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Electrical Properties and Crystal Structure of Barium Tantalum Sulfide, $BaTaS_3$[1]

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Barium tantalum sulfide, $BaTaS_3$, has been prepared and single crystals have been grown from a barium chloride flux. The crystal structure of $BaTaS_3$ has been refined by single-crystal analysis and the space group is $P6_3/mmc$ with two formula units per unit cell. The hexagonal cell dimensions are $a = 6.846 \pm 0.005$ and $c = 5.744 \pm 0.005$ Å. The calculated density is 5.91 g/cm³ and the observed density is 5.80 g/cm³. The structure was refined with the use of anisotropic temperature factors to a final R factor on F of 0.087 for 186 independent reflections above background. $BaTaS_3$ was found to be isostructural with $BaVS_3$ and $CsNiCl_3$. The structure is based on the hexagonal close packing of BaS_3 layers and consists of infinite chains along the c axis formed by face-shared octahedra; the Ta cations occupy all the S_6 octahedra and are spaced midway between the close-packed layers. Low-temperature X-ray studies show that there are no temperature-dependent crystallographic transitions between 77 and 298°K. Pressed and sintered bars of polycrystalline $BaTaS_3$ indicate semiconductor behavior with an activation energy of 0.01–0.06 eV. This behavior is attributed to a distortion of the hexagonal structure as a result of the pressure used in preparing the bar. The electrical properties are discussed in terms of direct interactions between the tantalum cations in *adjoining* octahedra.

Introduction

Aslanov and Kovba[2] have reported the preparation of $BaTaS_3$ and have indicated that the compound is isostructural with $CsNiCl_3$.[3] The X-ray powder diffraction pattern for $BaTaS_3$ consisted of "relatively" few sharp lines and was indexed on the basis of a hexagonal cell with $a = 6.847$ and $c = 5.742$ Å. When the compound was ground with Pyrex glass, the X-ray diffraction lines of the type khl and $00l$ were found to be diffuse whereas lines of the type $hk0$ remained sharp. This behavior was attributed to preferred orientation. In addition, Aslanov and Kovba reported electrical properties that they recognized to be inconsistent. The compound showed a positive temperature coefficient of electrical conductivity, which is characteristic of a semiconductor, and yet the Seebeck coefficient was reported to be $\sim 20\ \mu V/deg$, which is in the range usually attributed to metallic behavior.

Barium vanadium sulfide, $BaVS_3$,[4] with which $BaTaS_3$ is isostructural, was shown to be metallic and the observed conductivity was attributed to the formation of conduction bands *via* vanadium–vanadium d-orbital overlap. The similarity of $BaVS_3$ and $BaTaS_3$ suggests that perhaps $BaTaS_3$ should be metallic. The observed positive temperature coefficient of conductivity is probably a property characteristic of the pressed bars and not representative of the intrinsic properties of the compound. It was decided, therefore, to prepare pure $BaTaS_3$ and study its electrical and crystallographic properties.

Experimental Section

Preparation.—$BaTaS_3$ was prepared by heating a mixture of barium sulfide, tantalum metal (99.95+%, Gallard-Schlesinger Corp.), and sulfur (99.9999+%, Gallard-Schlesinger Corp.) for 2 weeks at 600° and for 1 week at 1000° in an evacuated silica tube. The barium sulfide used in the preparation was prepared from barium carbonate ("Specpure," Johnson, Matthey and Co., Ltd.) according to the procedure described in ref 5.

Crystal Growth.—Single crystals of $BaTaS_3$ were grown using barium chloride as a flux. A mixture of the sulfide and the flux was sealed in an evacuated silica tube. It was necessary to heat the mixture under vacuum at 150° for several hours before sealing in order to remove all of the water of hydration from the barium chloride. The evacuated silica tube was then sealed within a second silica tube to prevent any exposure of the melt to the atmosphere. The inner tube had a tendency to devitrify and crack. The double-tubed sample was heated to 1050° and held at that temperature for 12–24 hr. The furnace was programmed from 1050 to 800° at 3°/hr and then to room temperature at 50°/hr. The melt was extracted with cold water, filtered, and washed with acetone. The yield of crystals was very small and the largest crystals ($\sim$1 mm in length) could be separated from the polycrystalline material by passing the mixture through a series of sieves. The crystals were black and grew as first-order hexagonal prisms $[10\bar{1}0]$.

