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Resistance Anomaly in Quasi-One-Dimensional Sulfide $BaNbS_{3+\delta}$

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Single-phase specimens of hexagonal $BaNbS_{3+\delta}$ ($2.93 \leq 3+\delta \leq 3.06$) have been successfully prepared by the sulfurization method using CS_2. The lattice constants, a and c, are less sensitive to the value of δ in the region of $-0.07 \leq \delta \leq 0.06$. $BaNbS_{2.93}$ indicates a semiconductor-to-semiconductor gradual transition around 100 K. On the other hand, $BaNbS_{3+\delta}$ ($2.96 \leq 3+\delta \leq 3.06$) shows hump-shaped anomalous behaviors in the resistivity. Although the anomalies in the electrical resistivity have been observed, all the samples have indicated no anomaly in their magnetic susceptibility. The magnetic susceptibilities are nearly temperature independent with extremely small Curie-like behavior at low temperatures. $BaNbS_{2.98}$ does not undergo a structural phase transition and there is no change in symmetry down to 80 K, above which the hump-shaped anomaly is clearly found. The relationship in the resistance anomaly between $BaNbS_{3+\delta}$ and $BaVS_3$ seems to be significant and to have an important role in clarifying the mechanism of these anomalies.

Key Words: **Ternary sulfide; $BaNbS_{3+\delta}$; sulfurization method; quasi-one-dimensional conductor; X-ray diffraction; resistance anomaly; semiconductor-to-semiconductor transition; magnetic susceptibility.**

INTRODUCTION

Four sulfides, $BaTiS_3$ (1), $BaVS_3$ (2), $BaNbS_3$ (3), and $BaTaS_3$ (4), have been reported in the Ba-M-S (M = transition metals) systems. They have a hexagonal $BaNiO_3$ type structure with a space group of $P6_3/mmc$ at room temperature (1–4). This structure is known to have a quasi-one-dimensional anisotropic crystal structure which is characterized by linear chains of M ions running parallel to the c-axis as shown in Fig. 1. Each M ion is located at the center of an octahedron consisting of six sulfur ions. The chains are separated by large barium ions to enhance the one-dimensionality.

A great deal of research for $BaVS_3$ has been made by many workers (2, 5–11). It has been well known that $BaVS_3$ is a metal and undergoes a metal-to-semiconductor transition around 70 K accompanied by sharp peak in the susceptibility (5–10). The magnetic properties in low temperature have been the subject of controversy and remains unclear. Much effort has been made to explain the origin of the metal-to-semiconductor transition and the magnetic properties of $BaVS_3$. However, not all experimental results of $BaVS_3$ have been explained consistently and the physical properties have not been comprehensively understood yet.

In contrast with $BaVS_3$, only a few studies have been carried out on an isostructural $BaNbS_3$. It has been known that $BaNbS_3$ is a compound characterized as semiconducting and stoichiometric with hexagonal structure. Contrary to the earlier reports, Donohue *et al.* (12) have claimed that this compound is able to be nonstoichiometric with 20% Nb vacancies regardless of the synthetic procedures or the starting reagent ratios of Ba/Nb. They have shown that this compound is capable of being a single phase in the nonstoichiometric composition with Nb atoms down to $BaNb_{0.8}S_3$, which requires formally d^0 configuration with a pentavalent state of Nb. This Nb^{5+} state is in agreement with the observed diamagnetic and semiconducting behaviors (12).

Recently, new results have been reported by some workers (3, 13–15). Matsuura *et al.* (13, 14) have reported that $BaNbS_3$ shows slight diamagnetism below 300 K and a metal-to-semiconductor transition around 620 K in its electrical resistivity. They have indicated that Nb in semiconductive $BaNbS_3$ has d^1 configuration with tetravalent state on the basis of the result of X-ray photoelectron spectroscopy (XPS) and suggested that this transition might be caused by the formation of Nb–Nb dimers at temperatures below 620 K (13, 14). Yan *et al.* (15) have reported on the synthesis and physical properties of stoichiometric $BaNbS_3$ and sulfur-deficient phase $BaNbS_{3-\delta}$. Yan *et al.* have concluded that single-phase $BaNbS_3$ is exactly stoichiometric and the Nb-deficient phase $BaNb_{0.8}S_3$ cannot be prepared. Furthermore, they have found that stoichiometric $BaNbS_3$ is metallic from 300 to 30 K and the

