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Physical Properties of a New Barium Niobium Sulfide, $BaNb_2S_5$

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A new barium niobium sulfide, $BaNb_2S_5$, has been successfully synthesized. The X-ray powder diffraction pattern is indexed on the basis of a hexagonal unit cell with the lattice constants $a = 3.32$ Å and $c = 24.88$ Å. $BaNb_2S_5$ is metallic in electrical resistivity down to 1.9 K and shows paramagnetism in magnetic susceptibility down to 60 K. Thermoelectric power data indicate that $BaNb_2S_5$ is a *n*-type metal at temperatures higher than ~30 K from the standpoint of a single band model.

Introduction

To date, four different compounds, $BaNbS_3$, $Ba_{16.5}Nb_9S_{42}$, Ba_2NbS_5, and $Ba_9Nb_4S_{21}$, have been reported for the Ba–Nb–S system. We previously reported magnetic and transport properties of $BaNbS_3$ and $Ba(Nb, V)S_3$ (*1, 2*). $BaNbS_3$ is considered to be isostructural with $BaVS_3$. $BaVS_3$ has a quasi-one-dimensional anisotropic crystal structure, being characterized by linear chains of V^{4+} running parallel to the *c*-axis (*3*).

In this work, we synthesized a new barium niobium sulfide, $BaNb_2S_5$, and characterized it in terms of electrical resistivity, dc magnetic susceptibility, and thermoelectric power.

Experimental Procedure

$BaNb_2S_5$ was prepared by the following procedure. High purity powders of $BaCO_3$ and Nb_2O_5 were mixed in ethanol solvent for the composition with the cation ratio Ba : Nb 1 : 2. The mixed powder was calcined at 800°C for 5 hr in a mixed gas of H_2S and Ar. The resultant powder was ground and recalcined twice. The calcined powder was pressed into pellets and fired at 800°C in H_2S–Ar gas flow. The pellets were encapsulated in evacuated silica tubes and single-phase ceramic samples were obtained by sintering at 800°C for 60 hr.

The ratio of Ba to Nb was analyzed by an electron-probe microanalyzer (JEOL : Model JXA-8621). The sulfur content was analyzed by using a thermogravimetric technique. That is, the sample was heated at the rate of 5°C/min in O_2 gas flow in order to change the sulfide sample to an oxide. The resultant oxide sample was analyzed by X-ray powder diffraction and then the sulfur content was calculated from the difference in weight between the sulfide sample and the resultant oxide.

X-ray powder diffraction was performed

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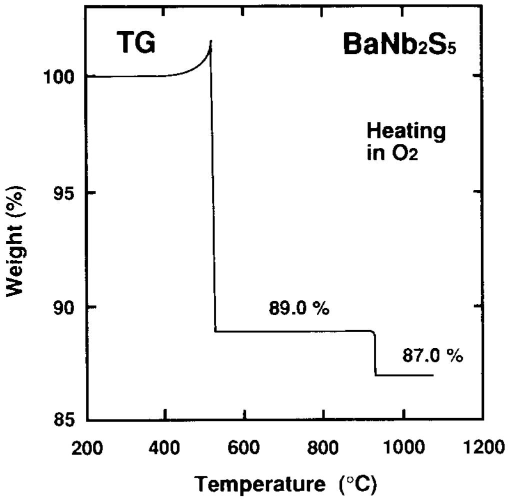

FIG. 1. Thermogravimetric (TG) curve of $BaNb_2S_5$ sample heated in O_2 gas flow.

by an X-ray diffractometer using Cu$K\alpha$ radiation (MAC Science Model : MXP[18]). As the obtained sample was strongly oriented along the c-axis, further structural refinement was not possible. Electrical resistivity was measured down to 1.9 K, employing a standard four-probe technique. Direct current magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design : Model MPMS). Thermoelectric power measurements were made in the temperature range 10 to 310 K applying a temperature difference of 0.3 K.

Results and Discussion

Electron probe microanalysis (EPMA) showed that the Ba : Nb ratio in the sulfide sample was 1 : 2. This ratio is in good agreement with the initial ratio of Ba and Nb. Figure 1 shows the thermogravimetric (TG) curve of the sample heated in O_2 gas flow. The TG curve shows that the final weight of the sample is 87% of the initial weight. The resultant oxide was found to be a mixture orthorhombic and hexagonal $BaNb_2O_6$ by X-ray powder diffraction. Therefore, since the weight ratio between the starting $BaNb_2S_x$ and the resultant $BaNb_2O_6$ was found to be 100 : 87, the chemical composition of the initial sulfide should be given by $Ba_1Nb_2S_5$.

