

Synthesis and Electrical Properties of Barium Uranium Sulfides

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Barium uranium ternary sulfides, BaUS₃ and BaU₂S₅, were synthesized in a single phase by the reaction of (Ba, UO₂)(NO₃)₂ at Ba/U=1 and 0.5 with carbon disulfide at 1273 K for 6 h. They crystallized in orthorhombic structure with space group, Pnma. The lattice parameters *a*, *b* and *c* are 7.493, 10.38 and 7.238 Å for BaUS₃ and 7.525, 8.475 and 11.858 Å for BaU₂S₅, respectively. The electrical conductivity of these compounds increased with increasing temperature above 200 K, below which however, it was nearly temperature independent. The Hall coefficient suggested that they are n-type semiconductors.

Key words: Uranium, Barium, Sulfide, Synthesis, Electrical conductivity, Hall effect

I. Introduction

The formation of barium uranium mixed sulfides, BaUS₃ and BaU₂S₅, has been reported by Brochu et al.^{1,2)} According to them, BaUS₃ was formed by heating BaUO₄ in a CS₂ gas at 1073 K for 12 h. BaUS₃ was also obtained by solid-solid reaction of b-US₂ and BaS in a sealed evacuated quartz ampoule at 1373 K for 48 h. BaUS₃ has an orthorhombic perovskite type structure¹⁾ with space group Pnma. The density of BaUS₃ determined by CCl₄ displacement method was 5.60 g cm⁻³. Magnetic susceptibility showed the Curie-Weiss type change at temperatures between 300 and 800 K. The effective Bohr magnetons of 3.20 suggested the uranium in BaUS₃ to be in a tetravalent state.¹⁾

A series of MU₂S₅ compounds (M=Ca, Sr, Ba) were synthesized²⁾ by the reaction of MU₂O₇ with CS₂ gas at 1123 K for 24 h. These compounds crystallize in an orthorhombic U₃S₅ type structure with space group Pnma. The density of BaU₂S₅ determined by CCl₄ displacement method was 6.80 g cm⁻³. The magnetic susceptibility of BaU₂S₅ showed that this compound was paramagnetic at low temperatures between 86 and 295 K with uranium oxidation state +4. As for the electrical properties such as electrical conductivity and Hall effect, however, no study has been reported yet.

The first aim of this work is to synthesize the barium uranium mixed sulfides by the reaction of mixed nitrates with CS₂ and by the reaction of BaS and US₂ in a sealed evacuated ampoule. According to our experiences to prepare sulfides,^{3,4)} the sulfurization reaction proceeds more rapidly when easily decomposable sulfates are used as starting materials. Because nitrates decompose generally at much lower temperatures than the corresponding

oxides, the same effect can be expected for the reaction of the nitrates in the present case. The second aim is to study the electrical properties of BaUS₃ and BaU₂S₅ by measuring electrical conductivity and Hall coefficient by the van der Pauw method in a temperature range of 15-300 K.

II. Experimental Procedure

1. Materials

Analytical grade CS₂ (b.p.=319-320 K and max. H₂O=0.02%) and BaCO₃ were obtained from Wako Pure Chemicals Ind. Ltd. and used as received. Both N₂ and H₂ gases of 99.99% purity were purchased from Nippon Sanso Co., Ltd.

Uranium metal turnings were dissolved in HNO₃ and purified by solvent extraction with TBP (tributyl phosphate).⁵⁾ Ammonium diuranate precipitate was changed to UO₃ by heating in air at 500°C. The main impurities in the UO₃ were 54 ppm Pd and 94 ppm Tm by ICP analysis. Uranyl sulfate trihydrate was obtained by dissolving the UO₃ in dilute H₂SO₄ followed by evaporation of the solutions to dryness under an IR lamp.

2. Preparation of sulfides

The experimental setup of the reaction apparatus has been described elsewhere.⁶⁾ For preparing b-US₂, the weighed amount of UO₂SO₄·3H₂O on a graphite boat was set in a horizontal resistance tube-furnace. The sample was heated up to 1073 K and kept at this temperature for 4 h in a flow of the mixed gas of CS₂ and N₂ which was obtained by bubbling the N₂ gas through liquid CS₂ at a rate of 100 ml min⁻¹. After the reaction, the sample was cooled to room temperature in the same gas flow. The product was identified as a single phase b-US₂ by X-ray powder analysis.⁷⁾ In a similar manner, BaS was pre-

pared by the reaction of BaSO_4 with CS_2 at 1073 K. BaS was formed in a single phase as ascertained by the X-ray diffraction analysis.⁹⁾ The mixtures of b-US₅ and BaS in the calculated amounts (for BaUS_3 and BaU_2S_5) were heated with 2 wt% sulfur in sealed evacuated quartz ampoules at 1273 K for one week.