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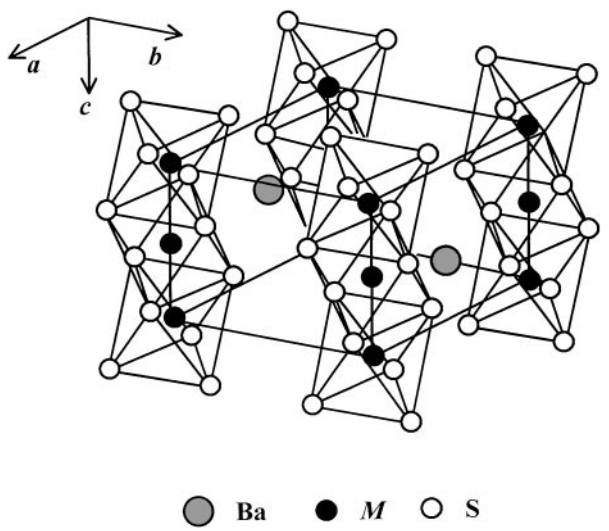

FIG. 1. Schematic drawing of the crystal structure of $BaMS_3$ (M = Ti, V, Nb, Ta) of a hexagonal $BaNiO_3$-type structure with space group of $P6_3/mmc$.

sulfur-deficient $BaNbS_{2.89}$ shows a semiconductor-to-metal transition at 130 K (15). Kim *et al.* (3) have also shown a similar anomaly at around 220 K in the stoichiometric $BaNbS_3$, where they attributed the resistance anomaly to the coexistence of metallic $BaNb_2S_5$ (16) and semiconductive $BaNbS_{3-\delta}$.

Temperature dependence of electrical resistivity of $BaNbS_3$ is extremely sensitive to its stoichiometry and these resistance anomalies seem to be intrinsic phenomena in $BaNbS_3$. Careful and extensive systematic investigation is required to clarify the resistance anomaly. In particular, the high-quality sample preparation and the precise control of the value of δ indicating the sulfur nonstoichiometry are crucial. A well-defined specimen with a definite value of δ can lead to a general agreement of the experimental results from the present hard situation suffering from the different data of sample to sample reported previously. In this paper, we have successfully obtained single phase $BaNbS_{3+\delta}$ specimens using a sulfurization method following a chemical reaction using CS_2. We will report the new systematic results of electronic and magnetic properties of $BaNbS_{3+\delta}$ ($2.93 \leq 3 + \delta \leq 3.06$). The value of δ has been determined by the weight difference between the starting compounds and the final product for the chemical reaction. Unfortunately, the value of δ is not so accurate because of the lack of rigorous chemical analysis and very precise microanalysis. In spite of the uncertainties about the exact composition, a successive coherent change in the temperature of anomalous maxima in the resistivity is found. X-ray diffraction at 80 K has been performed to confirm the absence or existence of the symmetry change due to the structural phase transition. It is our hope that the measurements presented below will be fruitful and helpful.

EXPERIMENTAL

Sample Preparations

$BaNbS_{3+\delta}$ were prepared by the sulfurization method using CS_2. Figure 2 is a schematic illustration of the experimental apparatus of sulfurization synthesis using CS_2. The starting materials, $BaCO_3$ (purity 99.99%, -300 mesh) and Nb_2O_5 (99.9%, -300 mesh) 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 700°C (30°C/min) in an 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 was empirically determined. The sulfurization was made through gradual chemical reactions in which sulfur was substituted for oxygen in the starting materials at 700°C for 5 h. Excess CS_2 gas not being used for the reaction was safely trapped in a cold trap and a NaOH aqueous solution outside the furnace. After cooling down to room temperature (5°C/min), resultant powders,

