

Synthesis, sintering, specific heat and magnetism of Eu_3S_4 by low-temperature CS_2 -gas sulfurization of Eu_2O_3 nanospheres

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Single-phase Eu_3S_4 was obtained via CS_2 gas sulfurization of Eu_2O_3 nanospheres at 773 K for longer than 0.5 h. The primary particle size of Eu_3S_4 became larger than that of Eu_2O_3 during the sulfurization process. Pure synthetic Eu_3S_4 powders were unstable and transformed to EuS at 873 K under vacuum. Eu_3S_4 compacts were sintered in temperature range of 773 K to 1173 K and they transformed to EuS at 1473 K during spark plasma sintering. Specific heat of sintered Eu_3S_4 did not show an anomalous behavior in the range of 2 K to 50 K. The magnetic susceptibility of polycrystalline Eu_3S_4 followed a Curie-Weiss law from 2 K to 300 K. Magnetization of polycrystalline Eu_3S_4 was larger than that of single crystal Eu_3S_4 when the magnetic field was less than 3.5 kOe.

Keywords: Eu_3S_4 ; mixed-valence compound; inhomogeneous compound; CS_2 -gas sulfurization; specific heat; magnetic properties

1. Introduction

Homogeneous mixed-valence compounds have attracted much attention in recent years because of valence fluctuations, which in their inhomogeneous mixed-valence counterparts are due to thermally activated hopping between equivalent cation sites [1–3]. A prominent inhomogeneous mixed-valence compound Eu_3S_4 with equivalent Eu sites at room temperature, but inequivalent Eu^{2+} and Eu^{3+} sites at low temperature, represents an ideal test case [4]. Cubic Eu_3S_4 crystals can act as sites for nucleation to accelerate the formation of $\gamma\text{-La}_2\text{S}_3$ during the nucleation process, which is advantageous for the preparation and stabilization of $\gamma\text{-La}_2\text{S}_3$ at low temperature [5].

Eu_3S_4 powders are generally prepared by reaction of Eu or EuS and sulfur [6, 7] or H_2S -gas sulfurization of Eu_2O_3 [8]. Eu_3S_4 powder samples were prepared from a mixture of EuS powder (ground-up crystal) and slight excess

of sulfur which were sealed in an evacuated quartz tube and fired at 600 °C for 3 days [6]. Shafer [8] studied H_2S -gas sulfurization of Eu_2O_3 , conducted for several days. However, it was impossible to prepare single phase Eu_3S_4 by H_2S gas sulfurization due to oxygen contamination in Shafer research. Compared with H_2S , CS_2 is a more effective sulfurization agent, which has been proven during the preparation of binary rare-earth sesquisulfides from their oxides [9]. To check the possibility of synthesis of single phase Eu_3S_4 by CS_2 -gas sulfurization at lower temperature, Eu_2O_3 nanospheres with larger specific surface area and smaller particle size were employed as starting material.

Thermal stability of mixed valence compound related to valence change and/or phase transformation is important for its application. The stability of mixed valence compound Yb_3S_4 was sensitive to temperature and atmosphere in our former research [10]. Similar to ytterbium, the valence of europium is strongly dependent on temperature and valence change may cause transformation of Eu_3S_4 to EuS [11]. Moreover, there is little

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reported about the stability of Eu_3S_4 . Therefore, the stability of Eu_3S_4 was investigated under vacuum.

The mixed valence compound systems show anomalies in their physical properties [12]. The lattice constant or unit cell volume of the mixed valence compound Eu_3S_4 is usually the first indication of the mixed valence behavior. Magnetic susceptibility χ and specific heat can also reflect the order-disorder phase transition due to temperature activated electron hopping. The magnetic susceptibility χ and specific heat of single crystal Eu_3S_4 have been investigated to understand the charge-order structure and phase transformation [11]. Unlike in the previous studies, we employed polycrystalline Eu_3S_4 obtained by CS_2 -gas sulfurization as a starting material.

