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The Preparation and Properties of $BaTa_{0.8}S_3$, $BaNb_{0.8}S_3$, and $BaTa_{0.8}Se_3$

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Compounds of the formulas $BaTa_{0.8}S_3$, $BaNb_{0.8}S_3$, and $BaTa_{0.8}Se_3$ were prepared by two methods: reaction of the elements in evacuated silica tubes and reaction of H_2S over mixtures of $BaCO_3$ and $0.4Ta(Nb)_2O_5$. They have the hexagonal $BaNiO_3$-type structure and are diamagnetic semiconductors. From the stoichiometries and properties we conclude that Nb and Ta are pentavalent.

Introduction

Compounds of the formula $BaTaS_3$ and $BaTaSe_3$ are reported to be semiconductors and have the hexagonal $BaNiO_3$ structure (*1*, *2*, *3*). In this structure, continuous strings of face-sharing octahedra extend in the *c* axis direction. As reported (*3*), the Ta–Ta distance within the strings is 2.871 Å, which is small enough to expect metal–metal bonding and metallic conduction. The observed semiconductivity rather than metallic conductivity has prompted speculation that the large spin-orbit coupling of Ta^{4+} stabilizes the semiconducting state (*4*).

As part of a larger study of compounds of this type and to resolve the question of semiconductivity and bonding, we studied the synthesis and bonding of $BaTaS_3$.

Experimental

Compositions of varying Ba:Ta and Ba:Nb ratios were prepared by two methods: by heating sealed evacuated silica tubes containing the elements plus a small amount of iodine, and by passing H_2S over finely ground mixtures of $BaCO_3$ and Ta_2O_5 or Nb_2O_5.

Ba, obtained 99.5% pure from ESPI, was cut and weighed in a N_2-filled dry box. Ta and Nb powders of 99.95% purity and S and Se of 99.999% purity obtained from ROC/RIC were weighed in air and with about 5 mg I_2/cm^3 were sealed in evacuated silica tubes which were coated on the inside by carbon from pyrolysis of toluene. The tubes, measuring 15 mm o.d. × 12 mm × 6 in., were heated in natural gradient furnaces with the ends containing the metals at about 350 to 400°C; the other ends extended to the cooler furnace openings. After about 12 hr, the temperature was raised to 600°C for 12 hr, then to 800°C for 12 hr. When all the S was taken up, the tubes were opened; the products were reground, sealed in evacuated silica tubes, and heated in a muffle furnace between 800° and 1100°C for 48 hr. The products formed as black sintered masses with no chemical transport.

Reactions were also carried out by grinding together spec pure $BaCO_3$ and Ta_2O_5 or Nb_2O_5 weighed in varying mole ratios. The mixtures were placed in silica boats and heated between 800 and 1100°C in a stream of reagent-grade H_2S obtained from Mathieson Co. Products were heated from 24 to 48 hr with at least one regrinding to ensure complete reaction.

All products were characterized by X-ray powder diffraction chemical analysis, and pycnometric density measurements. Cell dimensions were refined using a computerized least-squares technique to standard errors of about 0.001 Å.

The magnetic susceptibilities were measured by the conventional Faraday method using a Cahn RG microbalanace, a field gradient $H(\partial H/\partial X)$ of the order 4×10^7 Oe^2/cm at 1.7×10^4 Oe, and $HgCo(CNS)_4$ as calibrant.

Electrical resistivities were measured by the ordinary four-probe method, using bars cut from single crystals or sintered compactions.

Results and Discussion

The starting compositions and X-ray analysis of the products are shown in Table I. Single-phase material was obtained only when starting cation ratios were Ba/0.8 Ta or Ba/0.8 Nb. The starting formulas $BaTaS_3$, $BaTaSe_3$, and $BaNbS_3$, even after repeated grindings and heatings, always yielded two-phase products: (1) the $BaNiO_3$-type phase for which the refined cell parameters are shown and (2) an unidentified phase designated as "TaS_2 type" because of the plate-like habit of the crystals and the presence of the strongest peak in the case of the sulfides at $d = 6.2$ Å. The second strongest line is at $d = 4.13$ Å. It is, however, not TaS_2. The strongest peak in TaS_2 is at 6.01 Å (ASTM 2-137).

TABLE I

COMPOSITIONS PREPARED IN THE SYSTEM $Ba(Ta, Nb)_{1\pm x}X_{3-x}$

Starting Composition	Cell Dimensions *a*	Cell Dimensions *c*	Extra phases present
$BaTaS_3$	6.847	5.760	TaS_2 type
$Ba_{0.9}TaS_3$	6.843	5.771	TaS_2 type
$BaTa_{1.05}S_3$	6.867	5.762	TaS_2 type
$BaTa_{0.9}S_3$	6.840	5.775	TaS_2 type
$BaTa_{0.8}S_3$	6.826	5.776	none
$BaTaS_{2.8}$	6.869	5.780	TaS_2 type
$BaTaS_{2.7}$	6.869	5.789	TaS_2 type
$BaTa_{0.8}S_{2.7}$	6.874	5.752	BaS (weak)
$BaCO_3/0.45Ta_2O_5$	6.829	5.776	TaS_2 type (weak)
$BaCO_3/0.5Ta_2O_5$	6.828	5.776	TaS_2 type
$BaCO_3/0.4Ta_2O_5$	6.833	5.779	none
$BaTaSe_3$	7.125	6.060	$TaSe_2$ type
$BaTa_{0.8}Se_{2.9}$	7.119	6.086	weak, unidentified
$BaTa_{0.8}Se_3$	7.108	6.030	none
$BaNb_{0.8}S_3$	6.831	5.764	none