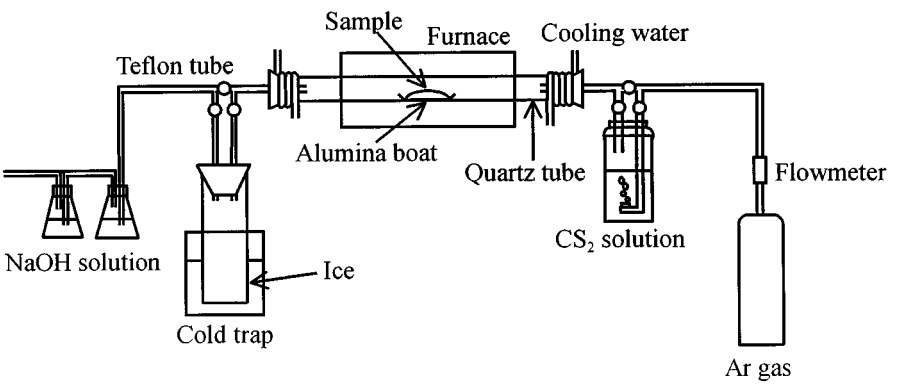

FIG. 2. Schematic illustration of experimental apparatus of sulfurization synthesis using CS_2.

which stuck fast to each other, were ground and pressed into pellets. Subsequently, these pellets were resulfurized at 900–1000°C for 5 h. Finally, the resultant pellets were reground and repressed into rectangular bars of about $2.0 \times 2.0 \times 10.0$ mm^3. In order to obtain and to control the different values of δ, the bars were sulfurized at certain different temperatures for 5 h for each specimen. These final heat treatments were made at 700–1000°C.

The values of $3 + \delta$ were carefully estimated with the use of the weight difference method. Although the real chemical reaction is not examined, a tentative resultant reaction is postulated as

$$4BaCO_3 + 2Nb_2O_5 + (6 + 2\delta)CS_2 \rightarrow 4BaNbS_{3+\delta} + (10 + 2\delta)CO_2 + (1 - 2\delta)O_2. \quad [1]$$

The weight difference between the starting compounds ($4BaCO_3 + 2Nb_2O_5$) and the product compound ($4BaNbS_{3+\delta}$) gives the value of $3 + \delta$. Here, we assume that the heavy elements of Ba and Nb do not sublimate in the reaction. This assumption was supported by the chemical (15) or combustion (3) analyses of Ba and Nb. The $3 + \delta$ in $BaNbS_{3+\delta}$ was determined from

$$3 + \delta = 10.299 \times [(W_{pro} \times W'_{pro} \times W''_{pro})/(W_{in} \times W'_{in} \times W''_{in})] - 7.180, \quad [2]$$

where W_{pro}, W'_{pro}, and W''_{pro} are weight of product compound and W_{in}, W'_{in}, and W''_{in} are weight of the starting compound for first, second, and final heart treatment, respectively. To prevent loss of recovery, the whole weight of powder or pellets with the alumina boat was measured before and after the reaction. The weight of the alumina boat did not changed after the reaction.

The weights of specimen were carefully measured to obtain the value of $3 + \delta$. We tried to prepare sulfur-rich specimen with the value of $3 + \delta$ greater than 3.06 by annealing with extra sulfur in an evacuated quartz tube. Single-phase specimen could not be obtained. Furthermore, single-phase specimen of the Nb-deficient phase $BaNb_{0.8}S_3$ could not be prepared using our method, which was consistent with the result of Yan *et al.* (15), where they indicated that the reaction $BaNbS_{3+\delta-\gamma} + \gamma S \leftrightarrow BaNbS_{3+\delta}$ was reversible.

The value of $3 + \delta$ contains the appreciable experimental errors. The errors in the value of $3 + \delta$ are less than ± 0.05 at most. We have tried X-ray pattern fitting by using the Rietveld method to determine the precise value of $3 + \delta$. However, with our analytical skill, we have been unable to determine exactly the values of $3 + \delta$. Unfortunately, a very precise microanalysis could not be made in our laboratory. Even though our weight difference method is primitive and the value of δ includes errors from the intermediate process, the experimental results of the value of δ would be fairly reliable because many times experiments showed excellent convergence. Our systematic experimental results support strongly the dominant sulfur nonstoichiometry by Yan *et al.* (15).

Measurements

Powder X-ray diffraction patterns at room temperature and 80 K were measured with a conventional diffractometer using diffracted beam monochromatized Cu$K\alpha$ radiation. The measurements were performed from $2\theta = 10^\circ$ to 60° with an interval of 0.02°. Lattice constants were determined by extrapolation to Bragg angle $2\theta = 180^\circ$, 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 a temperature range of 4.2 to 800 K. Sintered rectangular bar samples with the dimensions of about $2.0 \times 2.0 \times 10.0$ mm^3 were used for measurements of ρ. The filling densities of the sintered specimens were about 75%. Four copper wires were connected to the sample by silver paste (Tokuriki Chemical Research Co., Ltd., SILBEST P-1731) and the electrical contacts were secure. To prevent oxidation of sample, the measurements of ρ were carried out under He gas atmosphere which played also a role in thermal exchange. The *dc* current was applied in both directions alternately and taking the average values of the observed voltage to compensate for the thermal electromotive force.