In this study, the formation of Eu_3S_4 has been investigated via CS_2 -gas sulfurization of nanoscale Eu_2O_3 powders in the temperature range of 573 K to 773 K to understand the influence of characteristics of raw material Eu_2O_3 on the preparation of Eu_3S_4 . The stability of sulfurized Eu_3S_4 was systematically evaluated under vacuum to check the process of Eu_3S_4 -to- EuS transition. Synthetic Eu_3S_4 was sintered from 773 K to 1473 K by spark plasma sintering (SPS). Heat capacity and magnetism of sintered Eu_3S_4 were measured and compared with those of single crystal Eu_3S_4 prepared from EuS and sulfur [6].

2. Experimental

Eu_2O_3 powder (99.99 %, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) was employed as a raw material. The sulfurization experiment was conducted using the following procedure. A silica boat loaded with Eu_2O_3 was inserted into a silica-glass tube in a furnace (ARF3-500-60KC, Asahi Rika Mfg. Co., Ltd.) and then the tube was evacuated to a pressure less than 0.1 Pa. After the tube was filled with argon gas, the boat was heated to the setting temperature. Reagent-grade liquid CS_2 (Kanto Chemical Co., Tokyo, Japan) was introduced into the reactor by carrier argon gas flowing through a bubbler at a flow rate of 1.67 mL/s. The reactor system was cooled to room temperature in a stream

of Ar gas. CS_2 gas sulfurization process was described in our previous reports [9, 13]. The sulfurization experiments were continued at different temperatures from 573 K to 773 K for 0.5 h to 8 h. Stability of the synthesized Eu_3S_4 powders was evaluated under vacuum. Eu_3S_4 powder was placed on a BN boat (inner diameter 15 mm) and held at temperatures from 773 K to 1773 K (200 K of temperature interval) for 1 h under a pressure lower than 1.4×10^{-3} Pa. Eu_3S_4 powders were sintered by spark plasma sintering from 773 K to 1473 K for 3 h under vacuum of 7×10^{-3} Pa.

X-ray diffraction (XRD, model Rint-Ultima+, Rigaku Corp., Tokyo, Japan), with monochromatic $\text{CuK}\alpha$ radiation at 40 kV and 20 mA, was used to identify the synthesized products. The lattice parameters of the products were also calculated from the data acquired with a scan step of 1.0×10^{-3} degree for 2 s. The morphology of synthesized powders was characterized by scanning electron microscopy (SEM, JSM-5310LV, JEOL Ltd., Tokyo, Japan). Particle size distributions of EuS were measured by laser diffraction particle size distribution analyzer (Nikkiso Co., Ltd., Japan). Magnetic susceptibility measurements of Eu_3S_4 compacts were performed between 2 K and 300 K with a magnetic properties measurement system (MPMS, Quantum Design Inc.). Low temperature magnetization of Eu_3S_4 was performed down to 2 K by MPMS and specific heat of Eu_3S_4 was measured with Physical Property Measurement System (PPMS; Quantum Design Inc.) in the temperature range of 2 K to 300 K in zero magnetic field using thermal relaxation method. The specific surface area (hereinafter referred to as SSA) of the synthetic products was measured using a surface area and pore size analyzer (Autosorb-1, Quantachrome Instruments, Florida, USA) with N_2 adsorption.

3. Results and discussions

3.1. Preparation of Eu_3S_4

Fig. 1 shows a TEM image of the Eu_2O_3 powder employed in this study. The particle size is about 50 nm and the specific surface area is 9.33 m^2/g . Because the Eu_2O_3 powder consists of fine

particles and possesses large specific surface area, its chemical reactivity is expected to be extremely high.

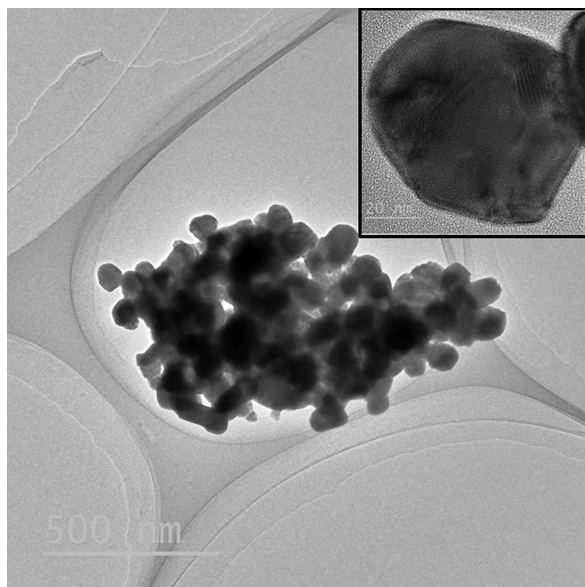


Fig. 1. TEM micrograph of nanoscale Eu_2O_3 powder.