Another method to prepare the barium uranium mixed sulfides is an open system reaction of the materials. To the purified uranyl nitrate solution of dilute HNO_3 , the calculated amount of BaCO_3 was dissolved. The solution was evaporated to dryness under an IR lamp. The solid $(\text{Ba,UO}_2)(\text{NO}_3)_2$ obtained was thoroughly ground in an agate mortar. $(\text{Ba,UO}_2)(\text{NO}_3)_2$ was decomposed and sulfurized by heating in a stream of the mixed gas of CS_2 and N_2 , which was prepared as mentioned above, at 1273 K for 3 h. The Ba/U atom ratios of $(\text{Ba,UO}_2)(\text{NO}_3)_2$ were 1 and 0.5 for BaUS_3 and BaU_2S_5 , respectively.

After the reaction, the products were ground for X-ray analysis and pelletized for electrical properties measurements.

3. X-ray diffraction analysis

The X-ray powder diffraction analysis was carried out with a diffractometer (Rigaku Type RAD-IC) using $\text{CuK}\alpha$ radiation (40 kV, 20 mA) monochromatized by curved pyrolytic graphite. Intensity and least-squares lattice parameter calculations were carried out with the programs LAZY-PULVERIX⁸⁾ and LCR2,¹⁰⁾ respectively.

4. Electrical measurements

The electrical conductivity and the Hall coefficient measurements were performed using four-probe van der Pauw method¹¹⁾ for the sintered pellets of BaUS_3 and BaU_2S_5 (10 mm in diameter). After four Cu lead wires were attached to the pellet with 90° separation, the pellet was set to the measuring device.¹²⁾ The device was cooled to 15 K in a vacuum by a helium refrigerator (Daikin UV202-CL). Then, the temperature of the pellet was raised with a tape heater at a rate of 0.5 K/min by a digital program controller (Chino KP-1000) up to room temperature. By applying a constant current of 10 mA (Advantest TR-6143) to the sample, the potential drop was measured by a voltmeter (Keithley Model-182) of which the input impedance was >10 GΩ. The hysteresis in the electrical conductivity was checked by lowering the temperature at the same rate from room temperature to ~15 K. For the Hall coefficient measurement, the magnetic field of 0.58 T was applied perpendicular to the sample with a electromagnet (Tamagawa WVM-3). The effect of magnetoresistance was minimized by changing the directions of the field and current, followed by averaging the Hall voltages.

III. Results and Discussion

1. Synthesis of BaUS_3 and BaU_2S_5

After the mixed nitrate $(\text{Ba,UO}_2)(\text{NO}_3)_2$ with the ratio Ba/U=1 was heated in the mixed gas of CS_2 and N_2 at

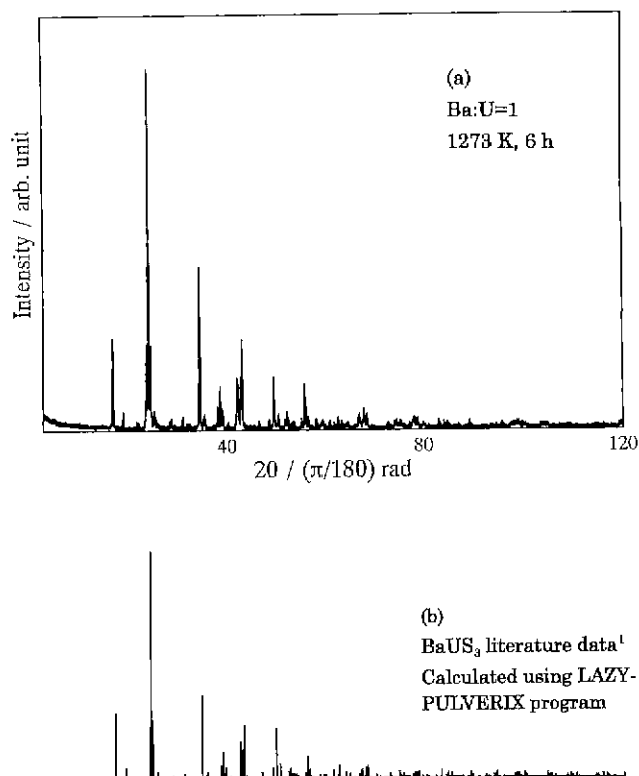


Fig. 1. X-ray diffraction pattern for the product obtained by heating $(\text{Ba,UO}_2)(\text{NO}_3)_2$ at 1273 K for 6 h (Ba/U=1), as compared with the literature data.