The X-ray powder diffraction pattern of the $BaNb_2S_5$ sample is shown in Fig. 2. The

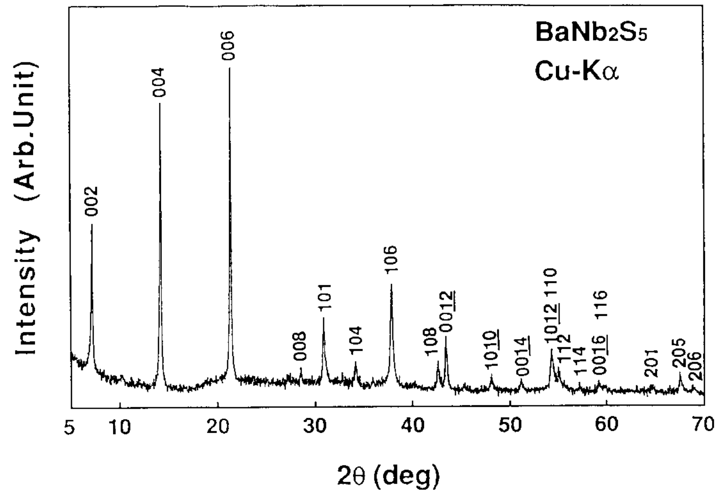

FIG. 2. X-ray powder diffraction pattern of $BaNb_2S_5$.

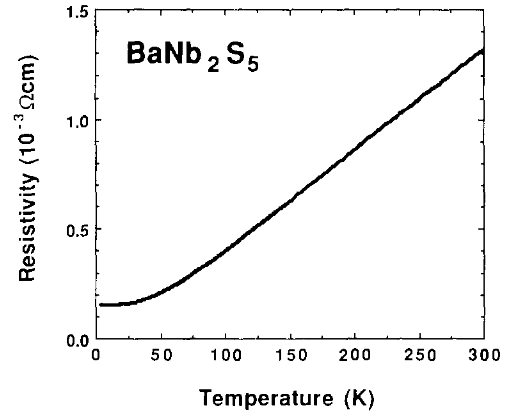

FIG. 3. Temperature dependence of electrical resistivity for BaNb$_2$S$_5$.

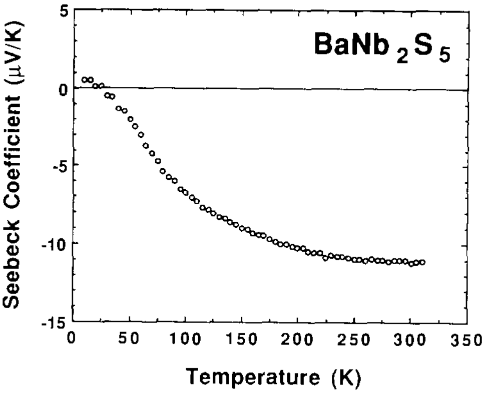

FIG. 5. Temperature dependence of the Seebeck coefficient for BaNb$_2$S$_5$.

peaks have been successfully indexed on the basis of a hexagonal unit cell with the lattice constants a = 3.32(5) Å and c = 24.88(4) Å. The indices assigned are shown in the figure. It can be seen in Fig. 2 that the intensities of the (00l) peaks are strong compared with the others. This fact suggests that BaNb$_2$S$_5$ may have a layered structure. This X-ray powder diffraction pattern is similar to that for BaTa$_2$S$_5$, which has lattice constants a and c of 3.32 and 25.13 Å, respectively (*4*). The a-axis length for BaNb$_2$S$_5$ is very close to that for BaTa$_2$S$_5$ but the c-axis length for BaNb$_2$S$_5$ is a little shorter than that for BaTa$_2$S$_5$.

