JOURNAL OF SOLID STATE CHEMISTRY 33, 277–281 (1980)

Electrical Transport Properties of a Nonstoichiometric Rare Earth Sulfide, $EuGd_2S_4$

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Received July 16, 1979; in revised form September 11, 1979

The electrical transport properties of nonstoichiometric $EuGd_2S_4$ prepared by heating under a high vacuum have been investigated. The samples heated were classified into two groups on the basis of their electrical transport behavior. One group comprised semiconducting materials heated at 1500 and 1600°C, for which the transport mechanism was found to be via electron hopping with activation energies ranging from 0.013 to 0.027 eV. Another group comprised metallic materials heated at 1700 and 1800°C. Their electrical transport was carried out through ordinary band conduction over the measured temperature range except at temperatures lower than 120°K, where hopping with a very small activation energy (~0.0035 eV) occurred predominantly.

Introduction

The rare earth sulfides with the Th_3P_4 structure, which can be described by the formula $Ln_{3-x}S_4$, are of interest because they exhibit a wide range of electrical and magnetic properties without changing crystal structure. Cutler and his co-workers (*1–3*) had studied in detail the electrical transport properties of $Ce_{3-x}S_4$. They observed a transition from a metallic (Ce_3S_4) to an insulator (Ce_2S_3) type of transport and suggested that the conduction electrons occupied a partially filled 5*d* band for Ce_3S_4.

On the other hand, it is known that rare earth sulfides $EuLn_2S_4$ have the same Th_3P_4-type crystal structure as $Ce_{3-x}S_4$ (*4*). We have previously reported (*5*) that a series of $EuLn_2S_4$ (*Ln* = La–Gd) compounds are all *p*-type semiconductors and their electrical conductivity is sensitive to sulfur vapor pressure. These compounds should be insulators if they are stoichiometric, since Eu ion in these compounds is divalent and *Ln* ion trivalent as shown from the magnetic susceptibility measurements. In practice, the physical properties of $EuLn_2S_4$ seem to be affected by their stoichiometry because they have the Th_3P_4 structure which is stable over a wide composition range.

The aim of this paper is to investigate the influence of nonstoichiometry on the electrical transport phenomena of the rare earth sulfide $EuGd_2S_4$.

Experimental

Preparation of $EuGd_2S_4$ sample. The preparation details of the stoichiometric $EuGd_2S_4$ sample were similar to those described in Ref. (*5*). In order to obtain nonstoichiometric $EuGd_2S_4$ samples, stoichiometric $EuGd_2S_4$ was heated on a mo-

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0022-4596/80/090277-05$02.00/0

lybdenum plate in a induction furnace at various temperatures (1500–1800°C) for 3 hr under vacuum ($\sim 10^{-4}$ mm Hg).

Analysis. The atomic ratio (Eu:Gd) in the heat-treated compounds was determined with a Rigaku Denki X-ray fluorescent spectrometer equipped with a Si (Li) detector. The quantity of sulfur was determined by the conventional wet chemical analysis, S anion in the sample being oxidized into SO_4 anion by $CCl_4 + Br_2$ (2:1) solution and concentrated HNO_3. The content of sulfur was obtained as the weight of $BaSO_4$.

Measurements of the physical properties. The electrical conductivity measurements were carried out with a polycrystalline sintered pellet in an atmosphere of He (at about 1 atm) over a temperature range of 77–770°K. A very thin layer of Au was evaporated on pellet end faces, which were put in contact with Ag electrodes. From measurements of current-voltage characteristics, the contact between the sample and the electrode was found to be ohmic at both room temperature and 77°K. The dc two-probe method was adopted and the data obtained were calibrated with those obtained by the dc four-probe method at room temperature. Thermoelectric power measurements were made by the ordinary method. The sample used for this measurement was bar shaped and was held in place between two copper blocks. Thin layers of silver paste were applied to the copper/sample interface so that excellent ohmic contact was obtained. Temperature gradients were imposed by controlling the amount of power in heating elements wound on the copper blocks and were always less than 5°C. The thermoelectric power S was measured as a function of temperature over the range 120–400°K and whether the material was n-type or p-type, was judged by the sign of S.

The structure of the resulting materials was characterized by X-ray powder data from a Rigaku Denki "Rota-flex" diffractometer with a scintillation detector and Cu$K\alpha$ radiation.

The magnetic susceptibility data were obtained with a Shimazu magnetic balance MB-11.

Results and Discussion

Table I shows the atomic ratio of $EuGd_2S_4$ heated at various temperatures *in vacuo*. The composition of the nontreated sample was slightly different from that of the stoichiometric sample. This difference is presumably due to an analytical error, but the nontreated $EuGd_2S_4$ may be approximately taken as in stoichiometry. Heat treatment under high temperatures and high vacuum decreased the concentration of both Eu and S components in $EuGd_2S_4$. These components seem to sublime in the form of EuS and sulfur molecules. The final composition is regarded as Gd_3S_4. However, this compound actually decomposed upon heating at temperatures higher than 1900°C.