Analysis.—Polycrystalline $BaTaS_3$ was analyzed for barium and sulfur; the tantalum content was determined by difference. $BaTaS_3$ was oxidized in a stream of dry oxygen at 1000° and X-ray analysis indicated that the oxidation product consisted of a mixture of $BaSO_4$ and $BaTa_2O_6$. The per cent sulfur in the original sample was calculated assuming complete conversion to these products and the barium content was determined by precipitation as the sulfate. *Anal.* Calcd for $BaTaS_3$: Ba, 33 13; Ta, 43.66; S, 23.21. Found: Ba, 33.5; Ta, 43.4; S, 23.10.

The amount of chloride in the single crystals could not be determined by standard analytical techniques. However, several hundred milligrams of the polycrystalline sample from the crystal growth experiments was treated with concentrated nitric acid and silver nitrate was added to the resulting solution. Faint cloudiness was observed and, since under identical conditions 0.5 mg of sodium chloride yielded considerable precipitate, it was concluded that the amount of chlorine present in the crystals was less than 0.1%.

Physical Measurements.—Electrical resistivity as a function of temperature was determined on sintered bars of polycrystalline material. The temperature range studied was from 80 to 350°K. The bars used for these measurements were prepared by hot-

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[1] This work has been supported by ARPA and the U. S. Army Research Office, Durham, N. C.

[2] L. A. Aslanov and M. Kovba, *Zh. Neorgan. Khim.*, **9**, 2441 (1964); *Russ. J. Inorg. Chem.*, **9**, 1317 (1964).

[3] G. N. Tishchenko, *Tr. Inst. Kristallogr. Akad. Nauk SSSR*, **11**, 93 (1955).

[4] R. A. Gardner, M. Vlasse, and A. Wold, *Acta Cryst.*, **B25**, 781 (1969).

[5] G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 2, 2nd ed, Academic Press, New York, N. Y., 1965, p 938.

pressing the polycrystalline powder at 142,000 psi and 300°. These conditions were maintained for 12 hr under a flowing argon atmosphere.

Electrical resistivity was determined on the bars by a conventional potential-probe method using spring-loaded gold-plated contacts. Seebeck coefficients were measured by means of a differential method using an ice bath as a constant cold junction. The copper contacts to the sample and lead wires required a correction to the measured coefficient of approximately 3 μV/deg. The Seebeck coefficient reported is that measured at room temperature and includes the lead wire correction.

Collection and Reduction of X-Ray Data.—Powder samples were examined by X-ray diffraction methods using a high-intensity copper source (λ(Cu Kα_1) 1.5405 Å) of focal spot size 1.2 × 3.0 mm. The diffracted X-rays were monochromatized (AMR-202 focusing monochromator) and detected by a Norelco scintillation counter. Lattice dimensions at 25° were determined from single-crystal rotation and Weissenberg photographs calibrated with sodium chloride. For $BaTaS_3$ $a = 6.846 \pm 0.005$ and $c = 5.744 \pm 0.005$ Å (λ(Mo Kα_1) 0.70926 Å), which are in excellent agreement with the data of Aslanov and Kovba.[2] The reported errors for the single-crystal cell parameters represent the average deviations in the observed cell constants. The pycnometrically measured density was $d = 5.80$ g/cm^3, which indicated a cell containing two formula units. The calculated density was $d_c = 5.91$ g/cm^3.

