, *J. Low Temp. Phys.* **105,** 1511 (1996).
6. M. Onoda, M. Saeki, and Y. Yajima, *J. Solid State Chem.* **105,** 354 (1993).
7. K. Matsuura, T. Wada, T. Nakamizo, H. Yamauchi, and S. Tanaka, *J. Solid State Chem.* **94,** 294 (1991).
8. H. Nozaki, M. Saeki, and M. Onoda, *J. Solid State Chem.* **116,** 392 (1995).
9. K. H. Hellwege and A. M. Hellwege (Eds.), "Landolt–Börnstein," Group II, Vol. 8, p. 27. Springer-Verlag, Berlin, 1976.