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Magnetic and ^{151}Eu Mössbauer spectroscopic studies on rare earth bismuth sulfides, $EuLnBiS_4$ (Ln = Eu, Gd)

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ABSTRACT

Ternary and quaternary rare earth bismuth sulfides $EuLnBiS_4$ (Ln = Eu, Gd) have been investigated by X-ray diffraction, ^{151}Eu Mössbauer spectroscopy, and magnetic susceptibility measurements. Both compounds have the orthorhombic $CaFe_2O_4$-type structure with space group *Pnma*. In Eu_2BiS_4, Eu^{2+} and Eu^{3+} ions occupy two crystallographically independent sites. The ^{151}Eu Mössbauer spectra for Eu_2BiS_4 indicate that the Eu^{2+} and Eu^{3+} ions exist in the molar ratio of 1:1, and the Debye temperatures of Eu^{2+} and Eu^{3+} are 175 and 230 K, respectively. Magnetic susceptibility measurements for Eu_2BiS_4 and $EuGdBiS_4$ reveal that an antiferromagnetic transition occurs at 2.8 and 6.5 K, respectively.

1. Introduction

It is well known that mixed-valence europium sulfides show an interesting electronic and magnetic behavior. For example, Eu_3S_4 has the Verwey transition at 186 K [1] and the ferromagnetic transition at 3.1 K [2]. $EuPd_3S_4$ shows an electron hopping between Eu^{2+} and Eu^{3+}, and has the antiferromagnetic transition at 3 K [3]. Similar electron hopping between Eu^{2+} and Eu^{3+} has been observed in $Eu_5Zr_3S_{12}$ [4], $Na_{1.515}EuGeS_4$ [5], and $(EuS)_{1.173}NbS_2$ [6]. $Eu_5Sn_3S_{12}$ is metamagnetic and has two field-dependent antiferromagnetic phases at low temperatures [7–9].

In these compounds, the europium ions have two oxidation states. In general, the divalent state of Eu is stable in sulfides, but some compounds contain trivalent europium. Flahaut noted that they are classified into two types [10]. In the case of compounds containing only Eu^{3+} ions, there is necessarily a strongly electronegative anion, or a second weakly electronegative cation. For compounds containing both Eu^{2+} and Eu^{3+}, such as Eu_3S_4 and $EuPd_3S_4$, ^{151}Eu Mössbauer spectroscopic measurements were performed to investigate the mixed-valence state of Eu [3,11]. These compounds show the occurrence of the electron transfer and/or the electron hopping between Eu^{2+} and Eu^{3+}, which may stabilize the Eu^{3+} ions.

Ternary europium bismuth sulfide Eu_2BiS_4 has been reported to crystallize in the orthorhombic $CaFe_2O_4$-type structure with space group *Pnma* [12]. The schematic structure of Eu_2BiS_4 is illustrated in Fig. 1. This compound has the formal oxidation state of $Eu^{2+}Eu^{3+}Bi^{3+}S^{2-}{}_4$, and the Eu^{2+} and Eu^{3+} ions occupy crystallographically different sites. The situation for Eu_2BiS_4 is different from the case of the above-mentioned sulfides and is similar to that for Eu_2CuS_3 [13], i.e., Eu_2BiS_4 has two crystallographically distinguishable sites for Eu^{2+} and Eu^{3+} ions. However, none of the studies on the electronic and magnetic properties for this mixed valence compound has been carried out.

In this study, two polycrystalline samples of $EuLnBiS_4$ (Ln = Eu, Gd) were prepared. Their magnetic susceptibilities were measured in the temperature range from 1.8 to 300 K and ^{151}Eu Mössbauer spectrum measurements were performed from 20 to 300 K.

2. Experimental

2.1. Sample preparation

Two europium bismuth sulfides, Eu_2BiS_4 and $EuGdBiS_4$, were prepared by the solid-state reaction. As starting materials, rare earth sesquioxides (Eu_2O_3, Gd_2O_3), powder sulfur (S), and powered Bi metals were used. Europium monosulfide EuS was prepared by heating europium sesquioxide (Eu_2O_3) on a graphite boat at 1073 K for 10 h in a flowing gaseous CS_2 by bubbling the nitrogen gas through liquid CS_2. Eu_3S_4 was prepared by heating stoichiometric mixtures of EuS and S powders in a quartz ampoule at 1073 K for 24 h. Gadolinium sesquisulfide (Gd_2S_3) was obtained by heating Gd_2O_3 in a flowing atmosphere of CS_2 gas at 1473 K for 2 h. Bismuth sesquisulfide (Bi_2S_3) was prepared by heating stoichiometric amounts of Bi and S powders at 823 K for 6 h. Then, stoichiometric mixtures of Eu_3S_4, Gd_2S_3, and Bi_2S_3 were intimately ground and pressed into pellets. They were heated in a quartz ampoule at 1223 K for 12 h.