The Laue symmetry for $BaTaS_3$ was found to be 6/mmm. Systematic extinctions, determined from zero- and upper-layer Weissenberg and precession photographs, occurred only for $hh\overline{2h}l$: $l = 2n + 1$. In addition, structural absences $h - k = 3n$ for $l = 2n + 1$ were observed. These absences are consistent with the space groups P6$_3$mc, P$\bar{6}$2c, and P6$_3$/mmc. Piezoelectric and pyroelectric measurements were not made since conducting crystals do not show these effects.[6]

A single crystal of $BaTaS_3$, in the form of a hexagonal prism (0.04 mm long and 0.02 mm maximum diameter) was mounted about its c axis and again remounted on the a axis. Multiple-film equiinclination Weissenberg photographs were taken with Zr-filtered Mo Kα radiation about the a axis (h = 0–7) and the c axis (l = 0–6). Intensities were measured visually by comparison with a standard intensity scale. These data were scaled and averaged to give a total of 186 independent reflections. The intensity data were corrected for extended spot-shape and Lorentz and polarization effects.[7] The interfilm and interlayer scaling was carried out by the usual scaling algorithms.[8] Absorption correction was applied using Burnham's algorithm.[9] The crystal measured had an irregular shape; however, it could not be ground to a sphere since it was very brittle.

Solution and Refinement of the Structure.—An inspection of the three-dimensional Patterson function, calculated using the NRC-8 Fourier program of Ahmed, *et al.*,[10] indicated that the tantalum, barium, and sulfur atoms occupy the positions (2a), (2b), and (6c) in space group P6$_3$mc or (2a), (2d), and (6h) in either P$\bar{6}$2c or P6$_3$/mmc.[11] The approximate positional parameters were determined to be (0, 0, 0) for Ta, ($^1/_3$, $^2/_3$, $^3/_4$) for Ba, and (x, $2x$, $^1/_4$) with $x \simeq {}^1/_6$ for S. The trial positional parameters were identical with those used by Aslanov and Kovba.[2] Although all three space groups were possible, it was decided initially to refine the structure in the centrosymmetric P6$_3$/mmc. A full-matrix least-squares refinement was carried out using the Busing, Martin, and Levy ORFLS[12] program modified to make real and imaginary anomalous dispersion corrections. The atomic scattering factors for S^{2-} were taken from ref 13, and those for Ba^{2+} and Ta^{4+} were the values given by Thomas and Umeda.[14] The necessary parameters used for the anomalous dispersion correction were those given by Dauben and Templeton.[15] Weights were assigned to each reflection according to the scheme of Cruickshank,[16] *i.e.*, $w = (A + BF_o + CF_o^2)^{-1}$, with $A = 2F_{\min}$ ($F_{\min} = 3$), $B = 1.0$, and $C = 2/F_{\max}$ ($F_{\max} = 302$).

The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized where F_o and F_c are the observed and calculated structure factors and w is the weight defined above. The unobserved reflections were assigned zero intensity and given zero weight in the refinement. For the refinement procedure, one over-all scale factor was used.

Several cycles of isotropic least-squares refinement led to

$$R = \frac{\sum||F_o| - |F_c||}{\sum|F_o|} = 0.106$$

$$wR = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2}\right]^{1/2} = 0.119$$

The refinement was continued in the centrosymmetric space group with three cycles of anisotropic calculations. The final values of R and wR for the observed data were 0.087 and 0.093, respectively. The application of Hamilton's[17] significance test indicates that the results are significant at the 0.005 level. The final positional and thermal parameters of this refinement are given in Table I. Interatomic distances, bond angles, and standard deviations were calculated using the Busing, Martin, and Levy ORFFE[18] program and are shown in Table II. The final structure factors are given in Table III for observed reflections only. Those reflections too weak to observe had, at the end, calculated structure factors whose magnitude did not exceed the minimum observable magnitude in nearby regions of reciprocal space.

TABLE I

POSITIONAL AND THERMAL PARAMETERS[a,b]

Atom	x	z	β_{11}	β_{22}	β_{33}
S	0.1686 (9)	$^1/_4$	11 (3)	59 (2)	78 (2)
Ta	0	0	27 (3)	27 (3)	74 (7)
Ba	$^1/_3$	$^3/_4$	81 (6)	81 (6)	82 (11)

[a] The standard deviations are shown in parentheses and refer to the last position of the respective values. [b] The temperature factor expression used was $\exp[10^{-4}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12})]$. Constraints placed on the β_{ij}'s are: for sulfur, $\beta_{11} = 2\beta_{12}$; for tantalum and barium, $\beta_{11} = \beta_{22} = 2\beta_{12}$.