1273 K for 6 h, the black product was obtained. The X-ray powder diffraction pattern for the product is shown in Fig. 1. The diffraction pattern of BaUS_3 calculated by the LAZY-PULVERIX program using the literature crystal data¹¹⁾ is also given in the figure. From Fig. 1a and 1b, it is seen that the product is a single phase BaUS_3 . The crystal is orthorhombic with space group $Pnma$. The lattice parameters were calculated by the Nelson-Riley least-squares method on the LCR2 program to be $a=7.439\pm 0.003$, $b=10.380\pm 0.004$, $c=7.238\pm 0.003$ Å. These values are in good agreement with the values of $a=7.44\pm 0.02$, $b=10.38\pm 0.02$, $c=7.24\pm 0.02$ Å reported by Brochu et al.¹¹⁾

The X-ray diffraction patterns of the product obtained by the reactions of $(\text{Ba,UO}_2)\text{NO}_3$ of Ba/U ratio=0.5 with CS_2/N_2 gas at 1273 K for 2 h is shown in Fig. 2. The diffraction pattern of BaU_2S_5 calculated by the LAZY-PULVERIX program using the literature crystal data²⁾ is also given in the figure. Since no significant difference is observed in the two patterns, BaU_2S_5 is seen to be obtained as a single phase. BaU_2S_5 has an orthorhombic structure with space group $Pnma$ which is isostructural with U_3S_5 . By using the Nelson-Riley least-squares method on the LCR2 program, the lattice parameters of BaU_2S_5 were calculated to be $a=7.525\pm 0.005$, $b=8.475\pm 0.006$, $c=11.858\pm 0.005$ Å. These values are in good agreement with the values of $a=7.53\pm 0.02$, $b=8.49\pm 0.02$, $c=11.82\pm 0.02$ Å reported by Brochu et al.²¹⁾

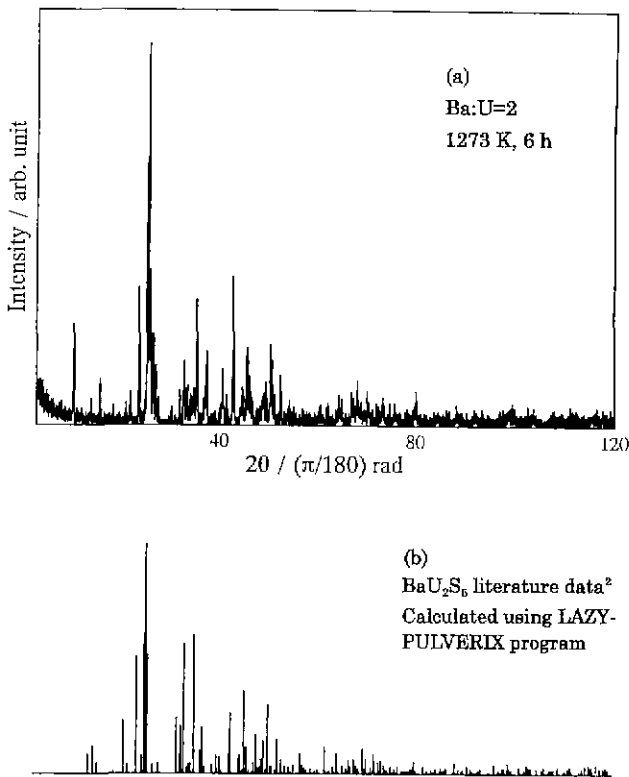


Fig. 2. X-ray diffraction pattern for the product obtained by heating $(\text{Ba}, \text{UO}_2)(\text{NO}_3)_2$ at 1273 K for 6 h ($\text{Ba}/\text{U}=2$), as compared with the literature data.