Fig. 2 shows typical XRD patterns of the products prepared by CS_2 sulfurization of Eu_2O_3 powder at different temperatures from 573 K to 773 K for 8 h. There is no componential variation after sulfurization at 573 K. Diffraction peaks of Eu_3S_4 and EuS_2 were detected at 673 K, indicating the start of sulfurization reaction. Eu_3S_4 , as a sole product, was obtained via sulfurization at 773 K for 8 h (JCPDS standard card PDF #01-074-7272).

To illustrate the influence of sulfurization conditions on the formation and growth of Eu_3S_4 , lattice parameters of Eu_3S_4 sulfurized at 773 K for different time intervals are shown in Fig. 3. Lattice parameter of Eu_3S_4 increases with the rise of sulfurization time except for the sulfurization of 2 h. For shorter sulfurization time, lattice parameter of Eu_3S_4 is smaller than that reported (8.534 Å, PDF #01-074-7272), which may be caused by oxygen or carbon impurity. When the sulfurization time is longer than 3 h, lattice parameter of Eu_3S_4 is close to the theoretical value. The value of the lattice parameter is sensitive to the number of vacancies in the sample [6]. The lattice parameter of the present sample is similar to those of the samples grown

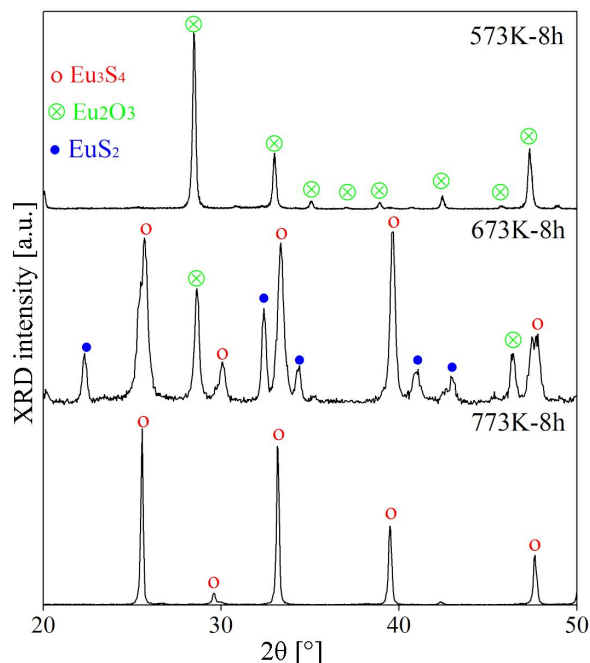


Fig. 2. XRD patterns of sulfurization products.

by Davis *et al.* [14] ($a = 8.519$ Å to 8.532 Å) and by Massenet *et al.* [6] ($a = 8.51$ Å). However, vacancies with the activation energy 0.163 eV [15] are also possible, which is satisfactorily close to the values reported previously [6, 14, 16].

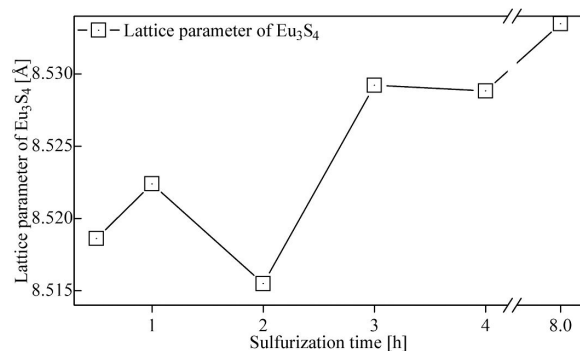


Fig. 3. Lattice parameter of Eu_3S_4 sulfurized at 773 K for 0.5 h to 8 h.