The above results indicate that a reasonable refinement was obtained in the centrosymmetric P6$_3$/mmc space group. In the absence of any stereochemical evidence which would show that the choice is incorrect, the centrosymmetric group is assumed.

Low-Temperature X-Ray Study.—Powder samples of $BaTaS_3$ were mixed with collodion and amyl acetate and spread on an aluminum-backed slide with a copper–constantan thermocouple attached to the slide. The sample was examined using

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(6) W. G. Cady, "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. VI, 1st ed, National Research Council of U. S., McGraw-Hill Book Co., New York, N. Y., 1929, p 208.

(7) K. Lonsdale, *Acta Cryst.*, **17**, 308 (1964).

(8) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *ibid.*, **18**, 129 (1965).

(9) C. W. Burnham, Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1961.

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(17) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(18) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

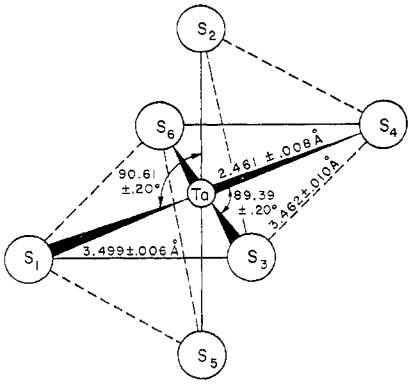

Figure 1.—Tantalum-occupied sulfur octahedron with bond distances and angles. Dashed lines indicate the planes of close-packed layers. Errors noted represent standard deviations.

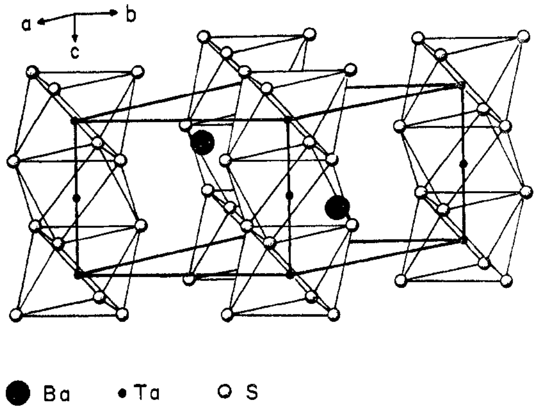

Figure 2.—Structure of $BaTaS_3$ showing chains of face-sharing sulfur octahedra. The hexagonal unit cell is outlined with bold lines.

Table II

Selected Interatomic Distances and Angles of $BaTaS_3$[a]

Atoms	Dist, Å	Atoms	Angle, deg
S_1–Ta_1	2.461 (8)	S_1–Ta_1–S_2	90.61 (20)
S_1–Ba_2	3.423 (3)	S_1–Ta_1–S_6	89.39 (20)
S_2–Ba_2	3.474 (6)	S_1–Ta_1–S_4	180.0 (9)
S_1–S_2	3.499 (6)	Ta_1–Ba_2–Ta_2	39.93 (4)
S_1–S_6	3.462 (10)	S_1–Ba_2–Ta_2	35.82 (14)
Ta_1–Ta_2	2.872 (3)		
Ta_1–Ba_2	4.205 (3)		
Ba_1–Ba_2	4.886 (3)		

Rms Component of Thermal Displacement along Principal Axes (Å)

Atom	Axis 1	Axis 2	Axis 3
S	0.0335 (51)	0.1144 (154)	0.1250 (178)
Ta	0.0699 (57)	0.0699 (57)	0.1110 (53)
Ba	0.1173 (91)	0.1201 (81)	0.1205 (117)

[a] Errors in cell parameters are included in the standard deviations.