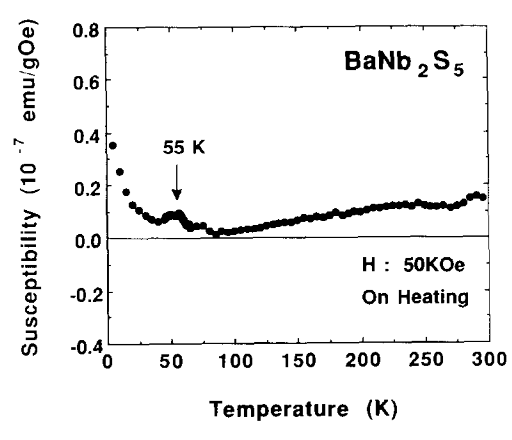

FIG. 4. Temperature dependence of magnetic susceptibility for BaNb$_2$S$_5$.

The temperature dependence of the electrical resistivity for BaNb$_2$S$_5$ is shown in Fig. 3. These data are parallel to those for BaTa$_2$S$_5$. The magnitude of resistivity is of the order of $10^{-4} \sim 10^{-3}$ Ω · cm and the temperature dependence is metallic in the temperature range between 1.9 and 300 K. The resistivity ratio, $R_{300\text{ K}}/R_{4.2\text{ K}}$, which is usually used for describing the purity of metals, has been estimated to be about 4.7.

The temperature dependence of dc magnetic susceptibility for BaNb$_2$S$_5$ is shown in Fig. 4. Since the susceptibility does not vary significantly in the temperature range between 40 and 300 K, it may be considered that BaNb$_2$S$_5$ exhibits a Pauli paramagnetism. The Curie–Weiss-like behavior (i.e., the increase in magnetic susceptibility as temperature lowers) below 40 K may be due to the appearance of some localized magnetic moments at low temperatures. Assuming that this part of the susceptibility curve obeys the Curie–Weiss law, the amount of the localized moments has been estimated to be very small, i.e., about 0.7% of the total magnetic moment when all the Nb^{4+} ions are assumed to be isolated. The weak peak around 55 K was observed only when the sample was cooled to 5 K quickly and heated to room temperature slowly. Cusps (or sharp peak) of this type were often observed for spin-glass states of alloys such as AuFe, which contained a small amount of magnetic impurities (*5*). Therefore, $BaNb_2S_5$ may have a spin-glass state around 55 K. Another possibility for the formation of the weak peak may be the influence of the antiferromagnetic transition of adsorbed oxygen in the sample, because molecular oxygen undergoes an antiferromagnetic transition around 43 K (*6*).

The temperature dependence of the thermoelectric power or the Seebeck coefficient for the $BaNb_2S_5$ sample is shown in Fig. 5. The Seebeck coefficient at 300 K is relatively small, being equal to $-11\ \mu$ V/K. On cooling, the sign of the Seebeck coefficient is negative and its absolute magnitude decreases monotonically as temperature lowers down to about 30 K. Below 30 K, the Seebeck coefficient is positive. The thermoelectric power experiment indicates that $BaNb_2S_5$ is a *n*-type metal at temperatures higher than ~30 K from the standpoint of a single band model.

In conclusion, we prepared single-phase samples of a new barium niobium sulfide, $BaNb_2S_5$, and investigated its magnetic and transport properties. The temperature dependence of electrical resistivity was metallic in the temperature range between 1.9 and 300 K. The magnetic susceptibility exhibited a spin-glass-like peak around 55 K and a Curie–Weiss-type paramagnetism below 40 K in addition to a Pauli paramagnetism. The thermoelectric power measurement indicated that $BaNb_2S_5$ was a *n*-type metal at temperatures higher than ~30 K from the standpoint of a single band model.

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References

1. K. Matsuura, T. Wada, T. Nakamizo, H. Yamauchi, and S. Tanaka, *Phys. Rev. B*, **43**, 13119 (1991).
2. K. Matsuura, T. Wada, T. Nakamizo, H. Yamauchi, and S. Tanaka, *in* "Advances in Superconductivity III" (Ed. by K. Kajimura and H. Hayakawa, Springer-Verlag, Tokyo, 1991), pp. 253–256.
3. R. A. Gardner, M. Vlasse, and A. Wold, *Acta Crystallogr. Sect. B*, **25**, 781, (1969).
4. M. Saeki, H. Nozaki, and M. Onoda, *Mater. Res. Bull.* **24**, 851 (1989).
5. V. Cannella and J. A. Mydosh, *Phys. Rev. B* **6**, 4220 (1972).
6. S. Gregory, *Phys. Rev. Lett.* **40**, 723 (1978).