Next, the weighed mixtures of $\beta\text{-US}_2$ and BaS (and a small amount of sulfur) with different ratios of Ba/U from 0.5 to 1.1 were heated in a sealed quartz tube at 1273 K for one week. The X-ray diffraction patterns for the obtained compounds are shown in Fig. 3. From the results, it is seen that the peaks of BaUS_3 were observed at ratios between 0.8 and 1.1, while BaU_2S_5 was obtained at a ratio $\text{Ba}/\text{U}=0.5$. In the above synthetic method using the closed system, the formation of a small amount of UOS was identified as an impurity in all the products. This may be caused by the reaction between $\beta\text{-US}_2$ and quartz glass at the high temperature of 1273 K. Uranium oxysulfide is known to be sometimes mingled in sulfides. Picon and Flahaut¹³⁾ have found the presence of UOS in uranium sulfides as an intermediate or impurity compound formed in the preparation reactions. In our previous study to prepare $\text{U}_{0.92}\text{Pd}_3\text{S}_4$ by heating the mixture of US_2 , Pd powder and sulfur in an evacuated sealed quartz tube, a small amount of UOS phase was also found to be formed.¹⁴⁾ Since the presence of the impurity phase may affect the electrical properties, the BaUS_3 and BaU_2S_5 compounds as single phases obtained by the reaction of the mixed nitrate and CS_2/N_2 gas were used for electrical conductivity and Hall coefficient measurements.

2. Electrical conductivity of BaUS_3 and BaU_2S_5

The logarithm of electrical conductivities, $\ln \sigma$, of BaUS_3 and BaU_2S_5 are plotted in Fig. 4 as a function of the re-

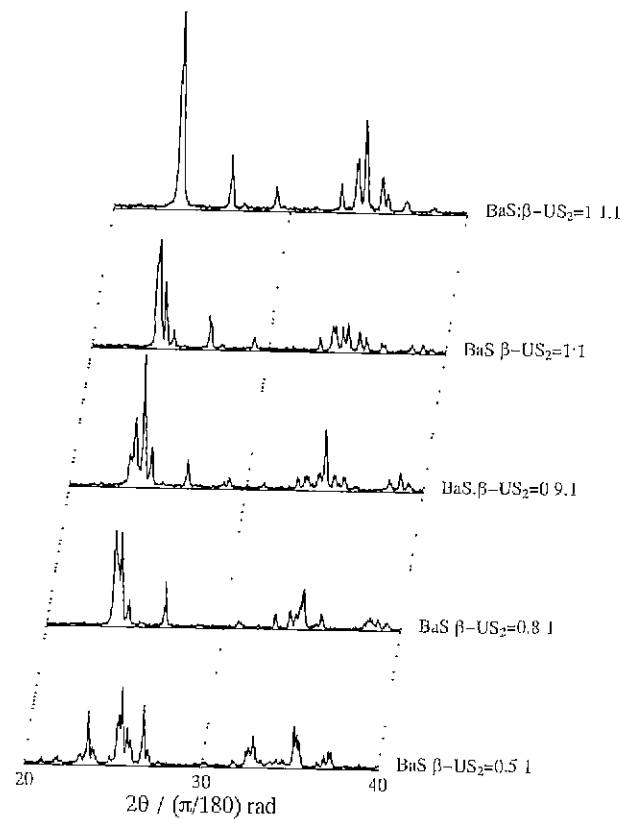


Fig. 3. X-ray diffraction pattern for the product obtained by heating the mixture of $\beta\text{-US}_2$ and BaS in a sealed quartz tube at 1073 K for one week.