Table III

Observed and Calculated Amplitudes (×2.679) (in electrons) for $BaTaS_3$

K	L	OBS	CALC
H=0			
0	2	60	52
0	4	267	264
0	8	132	122
H=1			
0	0	135	129
0	1	97	82
0	2	199	204
0	3	70	67
0	4	77	83
0	5	58	46
0	6	111	105
0	7	36	30
1	0	250	264
1	2	92	55
1	4	176	176
1	6	40	39
1	8	88	83
H=2			
0	0	59	56
0	1	175	179
0	2	230	238
0	3	129	135
0	4	46	44
0	5	103	99
0	6	137	128
0	7	65	68
1	0	107	114
1	1	92	73
1	2	156	175
1	3	63	59
1	4	78	80
1	5	47	42
1	6	102	96
1	7	27	28
1	8	53	40
2	0	302	303
2	2	35	21
2	4	230	220
2	6	9	12
2	8	96	108
H=3			
0	0	228	228
0	1	3	3
0	2	58	62
0	3	3	2
0	4	151	159
0	6	46	38
1	0	111	99
1	1	65	61
1	2	148	159
1	3	46	50
1	4	60	73
1	5	40	37
1	6	86	92
2	0	100	90
2	1	61	50
2	2	145	145
2	3	52	42
2	4	67	68
2	5	34	31
2	6	87	87
3	0	188	165
3	2	68	53
3	4	131	126
3	6	37	35
H=4			
0	0	71	54
0	1	118	127
0	2	178	189
0	3	101	109
0	4	31	40
0	5	99	84
0	6	104	112
0	7	43	58
1	0	174	180
1	2	71	56
1	4	129	135
2	0	56	48
2	1	117	105
2	2	157	160
2	3	96	92
2	4	45	37
2	5	76	71
2	6	102	99
3	0	98	81
3	1	57	37
3	2	105	110
3	3	21	33
3	4	71	64
3	5	18	26
3	6	56	70
4	0	104	102
4	2	8	3
4	4	165	144
4	6	6	0
H=5			
0	0	96	91
0	1	65	47
0	2	117	127
0	3	44	40
0	4	63	71
0	5	30	30
0	6	81	78
1	0	96	82
1	1	57	43
1	2	123	121
1	3	37	37
1	4	74	65
1	5	30	29
1	6	71	76
2	0	154	136
2	2	65	54
2	4	123	107
2	6	38	36
3	0	65	69
3	2	90	101
3	3	39	28
3	4	53	55
3	6	76	66
4	0	73	62
4	1	27	21
4	2	98	91
4	4	44	50
4	6	53	61
5	0	87	97
5	2	45	42
5	4	97	79
H=6			
0	0	199	210
0	4	162	164
1	0	79	71
1	1	43	32
1	2	111	108
1	3	37	28
1	4	44	57
1	6	63	70
2	0	40	41
2	1	77	75
2	2	120	122
2	3	59	66
2	4	38	34
2	5	52	53
2	6	85	80
3	0	112	105
3	2	52	47
3	4	85	86
4	0	46	37
4	1	61	55
4	2	96	98
4	3	63	49
4	4	27	31
5	0	62	57
5	1	20	16
5	2	71	66
6	0	114	101
6	2	7	10
6	4	96	83
H=7			
0	0	66	68
0	1	27	25
0	2	99	102
0	6	50	67
1	0	106	114
1	2	32	47
1	4	81	92
2	0	56	67
2	2	82	79
2	4	53	55
3	0	54	57
3	2	74	76
4	0	76	78
4	2	42	44
5	0	44	47
5	2	57	62
6	0	47	42
6	2	51	55
H=8			
0	0	35	39
0	1	59	64
0	2	99	109
0	3	46	57
0	6	68	72
1	0	61	61
1	2	60	78
2	0	120	126
2	4	86	102
5	0	58	60
5	2	46	36
6	2	59	56
H=9			
0	0	87	86
0	4	53	71
2	0	48	48
2	2	59	64
H=10			
0	2	70	79

monochromatized high-intensity copper radiation with a Norelco diffractometer. A temperature of approximately 77°K was reached by blowing liquid nitrogen directly on the sample. No crystallographic transition was observed between 77 and 298°K.