Magnetic susceptibility, χ, which refers to a magnetization divided by a constant field, M/H, was measured in a constant field of 10 kOe with a SQUID magnetometer (Quantum Design) over a temperature range of 10 to 300 K. The powder sample solidified with cyanoacrylate adhesives was used for the measurements of χ. Background contribution due to the cyanoacrylate adhesives was subtracted from the experimental results.

RESULTS

Figure 3 presents the powder X-ray diffraction patterns of $BaNbS_{3+\delta}$ at room temperature. All diffraction peaks have been indexed in terms of hexagonal symmetry with a space group of $P6_3/mmc$. The indices assigned are also shown in Fig. 3. It is obvious that, within the limit of our resolution ($\sim 5\%$), single-phase specimens have been obtained in the range of $2.93 \leq 3 + \delta \leq 3.06$. The lattice constants of $BaNbS_{2.93}$ are $a = 6.862$ and $c = 5.742$ Å and these of $BaNbS_{3+\delta}$ ($2.93 \leq 3 + \delta \leq 3.06$) are less sensitive to the δ within this composition range.

Figure 4 shows temperature dependence of the electrical resistivity of $BaNbS_{3+\delta}$ over the temperature range of 4.2 to 800 K. $BaNbS_{2.93}$ indicates a semiconductor-to-semiconductor gradual transition around 100 K. On the other hand,

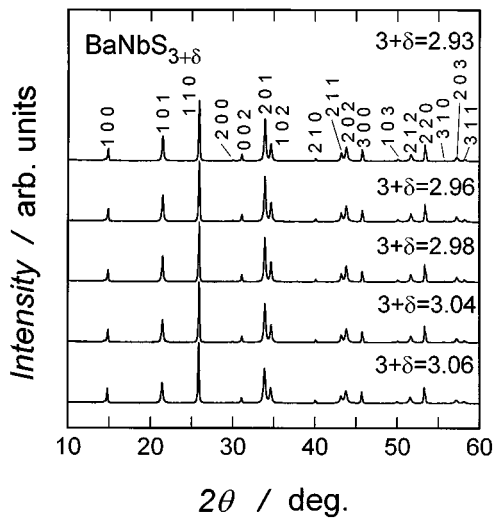

FIG. 3. Powder X-ray diffraction patterns of $BaNbS_{3+\delta}$ at room temperature.

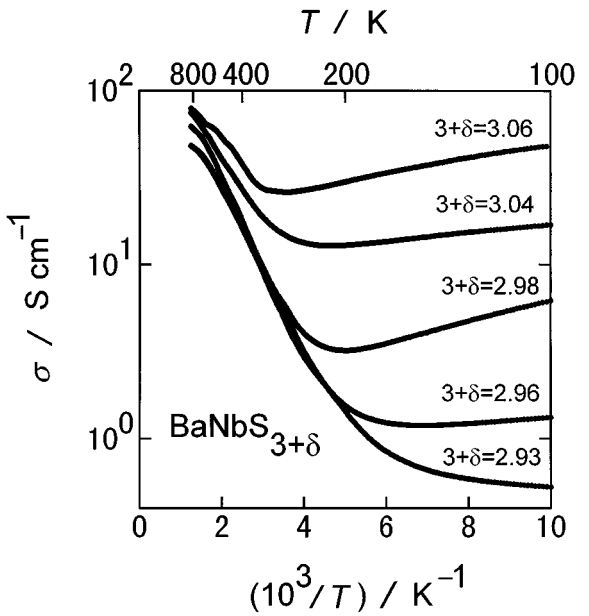

FIG. 5. Electrical conductivity for $BaNbS_{3+\delta}$ ($2.93 \leq 3+\delta \leq 3.06$) as a function of the inverse temperature $1/T$ over a temperature range of 100 to 800 K.