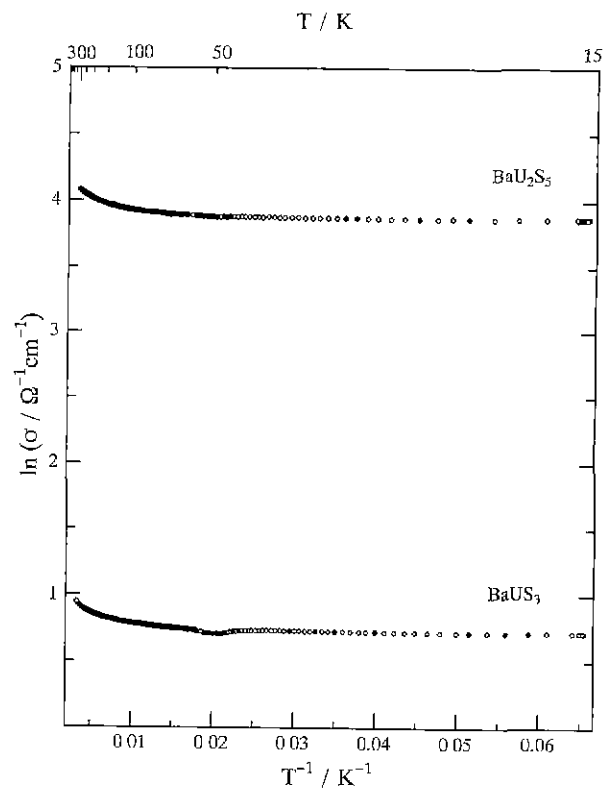


Fig. 4. $\ln \sigma$ of BaUS_3 and BaU_2S_5 as a function of $1/T$.

reciprocal temperature. Since no significant hysteresis loops were observed for the electrical conductivity values of these samples in the heating and cooling processes, the averaged values of the two processes are plotted in this figure. It is seen that $\ln s$ increases with increasing temperature at higher temperatures of $T^{-1} < 0.005$ (i.e. $T > 200$ K), while it shows a slight dependence below that temperature. From these results, the above two compounds seem to be semiconductive. The values of electrical conductivities for BaUS_3 and BaU_2S_5 at 300 K are 0.603 and 59.2 $\text{W}^{-1}\text{cm}^{-1}$, respectively. The electrical conductivity of BaUS_3 is about 10^2 lower than that of BaU_2S_5 . In terms of the relation, $\ln s = -E_a/RT$, the activation energy was calculated in the temperature range where $\ln s$ showed linear relation with temperature. The activation energies of BaUS_3 are 8.01 and 0.070 meV in the temperature ranges of 200–300 and 15–35 K, respectively. For BaU_2S_5 , they were 7.05 and 0.032 meV in the temperature ranges of 200–300 and 15–35 K, respectively. These values are very small compared with those of semiconductors¹⁵⁾ such as Si (5.4 eV) and Ge (744 meV) at 300 K.

3. Hall coefficient, carrier density and mobility for BaUS_3 and BaU_2S_5

The Hall coefficient (R_H) measured for BaUS_3 and BaU_2S_5 are shown in Fig 5. Since the polarities of R_H for BaUS_3 and BaU_2S_5 are negative, BaUS_3 and BaU_2S_5 are considered to be n-type semiconductor: The carrier is electron. The Hall coefficients for BaUS_3 and BaU_2S_5 do not

Table 1. Electrical Data for BaUS_3 and BaU_2S_5 at 300 K

Compound	σ ($\Omega^{-1}\text{cm}^{-1}$)	R_H (cm^3C^{-1})	n_c (cm^{-3})	μ_e ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
BaUS_3	0.603	3.55	1.1×10^{18}	9.41
BaU_2S_5	59.2	-6.7×10^{-1}	9.3×10^{19}	1.13×10^{-3}

show a significant change at temperatures ranging from 15 to 160 K, although they slightly decrease with scatter at temperatures higher than 160 K. From the Hall coefficient measured, hole mobility, m_h , and carrier density, n_c , at 300 K were calculated as 9.41 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and 1.1×10^{18} cm^{-3} , respectively, for BaUS_3 and 1.13×10^{-3} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and 9.3×10^{19} cm^{-3} , respectively for BaU_2S_5 . The carrier densities, n_0 , were calculated as 1.50×10^{18} cm^{-3} for BaUS_3 and 9.36×10^{19} cm^{-3} for BaU_2S_5 , respectively, by the equation $s = en_0 \exp(-E_a/kT)$. The value of n_0 of BaU_2S_5 is ca. 60 times larger than that of BaUS_3 , while the value of m_h is smaller by the order of 10^4 . From the above results, the low electrical conductivity of BaU_2S_5 is considered to be associated with the low mobility. The values of s , R_H , n_c and m_h for BaUS_3 and BaU_2S_5 at 300 K are listed in Table 1.