Results and Discussion

The structure of $BaTaS_3$ is based on the hexagonal close-packing of BaS_3 layers with the tantalum cations in one-fourth of the octahedral voids between the close-packed layers. In a close-packed array of barium and sulfur in a 1:3 ratio, only one-fourth of the octahedral voids between the layers are surrounded exclusively by the anions; these are the octahedra occupied by tantalum cations (see Figure 1). The site symmetry of the tantalum ion is $\bar{6}m2$ (D_{3h}). Figure 2 shows a representation of the structure of $BaTaS_3$. The diagram illustrates the fact that the structure consists of infinite chains of face-shared anion octahedra with the transition metal cations spaced midway between the anions of the close-packed layers. The structure also contains unoccupied octahedra with barium cations at two of their opposite corners and these octahedra share edges with the octahedra shown in Figure 2. The octahedra with barium cations at two of their corners are not shown in the diagram for the sake of simplicity. The X-ray diffraction pattern of $BaTaS_3$ powder is shown in Figure 3(a). The hexagonal indices are indicated for each peak.

The pressed and sintered bars that were to be used for electrical conductivity and Seebeck coefficient measurements were first examined by X-ray diffraction techniques in order to determine whether or not any oxidation of the samples occurred upon sintering. It was found that the bars prepared by the hot-pressing method showed a very pronounced distortion of the original structure as a result of pressing. Figure 3 shows the diffraction patterns for (a) powdered $BaTaS_3$, (b) a hot-pressed bar of $BaTaS_3$, and (c) a hot-pressed bar annealed 15 days at 1000°. The diagram clearly indicates the change of the diffraction pattern upon pressing and subsequent annealing. The peaks of the type *hk*0 remain sharp and peaks of the type *hkl* are all very diffuse. The effect is not due to preferred orientation since each side of the bar had the same diffraction pattern. One of the hot-pressed bars was cut along a face diagonal and the inner surface was X-rayed; the