$BaNbS_{3+\delta}$ ($2.96 \leq 3+\delta \leq 3.06$) show hump-shaped anomalous behaviors (a semiconductor-to-metal transition). It is noticed that the electrical resistivity of $BaNbS_{2.96}$ increases slightly below 40 K. The temperature indicating the rounded maximum resistivity ρ_{max} decreases systematically with decreasing values of $3+\delta$. Temperatures of ρ_{max} for $3+\delta = 2.96$, 2.98, 3.04, and 3.06 are 146, 200, 215, and 280 K, respectively. At high temperatures, all samples show a semiconductive behavior.

Figure 5 plots the electrical conductivity σ of $BaNbS_{3+\delta}$ as a function of reciprocal temperature $1/T$. The experimental results can be well reproduced by a single exponential expression in the wide temperature range between 300 and 700 K, except for $BaNbS_{3.06}$. Thus it seems that the major mechanism for the electrical conduction is thermal activation at high temperatures. An exponentially activated energy of q has been estimated using the formula

$$\sigma(T) = A \exp(-q/k_B T), \qquad [3]$$

where A is a temperature independent constant and k_B is the Boltzmann constant. The activation energies are about 0.07 eV for $3+\delta = 3.04$ and 0.1 eV for $2.93 \leq 3+\delta \leq 2.98$, which are slightly less than the values in the literature (3, 13, 14).

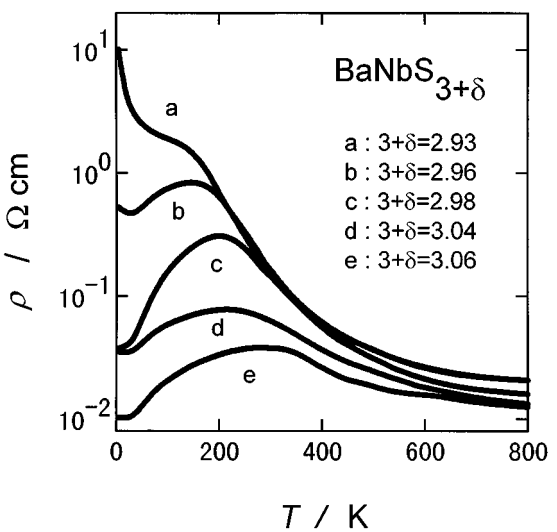

FIG. 4. Temperature dependence of the electrical resistivity of $BaNbS_{3+\delta}$ ($2.93 \leq 3+\delta \leq 3.06$) over a temperature range of 4.2 to 800 K.

Diamagnetic susceptibilities of $BaNbS_{3+\delta}$ have been observed below 300 K. The values of the diamagnetic susceptibilities at 300 K are in reasonable agreement with the results in the literatures (3, 12–14). Observed magnetic susceptibility χ_{obs} includes diamagnetic contribution χ_{core} due to the atomic core electrons for $BaNbS_{3+\delta}$; that is, $\chi_{obs} = \chi + \chi_{core}$. The following values are used for the corrections: $\chi_{core} = -\{24(Ba^{2+}) + 23(Nb^{4+}) + (3+\delta)\times 38(S^{2-})\}\times 10^{-6}$ emu/mol (17). After the corrections of χ_{core}, the magnetic susceptibilities, χ, of all samples are positive below 300 K. Figure 6 shows the temperature dependence of the magnetic susceptibility, χ, for $BaNbS_{3+\delta}$. As shown in Fig. 6, no anomaly has been detected in the all samples, while the anomalies have been observed in the electrical resistivity. The magnetic susceptibility, χ, can be expressed as

$$\chi = \chi_0 + C/(T-\theta), \qquad [4]$$

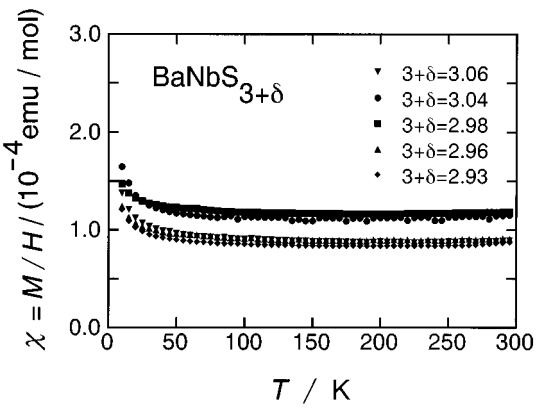

FIG. 6. Magnetic susceptibility versus temperature for $BaNbS_{3+\delta}$ ($2.93 \leq 3 + \delta \leq 3.06$) after subtraction of diamagnetic contribution due to the atomic core electrons.