Fig. 4 shows typical SEM micrographs of single-phase Eu_3S_4 formed by sulfurization at 773 K for 3 h to 8 h. The primary particles size and shape of Eu_3S_4 are similar to those of Eu_2O_3 powder, thus, it is easier for these particles to sinter and form secondary particles. Fig. 4c shows the

necks; the shape has changed, and the grains grew as the sulfurization time increased to 8 h. In case of Eu_3S_4 , fine primary particles agglomerated to form secondary particles. Moreover, the average size of the primary particles became larger when the sulfurization time increased. This behavior is similar to that of Eu_2O_3 nanowires subjected to H_2S -gas sulfurization [17]. A high sulfurization temperature destroyed the morphology of the nanowires, resulting in highly sintered agglomerated materials [17].

3.2. Stability of Eu_3S_4 under vacuum

Fig. 5 shows SEM micrographs of EuS synthesized by annealing Eu_3S_4 at temperatures of 873 K to 1673 K with temperature interval of 200 K for 1 h under vacuum. The particle size of the synthesized EuS ranges from 0.5 μm to 1 μm , which is similar to the particle size of the products treated under Ar/ CS_2 atmosphere or Ar atmosphere [4]. In contrast to the heat-treatment process under Ar or Ar/ CS_2 atmosphere, agglomeration of the EuS particles was exacerbated under vacuum, and the produced EuS began to sinter at 1273 K. Moreover, the particles bonded together and grain growth was observed with increasing temperature. The results of the heat treatment revealed that unlike the heat treatment in an Ar/ CS_2 atmosphere, the phase transformation from Eu_3S_4 to EuS under vacuum did not require high partial pressure of sulfur. Sulfur gas generated from Eu_3S_4 could be quickly removed under vacuum which facilitated conversion to EuS.

Fig. 6 shows particle size distribution of synthetic EuS annealed at 1073 K and 1473 K. The average particle size of EuS treated at 1073 K is 5.65 μm . However, the average particle size of EuS annealed at 1473 K is 5.58 μm , which is smaller than that of EuS annealed at 1073 K. Both EuS annealed at 1073 K and 1473 K have larger particles than Eu_2O_3 (4.15 μm).

3.3. Sintering, specific heat and magnetization of Eu_3S_4

XRD patterns of the reaction products sintered at 823 K to 1473 K by SPS are shown in Fig. 7.