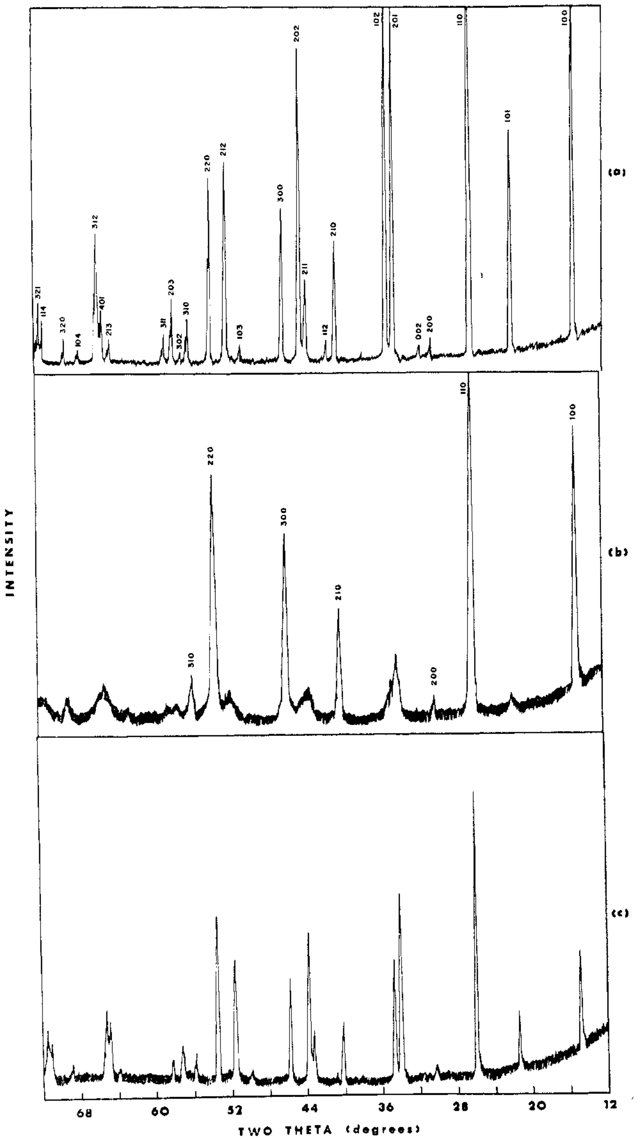

Figure 3.—X-Ray diffraction patterns for $BaTaS_3$: (a) powder; (b) sintered bar, pressed at 100,000 psi and 300°; (c) sintered bar, annealed 15 days at 1000°. Hexagonal indices are indicated in (a).

result was the same. Following the annealing of the bar, its X-ray pattern sharpens and approaches that of the prepressed sample.

Figure 4 shows a plot of log (resistivity) *vs.* $10^3/T_K$ for the hot-pressed bars. The room-temperature resistivity is approximately 2.5×10^{-1} ohm cm and $d(\ln \rho)/d(1/kT)$ ranges from 0.06 eV at room temperature to 0.012 eV at 80°K. The Seebeck coefficient -64 μV/deg is higher than the value of -20 μV/deg reported by Aslanov and Kovba,[2] but it is still within a range that may be considered characteristic of metallic materials.

Since $BaTaS_3$ is isostructural with $BaVS_3$, the application of Goodenough's theory[19] would lead one to anticipate metallic behavior for $BaTaS_3$. The critical distance, R_c, calculated for direct tantalum–tantalum interaction is 3.30 Å. The observed Ta–Ta distance in $BaTaS_3$ is 2.871 Å, and this value is clearly less than the critical distance. A possible explanation for the activation energy observed in the sintered bars, as indicated by the occurrence of the diffuse X-ray peaks observed in Figure 3(b), is that the pressure used to make the bars causes a distortion of the structure. $BaTaS_3$ has a hexagonal close-packed sequence of BaS_3 planes, and the octahedra containing the tantalum cations are all face-shared. Application of sufficient pressure can cause a change in the stacking sequence so that some of the octahedra share corners. The relatively low pressure used to prepare the bars is not sufficient to transform the hexagonal close-packed structure to a new type, but rather results in the small distortion along the *c* axis which is indicated by the X-ray pattern shown in Figure 3(b). It can be seen that reflections of the type *hk*0 are not affected by the pressure; however, the reflections involving the *l* index show considerable change. Longo and Kafalas[20,21] have recently reported on the pressure-induced transformations for compounds with similar structures ($BaRuO_3$, $Ba_{1-x}Sr_xRuO_3$). The distortion observed for $BaTaS_3$ is undoubtedly sufficient to affect the tantalum chains (shown in Figure 2) which are aligned along the *c* axis and hence interfere with the delocalization of the electrons along this direction.

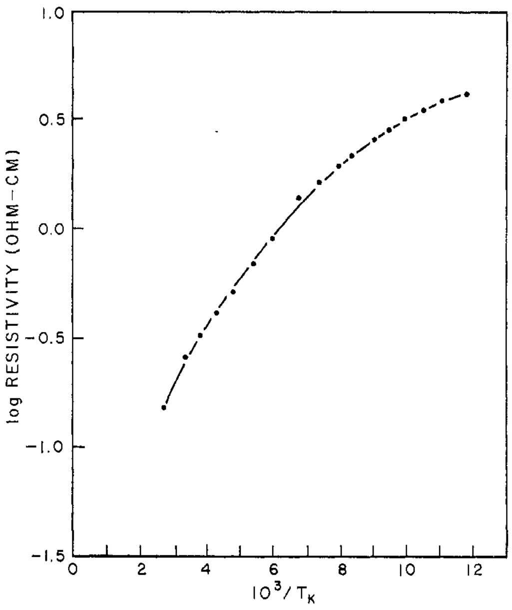

Figure 4.—Log (resistivity) *vs.* $10^3/T_K$ for $BaTaS_3$.

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