where χ_0 is the temperature independent term, C is the Curie constant, and θ is the Weiss temperature. For all samples of $BaNbS_{3+\delta}$, the effective magnetic moment per niobium ion from the Curie-Weiss term is about 0.04 μ_B, which is much less than that of the spin-only moment (1.73 μ_B) expected for an isolated Nb^{4+} ($S = 1/2$) ion. This low temperature Curie-Weiss term is due to the existence of localized spins at impurity sites and/or at other kinds of lattice imperfections. Then, the increase of χ at low temperatures is not intrinsic. The temperature independent term χ_0 may arise mainly from the Pauli paramagnetic contribution. Assuming the entire value of χ_0 is the Pauli paramagnetic contribution, the density of states at the Fermi energy $N(\varepsilon_F)$ (for both spin directions) is estimated by using the relation

$$\chi = \mu_B^2 N(\varepsilon_F). \qquad [5]$$

The density of states $N(\varepsilon_F)$ are about 0.99 states/eV·atom for $BaNbS_{3+\delta}$ ($2.96 \leq 3 + \delta \leq 3.06$).

A low-temperature X-ray diffraction measurement of $BaNbS_{2.98}$, which exhibits the hump-shaped anomaly at about 200 K, has been carried out at 80 K and room temperature. No structural phase transition has been observed, nor have weak extra peaks been detected within our resolution, these results are consistent with the result of Kim *et al.* (3).

DISCUSSION

Kim *et al.* (3) also have found a hump-shaped resistance anomaly for one specimen of $BaNb_{0.8}S_{3-\delta}$ and they have attributed this anomaly to the existence of a metallic impurity phase of $BaNb_2S_5$, in which this resistance anomaly is regarded as an insignificant phenomenon and as an extrinsic result. It is stressed that the present work demonstrates the systematic development of the resistance anomaly of $BaNbS_{3+\delta}$ for single phase specimens and consequently the anomalous behavior is inherent. More recently, similar anomalies have been reported in the isostructural $BaNbSe_3$ system by Ohtani *et al.* (18). $BaNb_{0.95}Se_3$ shows a semiconductor-to-metal transition at about 140 K in its electrical resistivity and similar transition has been observed in slightly Ba-deficient $BaNb_{0.95}Se_3$. Slightly Ba-rich $BaNb_{0.95}Se_3$ exhibits a semiconductor-to-semiconductor transition around 200–300 K.

In the selenide $BaNbSe_3$ system, the resistance anomalies are characterized in terms of the variations in Ba and Nb contents (18). Yan *et al.* (15) have concluded that $BaNbS_3$ and $BaNb_{0.8}Se_3$ can be prepared, however, $BaNb_{0.8}S_3$ and $BaNbSe_3$ cannot be prepared, which might be consistent with our results. In contrast with the selenide system, all our measurements seem to indicate the predominant role of the sulfur deficiency in the sulfide $BaNbS_3$ system. This assumption should be confirmed by a rigorous microanalysis method in the future.

$BaVS_3$ exhibits a structural phase transition from hexagonal to orthorhombic around 250 K with decreasing temperature, where the linear V chains turn into zigzag chains. Furthermore, $BaVS_3$ shows successively a metal-to-semiconductor transition ($\sim$70 K) and a para to antiferromagnetic transition ($\sim$35 K). On the other hand, $BaNbS_{3+\delta}$ has no lattice distortion, nor weak extra peak in X-ray diffraction data down to 80 K. Then, lattice distortion is not major factor in understanding the electronic state. The resistivity of $BaNbS_{3+\delta}$ is very sensitive to its stoichiometry; however, a simpler and more transparent discussion than that in the hard situation for $BaVS_3$ will be provided in the future.