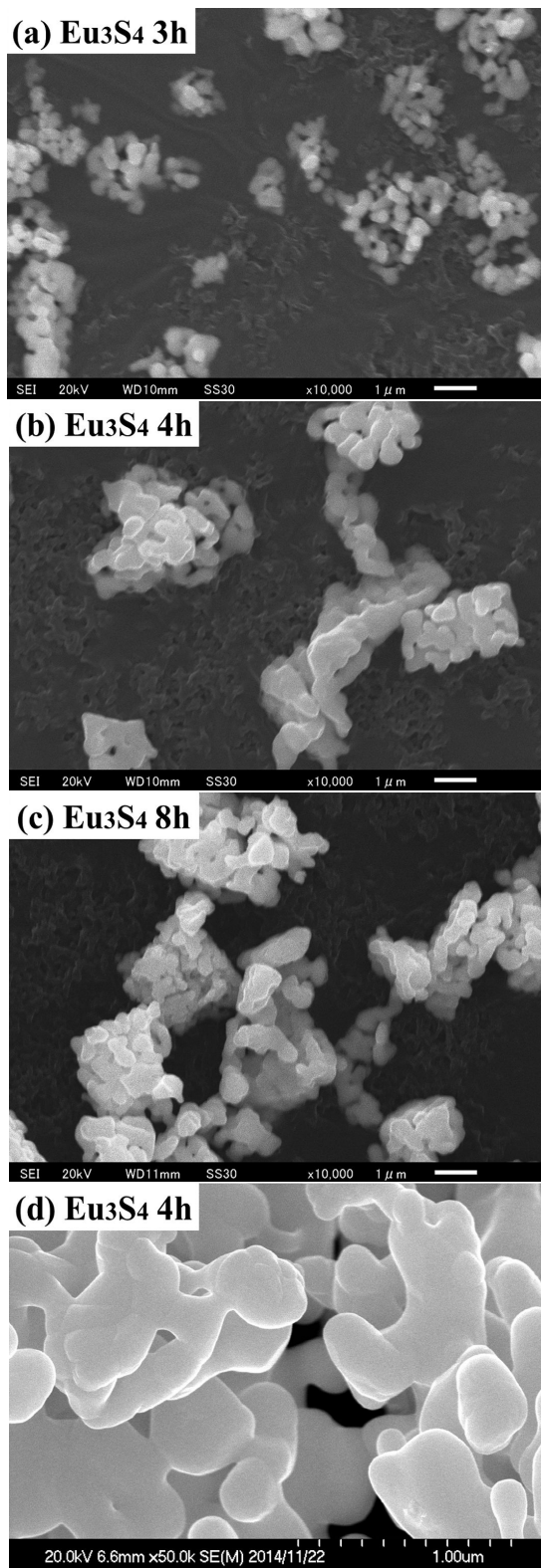


Fig. 4. SEM micrographs of Eu_3S_4 obtained by sulfurization of Eu_2O_3 at 773 K for 3 h (a), 4 h (b), 8 h (c), and its high-resolution SEM for 4 h (d).

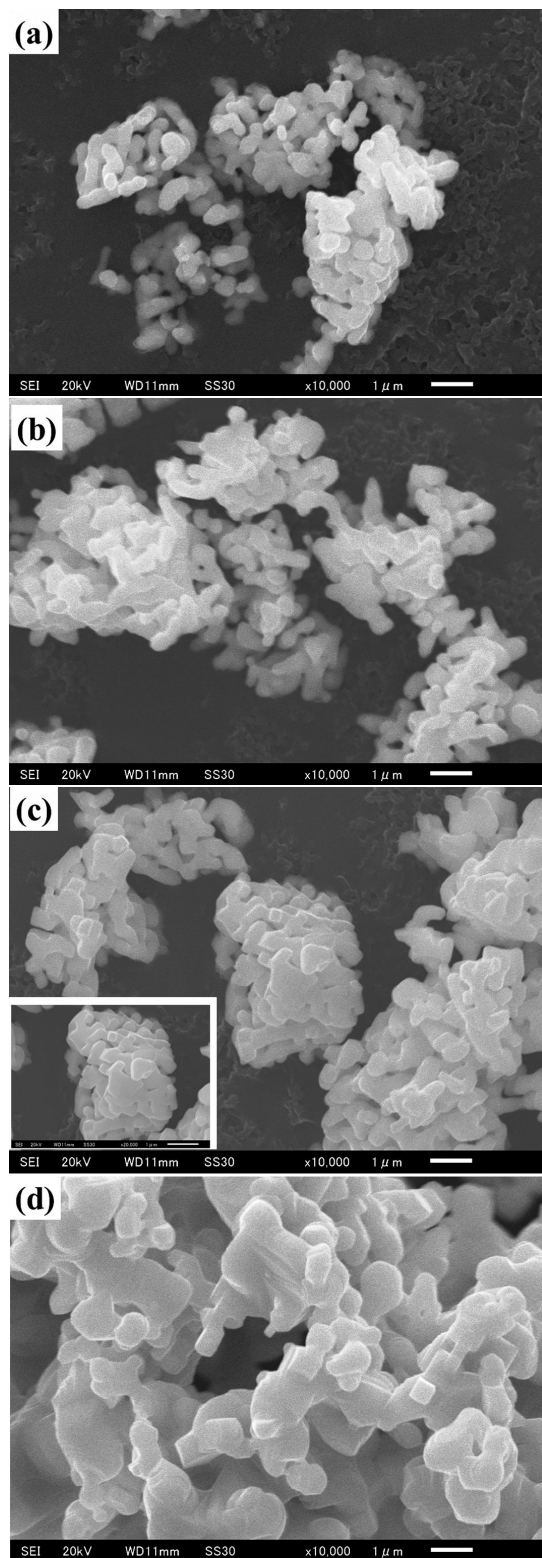


Fig. 5. SEM micrographs of synthetic EuS obtained by annealing Eu_3S_4 at 873 K (a), 1073 K (b), 1273 K (c), and 1673 K (d).

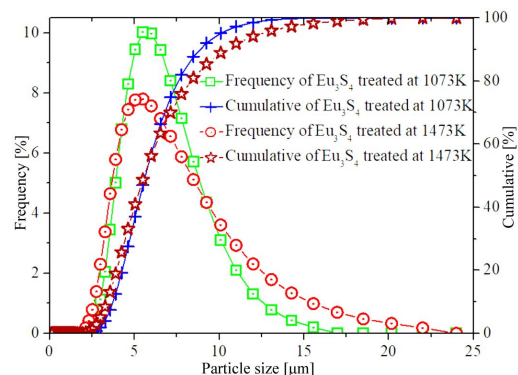


Fig. 6. Particle size distribution of EuS obtained by treating Eu_3S_4 at 1073 K and 1473 K.