Data on X-ray powder diffraction and magnetic measurements are given in Table II. The X-ray powder diffraction patterns of the heated samples were all indexed on the cubic Th_3P_4 structure. Since the diffuse X-ray diffraction patterns were obtained for the samples heated at higher temperatures, the samples seem to become poorer crystalline.

TABLE I

ATOMIC RATIO OF THE SAMPLES HEATED AT VARIOUS TEMPERATURES

Heating temp. (°C)	Atomic ratio		
	Eu :	Gd :	S
Nontreated	1.02	2	3.99
1500	1.01	2	3.98
1600	0.98	2	3.88
1700	0.88	2	3.81
1800	0.83	2	3.80

TABLE II

LATTICE CONSTANTS AND MAGNETIC DATA OF THE HEATED SAMPLES

Heating temp. (°C)	Lattice const. (Å)	μ_{cal} (μ_B)	μ_{eff} (μ_B)	θ_p (°K)
Nontreated	8.512	13.82	14.15	1.0
1500	8.518	13.82	13.54	5.6
1600	8.502	13.91	13.39	14.5
1700	8.499	13.80	13.31	27.5
1800	8.465	13.71	13.38	34.5

The magnetic susceptibility for all the samples was measured in the range 77–300°K. The susceptibilities obeyed the Curie–Weiss law in this range. Analysis of the linear portion of the $1/\chi_M$ vs T curve yields values of μ_{eff}, which are close to the theoretical values. On the other hand, it is very interesting that the heated materials possess a positive paramagnetic Curie temperature, θ_p. On the basis of this result, nonstoichiometric $EuGd_2S_4$ is expected to become a ferromagnetic material at low temperature, though stoichiometric $EuGd_2S_4$ is antiferromagnetic as reported by Lugscheider *et al.* (*6*). Magnetic measurements in the low temperature range 4.2–77°K are under way.

Electrical conductivity measurements were performed in the range 77–770°K. The temperature dependences of the conductivity are shown in Fig. 1. The conductivity of the heated samples was very high compared with that of the nontreated sample. The samples heated at 1500 and 1600°C have semiconducting behavior, while those heated at 1700 and 1800°C are metallic. The increase of conductivity resulting from the heat treatment does not seem to correspond to the increase of mobility but to the increase of the number of conduction electrons, which are supplied to a partially filled 5*d* band due to the removal of sulfur.

Figure 2 shows the temperature dependence of the thermoelectric power. The sign of the thermoelectric power S in all heated specimens is negative over the whole range of temperatures, indicating electron-type conduction, while the sign of the nontreated materials is positive. Linearity of the thermoelectric power S versus temperature T was obtained for all heated specimens. The temperature dependences of S can be classified into two categories: (I) the metallic materials, whose intercept

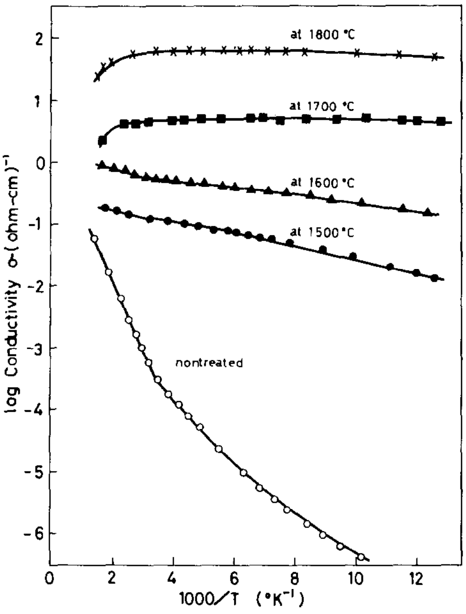

FIG. 1. Dependence of temperature on the electrical conductivity of $EuGd_2S_4$ heated at various temperatures *in vacuo* ($\sim 10^{-4}$ mm Hg).

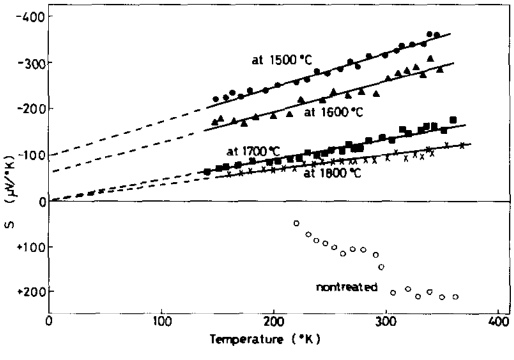

FIG. 2. Dependence of temperature on the thermoelectric power of $EuGd_2S_4$ heated at various temperatures.

of the S vs T plot at $T = 0$ is about zero; (II) the semiconductors, whose intercept at $T = 0$ corresponds to a finite value of S.