Fig. 6 shows the change of carrier density of BaUS_3 and BaU_2S_5 as a function of $1/T$. It is seen that the carrier density of these compounds does not change with temperature in the range from 15 to 160 K, while the density slightly increases with increasing temperature in the range higher than 160 K. Thus, both compounds are sup-

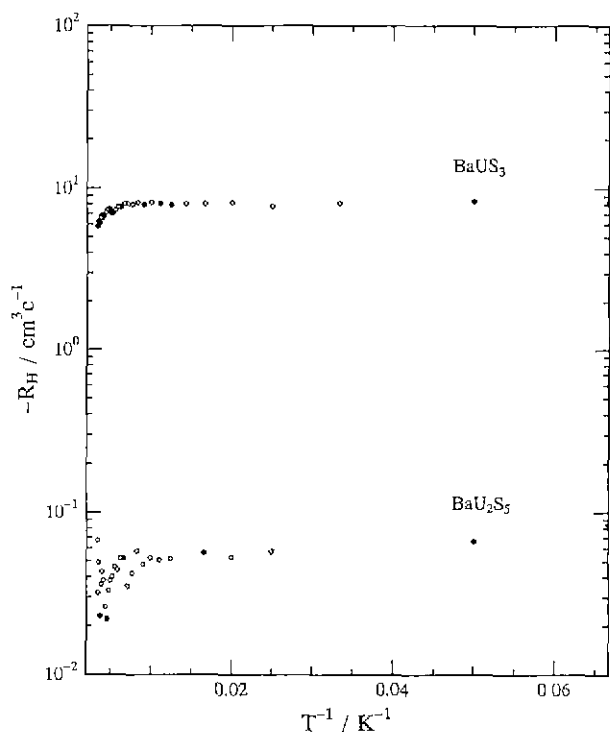


Fig. 5. Hall coefficient of BaUS_3 and BaU_2S_5 as a function of $1/T$.

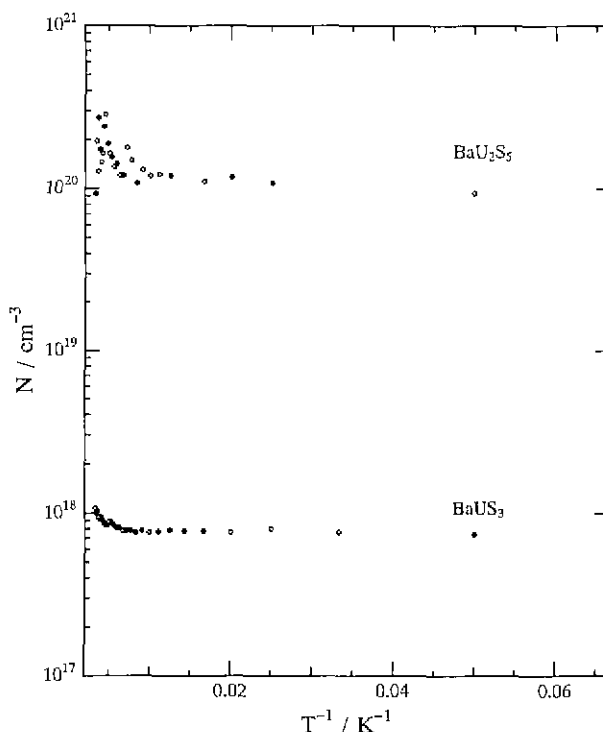


Fig. 6. Carrier density of BaUS_3 and BaU_2S_5 as a function of $1/T$.

posed to have a region of saturation conduction between 15 and 160 K and that of intrinsic conduction at temperatures higher than 160 K.

IV. Conclusions

Synthesis of barium uranium mixed sulfides, BaUS_3 and BaU_2S_5 , by the reaction of mixed nitrates with CS_2 and by the reaction of b-US₂ and BaS in a sealed evacuated ampoule was studied. The results are summarized as follows: 1) When $(\text{Ba, UO}_2)(\text{NO}_3)_2$ of Ba/U=1 and 0.5 were heated in a stream of CS_2/N_2 at 1273 K for 6 h, BaUS_3 and BaU_2S_5 were obtained having orthorhombic crystal structures with lattice parameters $a=7.493$, $b=10.38$, $c=7.238$ Å and $a=7.525$, $b=8.475$, $c=11.858$ Å, respectively. 2) By heating the mixture of b-US₂ and BaS at a molar ratio Ba/U=0.5 in sealed quartz ampoules, BaUS_3 were obtained at ratios between 0.8 to 1.1, while BaU_2S_5 was obtained. 3) The electrical conductivity of these compounds increased with increasing temperature above 200 K. below which, however, it was nearly temperature independent. 4) Hall coefficient suggested that they are n-type semiconductors.

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