At 823 K to 923 K, the diffraction peaks of Eu_3S_4 have not changed. As the sintering temperature increased up to about 1173 K, slight diffraction peaks of EuS were observed. This result suggests that Eu_3S_4 transformed into EuS on the surface of the compact at high sintering temperature. However, this transformation of Eu_3S_4 to EuS was inhibited due to closed graphite mold.

Specific heat measurements have been made on polycrystalline Eu_3S_4 ceramic bulk between 4 K and 50 K as shown in Fig. 8. The data of single crystal Eu_3S_4 prepared from EuS and sulfur were also included for comparison because the authors did not extend their measurements below 27.5 K [18]. The specific heat of polycrystalline Eu_3S_4 has no phase transformation peak from 4 K to 50 K. It is similar to the mixed-valence compound Yb_3S_4 and reported data [19]. The value of specific heat for polycrystalline Eu_3S_4 is smaller than that of single crystal Eu_3S_4 in the range of 27.5 K to 50 K [18]. Moreover, the specific heat of single crystal Eu_3S_4 exhibits a large peak at around 160 K [6] or 186 K [18] corresponding to the order-disorder transition, but the giant anomalous peak disappeared for the polycrystalline Eu_3S_4 as shown in the inset of Fig. 8.

Fig. 9 shows the temperature dependence of magnetic susceptibility χ and inverse magnetic susceptibility $1/\chi$ for Eu_3S_4 in the temperature range of 2 K to 300 K. There is no peak or any other abnormal behavior at the charge ordering transition around 160 K [6]. Furthermore, there is no anomaly

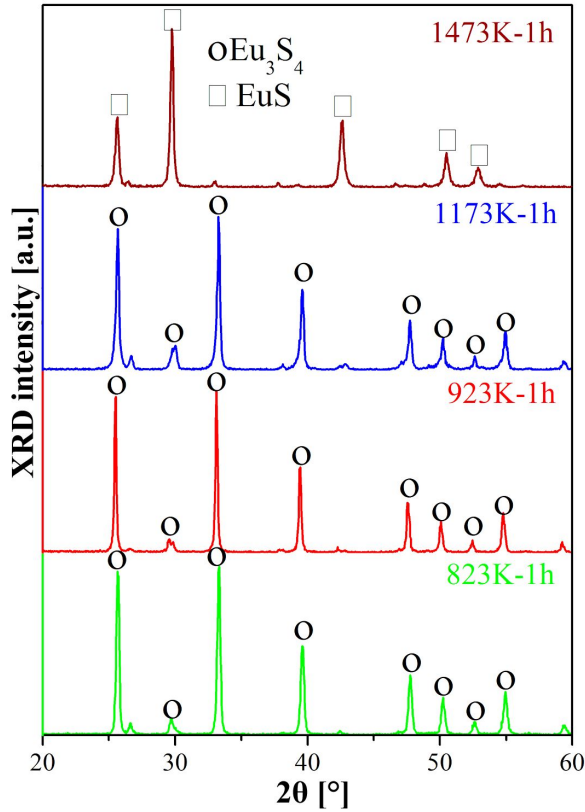


Fig. 7. XRD patterns of sintering products from Eu_3S_4 obtained by SPS.

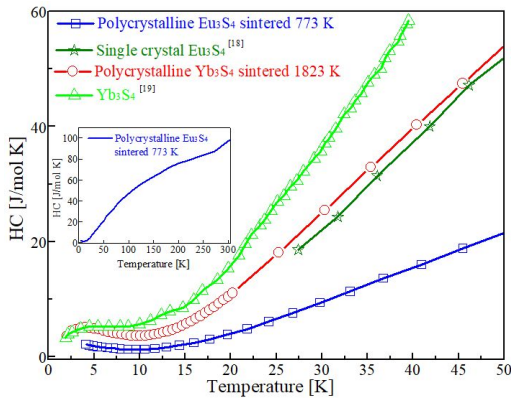


Fig. 8. Specific heat of Eu_3S_4 as a function of temperature.