The magnetic susceptibility of $BaNbS_{3+\delta}$ is essentially independent of the temperature below 300 K. From the viewpoint of the ionic picture for $BaNbS_3$, Nb atom has d^1 ($S = 1/2$) configuration and Nb^{4+} valence state. Nevertheless, $BaNbS_3$ does not indicate any static magnetic order, but shows small Pauli-para like constant term, essentially in the absence of localized magnetic moment. $BaNbS_3$ may provide an intriguing physical subject for Heisenberg antiferromagnetic ($S = 1/2$) quantum spin fluctuation in one-dimensional system. This spin fluctuation is modulated and mediated through the introduction of nonstoichiometry of sulfur atom. The spin-singlet formation and the electrical conductivity are strongly influenced by the nonstoichiometry of sulfur. Experimental verifications are needed, for example, NMR measurements could confirm the spin-singlet formation and photoemission spectroscopy may be able to give the power-law exponent of spectral function.

SUMMARY

Temperature dependence of the electrical resistivity of $BaNbS_3$ is very sensitive to its stoichiometry. The anomalies

in the electrical resistivity have been found, and the systematic study of $BaNbS_{3+\delta}$ samples with various δ has revealed that the anomalies are inherent in $BaNbS_{3+\delta}$. Although the anomalies in the electrical resistivity have been observed, all the samples do not show any anomaly in its magnetic susceptibility. No structural phase transition has been observed, nor have weak extra peaks been detected by the low-temperature X-ray diffraction measurement down to 80 K for $BaNbS_{2.98}$.

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REFERENCES

1. J. Huster, *Z. Naturforsch. B* **35,** 775 (1980).
2. R. A. Gardner, M. Vlasse, and A. Wold, *Acta Crystallogr. B* **25,** 781 (1969).
3. S.-J. Kim, H.-S. Bae, K.-A. Yee, J.-H. Choy, D.-K. Kim, and N.-H. Hur, *J. Solid State Chem.* **115,** 427 (1995).
4. R. A. Gardner, M. Vlasse, and A. Wold, *Inorg. Chem.* **8,** 2784 (1969).
5. M. Takano, H. Kosugi, N. Nakanishi, M. Shimada, T. Wada, and M. Koizumi, *J. Phys. Soc. Jpn.* **43,** 1101 (1977).
6. O. Massenet, R. Buder, J. J. Since, C. Sohlenker, J. Mercier, J. Kelber, and D. G. Stucky, *Mater. Res. Bull.* **13,** 187 (1978).
7. O. Massenet, J. J. Since, J. Mercier, M. Avignon, R. Buder, V. D. Nguyen, and J. Kelber, *J. Phys. Chem. Solids* **40,** 573 (1979).
8. K. Matsuura, T. Wada, T. Nakamizo, H. Yamauchi, and S. Tanaka, *Phys. Rev. B* **43,** 13118 (1991).
9. M. Nakamura, A. Sekiyama, H. Namatame, A. Fujimori, H. Yoshihara, T. Ohtani, A. Misu, and M. Takano, *Phys. Rev. B* **49,** 16191 (1994), and references therein.
10. T. Graf, D. Mandrus, J. M. Lawrence, J. D. Thompson, P. C. Canfield, S.-W. Cheong, and L. W. Rupp, Jr., *Phys. Rev. B* **51,** 2037 (1995), and references therein.
11. H. Imai, H. Wada, and M. Shiga, *J. Phys. Soc. Jpn.* **65,** 3460 (1996).
12. P. C. Donohue and J. F. Weiher, *J. Solid State Chem.* **10,** 142 (1974).
13. K. Matsuura, T. Wada, T. Nakamizo, H. Yamauchi, and S. Tanaka, *in* "Proceedings, 3rd International Symposium on Superconductivity (ISS'90), Advances in Superconductivity III" (K. Kajimura and H. Hayakawa, Eds.), Vol. 1, p. 253. Springer-Verlag, Tokyo, 1991.
14. K. Matsuura, T. Nakamizo, T. Wada, H. Yamauchi, and S. Tanaka, *Jpn. J. Appl. Phys.* **32,** Suppl. 32-3, 662 (1993).
15. J. Yan, K. V. Ramanujachary, and M. Greenblatt, *Mater. Res. Bull.* **30,** 463 (1995).
16. K. Matsuura, T. Wada, T. Nakamizo, H. Yamauchi, and S. Tanaka, *J. Solid State Chem.* **94,** 294 (1991).
17. K. H. Hellwege and A. M. Hellwege (Eds.) "Landolt-Börnstein" Group II, Vol. 8, p. 27. Springer-Verlag, Berlin, 1976.
18. T. Ohtani, S. Honji, and M. Takano, *J. Solid State Chem.* **132,** 188 (1997).