In the nearly free electron approximation the thermoelectric power S is commonly represented by

$$S = -\frac{\pi^2 k^2 T}{3e}\left(\frac{\partial \ln \sigma}{\partial E}\right)_{E=E_f}, \quad (1)$$

where E_f is the energy of the Fermi level at temperature T, k is the Boltzman constant, and σ is the conductivity at energy E. Assuming that the carriers are chiefly scattered by lattice vibrations in the metallic materials, in order to simplify the problem, Eq. (1) reduces to the form (7)

$$S = -\frac{\pi^2 k^2}{3e}\frac{T}{E_f}. \quad (2)$$

By means of Eq. (2) we can make a rough estimate of the Fermi energy E_f. The values of E_f calculated from the experimental values of the thermoelectric power are given in Table III for the samples heated at 1700 and 1800°C.

In cerium sulfide $Ce_{3-x}S_4$, each conduction electron is to be thought of as moving in the d band under the influence of the fluctuating random field due to the negative charges on the cation vacancies. This situation can be applied to the nonstoichiometric $EuGd_2S_4$ dealt with in this paper, since a number of cation vacancies are produced by the sublimation of the Eu atom. The conduction in such cases is via electron hopping from one localized state to another, and its mobility μ contains an activation energy W. As shown by Cutler and Mott (3), the conductivity σ in this type of conduction is represented by

$$\sigma = \sigma(E_f) = e\mu(E_f)N(E_f)KT, \quad (3)$$

where

$$\mu(E) = \mu_0(E)\exp[-W(E)/kT] \quad (4)$$

and

$$\mu_0 = C/kT. \quad (5)$$

$N(E)$ is the electron density at energy E, and C is a constant. When Eq. (3) is substituted in Eq. (1), one obtains

$$S = -\frac{\pi^2 k}{3e}\left[kT\frac{d\ln(\mu_0 N)}{dE} - \frac{dW}{dE}\right]. \quad (6)$$

Thus S should be a linear function of T for which the slope and intercept yield values of $d\ln(\mu_0 N)/dE$ and dW/dE for $E = E_f$. This is found to be true for the case of the semiconductors, that is, the samples heated at 1500 and 1600°C. The activation energy for the hopping conduction is given in Table III.

The relationship of the resistivity ρ vs temperature T for the specimen heated at 1800°C is shown in Fig. 3. This specimen exhibited a semiconducting behavior below 120°K and a metallic behavior above this temperature. Since a ferromagnetic transition point seems to be much lower than this temperature, as shown in Table II, it is

TABLE III

ELECTRICAL TRANSPORT PROPERTIES OF THE HEATED SAMPLES

Heating temp. (°C)	Conductivity σ at 300°K $(\Omega\text{-cm})^{-1}$	Type of conduction	Activation energy (eV)	Fermi energy (eV)
Nontreated	3.63×10^{-6}	p-type semi	0.10,0.22	—
1500	1.22×10^{-1}	n-type semi	0.020	—
1600	5.52×10^{-1}	n-type semi	0.013, 0.027	—
1700	4.51	Metallic	—	0.037
1800	5.94×10	Metallic	—	0.101

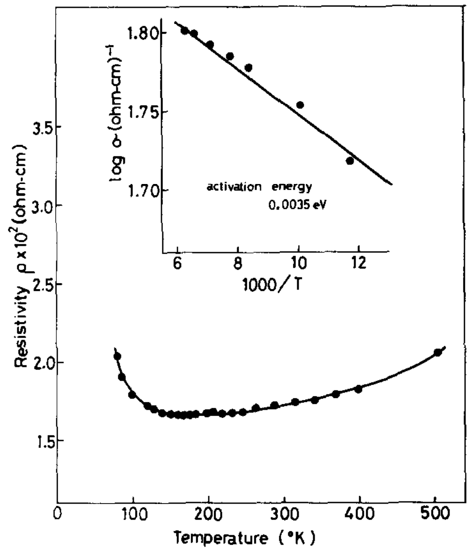

FIG. 3. Dependence of temperature on the electrical resistivity of $EuGd_2S_4$ heated at 1800°C.

understandable for this phenomenon that hopping conduction through a localized state at the bottom of the conduction band occurs below 120°K, while ordinary band conduction is predominant above this temperature. Such hopping conduction, whose activation energy was much smaller than that of the semiconducting samples heated at 1500 and 1600°C, was also observed in the specimen heated at 1700°C. In this case, variable range hopping may also occur because these samples were very poor crystalline, as observed in amorphous Ge and Si (*8*, *9*).

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