The cell dimensions of the $BaNiO_3$-type phases show variations indicating a narrow range in stoichiometry, apparently close to the formulas $BaTa_{0.8}S_3$ and $BaTa_{0.8}Se_3$.

The composition $BaTa_{0.8}S_3$ was established by chemical analysis and pycnometric density measurements on single-phase material prepared from oxide and H_2S. The results are shown in Table II.

The results strongly favor assignment of the formula $BaTa_{0.8}S_3$.

The density of $BaTa_{0.8}S_3$ was calculated assuming Ta vacancies. We see no evidence for ordering of vacancies, such as a superlattice, and conclude that the vacancies are random.

The magnetic susceptibility of $BaNb_{0.8}S_3$ was slightly temperature dependent, increasing from $\chi_M = -3 \times 10^{-5}$ at 300 K to $\chi_M = -3 \times 10^{-6}$ at 800 K. It is not clear whether this behavior is intrinsic or caused by an impurity. However, the magnetic susceptibility of nominal $BaTaS_3$ and $BaTaSe_3$ (i.e., $BaTa_{0.8}S_3$ containing the TaS_2 type impurity) was essentially independent of magnetic field from 8–17 kOe and temperature from 78–800 K. The susceptibility of the corresponding pure phases ($BaTa_{0.8}S_3$ and $BaTa_{0.8}Se_3$) at room temperature was the same as that of the nominal compositions and in the range expected for simple diamagnetism as shown in Table III.

TABLE II

CHEMICAL ANALYSIS AND DENSITY OF $BaTa_{0.8}S_3$

	Calc. $BaTaS_3$	Calc. $BaTa_{0.8}S_3$	Observed
% Ba	33.1	36.3	37.2
% Ta	43.7	38.3	37.8
% S	23.2	25.4	26.1
% O	—	—	0.14
density	5.91 g/cm^3	5.39 g/cm^3	5.38 g/cm^3

TABLE III

MOLAR MAGNETIC SUSCEPTIBILITIES (χ_M)

Starting Composition	χ_M ($\times 10^{-3}$)	Estimated diamagnetism from Pascals constants ($\times 10^{-3}$)
$BaTaS_3$[a]	$-(0.069 \pm 0.002)$	
$BaTa_{0.8}S_3$[b]	$-(0.071 \pm 0.002)$	-0.08
$BaTaSe_3$[a]	$-(0.082 \pm 0.002)$	
$BaTa_{0.8}Se_3$[b]	$-(0.083 \pm 0.002)$	-0.10

[a] Results are mean and standard deviations of measured values at ~15° intervals from 78 to 800 K.

[b] Results are at room temperature only.

The electrical resistivities on sintered pellets of $BaTa_{0.8}S_3$ and $BaTa_{0.8}Se_3$ show semiconduction. The resistivity of $BaTa_{0.8}Se_3$ at 298K is 6×10^2 Ω cm with $Ea = 0.4$ eV. The resistivity of $BaTa_{0.8}S_3$ at 298 K is 2.2×10^2 Ω cm with a constant activation energy between 298 and 570 K of 0.24 eV. In comparison Gardener et al. (*3*) reported measurements on sintered bars of $BaTaS_3$: $\rho 298$ K $= 2.5 \times 10^{-1}$ Ω cm with Ea ranging from 0.06 eV at 298 K to 0.012 eV at 80 K. If the second phase is a metallic conductor, the resistivity of $BaTa_{0.8}S_3$ might be lowered. We selected a crystal from a preparation of $BaTaS_3$ from the elements in which a large lump of Ta was used which did not completely react. The crystal showed the cell dimensions of $BaTa_{0.8}S_3$ and resistivity $\rho 298$ K $= 10^9$ Ω cm $Ea = 0.7$ eV. Thus the resistivity of $BaTa_{0.8}S_3$ can vary, probably because of impurities.

It is also possible that some Ta^{4+} may be present in compositions prepared with the stoichiometry $BaTaS_3$. This would lower the resistivity and could account for the slightly different lattice constants for different ratios of elements. Our results, however, indicate that the true formulas are $BaTa_{0.8}S_3$, $BaTa_{0.8}Se_3$, and $BaNb_{0.8}S_3$ and that Ta and Nb are pentavalent. We assume that the composition $BaNb_{0.8}Se_3$, although not prepared, would be analogous. As expected, the compounds are diamagnetic semiconductors.

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