at the Curie temperature of EuS ($T_c = 16$ K), indicating that no $\text{Eu}_2\text{O}_2\text{S}$ or EuS does exist as an impurity phase. The experimental inverse magnetic susceptibilities curve seems to contain two linear segments with different slopes above

and below 100 K. Both parts can be described by the Curie-Weiss law, $1/\chi = (T - \theta)/C$, where, above 100 K, $C_1 = 11.11$, $\theta_1 = 3.1$ and below 100 K, $C_2 = 7.94$, $\theta_2 = -28.9$. These values are in good agreement with those obtained by Davis et al. [14] and Massenet et al. [6], but the mentioned authors prepared Eu_3S_4 from a mixture of EuS and sulfur sealed in an evacuated quartz tube and fired at 600 °C for 3 days or pressing and sintering in evacuated quartz capsules at 800 °C for 72 h. Compared with the former studies, single phase Eu_3S_4 can be obtained by CS_2 -gas sulfurization of Eu_2O_3 nanospheres at 773 K.

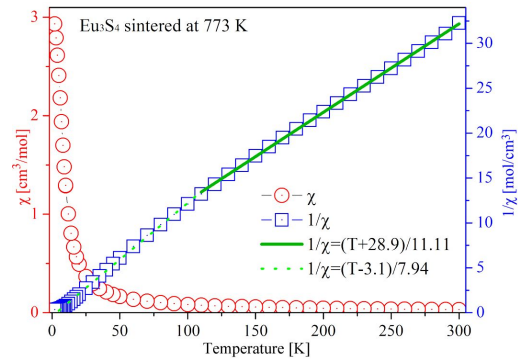


Fig. 9. Magnetic susceptibility of Eu_3S_4 as a function of temperature.

The magnetization versus H measured at 2 K was plotted in Fig. 10. In the high field limit, the magnetization tends to 55 emu/g, which is in a very good agreement with the experimental value of single crystal Eu_3S_4 . Compared with the single crystal Eu_3S_4 , polycrystalline Eu_3S_4 orders with a saturation magnetization of 55 $\text{emu} \cdot \text{g}^{-1}$ which is in excellent agreement with the value of 67 $\text{emu} \cdot \text{g}^{-1}$ predicted if only 1/3 of Eu^{2+} ($J = 7/2$) carry a moment. Similar to Sm_3S_4 [20], magnetic susceptibility of Eu_3S_4 can be interpreted by the combination of a Curie-Weiss component from Eu^{2+} and van Vleck component from Eu^{3+} above the ferromagnetic ordering temperature [6, 21].

4. Conclusions

In the evaluation of the effect of heat treatment on the phase transformation from Eu_3S_4 to EuS

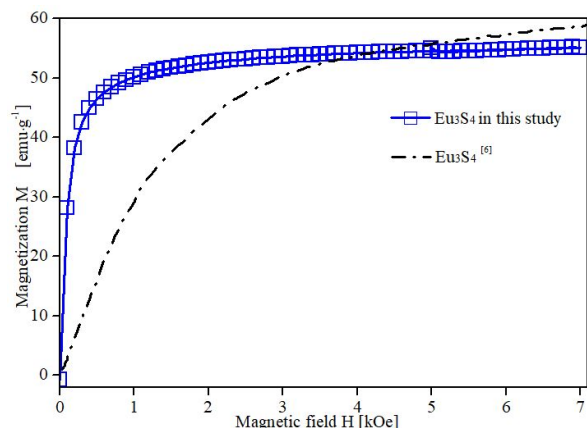


Fig. 10. Magnetization versus magnetic field H at 2 K.

at a fixed heat treatment time of 1 h, it was found that heat treatment at 873 K or higher in a vacuum atmosphere, yields single-phase EuS. Eu_3S_4 transformed to EuS above 1173 K during spark plasma sintering. Specific heat of polycrystalline Eu_3S_4 is similar to mixed-valence compound Yb_3S_4 and its saturation magnetization is $55 \text{ emu}\cdot\text{g}^{-1}$. The magnetic susceptibility of polycrystalline Eu_3S_4 is consistent with the Curie-Weiss law.

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