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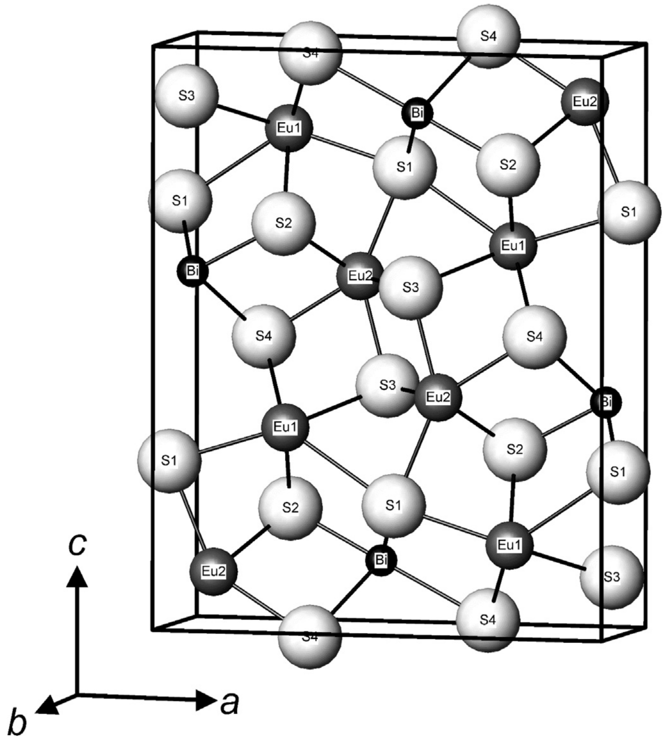

Fig. 1. Crystal structure of Eu_2BiS_4.

2.2. *Powder X-ray diffraction*

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with Cu-Kα radiation equipped with a curved graphite monochromator. The data were collected by step-scanning in the angle range of $10° \leq 2\theta \leq 120°$ at a 2θ step-size of 0.02°. The X-ray diffraction data were analyzed by the Rietveld technique, using the program RIETAN-FP [14] and the crystal structure was drawn by VESTA program [15].

2.3. *^{151}Eu Mössbauer spectra*

The ^{151}Eu Mössbauer spectra were measured in the temperature range between 20 and 300 K with a Mössbauer spectrometer VT-6000 (Laboratory Equipment Co.) in the constant acceleration mode using a radiation source $^{151}SmF_3$ (1.85 GBq). The spectrometer was calibrated with a spectrum of α-Fe at room temperature. The γ-rays were detected with a NaI scintillation counter. Europium trifluoride (EuF_3) was used as a reference standard for the chemical isomer shift. The sample was wrapped in an aluminum foil so as to have its average surface density of 10 mg (Eu) cm^{-2}.

2.4. *Magnetic susceptibility*

The temperature-dependence of the magnetic susceptibility was measured in an applied field of 0.1 T over the temperature range of 1.8 K ≤ T ≤ 400 K, using a SQUID magnetometer (Quantum Design, MPMS5S). The susceptibility measurements were performed under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. The former was measured upon heating the sample to 400 K under the applied magnetic field of 0.1 T after zero-field cooling to 1.8 K. The latter was measured upon cooling the sample from 400 to 1.8 K in the applied field of 0.1 T.

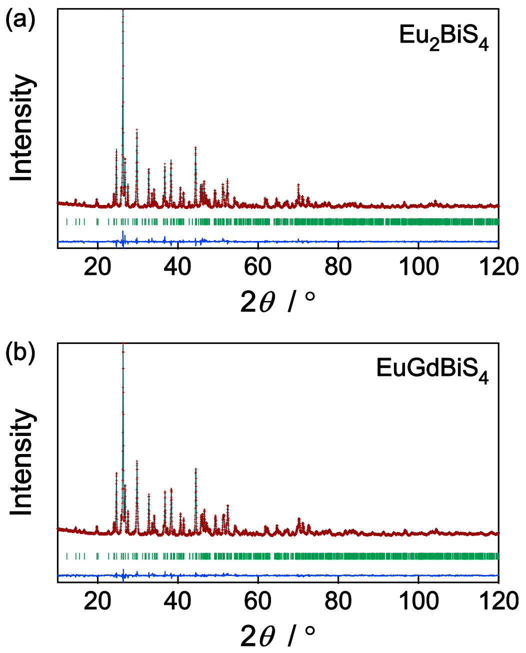

Fig. 2. Powder x-ray diffraction patterns and Rietveld refinements for (a) Eu_2BiS_4 and (b) $EuGdBiS_4$. The bottom trace is a plot of the difference between observed + (cross makers) and calculated (solid line) intensities. All allowed Bragg reflections are shown by vertical lines.

3. Results and discussion

3.1. *Structures of Eu_2BiS_4 and $EuGdBiS_4$*

Both the Eu_2BiS_4 and $EuGdBiS_4$ compounds were obtained as a single phase. The X-ray diffraction profiles were indexed on an orthorhombic cell with the space group *Pnma*, and their crystallographic parameters were refined by the RIETAN-FP program. Fig. 2(a) and (b) show the X-ray diffraction profiles of Eu_2BiS_4 and $EuGdBiS_4$, respectively. The calculated profiles are in good agreements with the observed ones (Eu_2BiS_4: $R_{wp} = 8.49\%$, $R_I = 2.08\%$; $EuGdBiS_4$: $R_{wp} = 7.13\%$, $R_I = 1.84\%$). The refined lattice parameters and positional parameters for Eu_2BiS_4 and $EuGdBiS_4$ are listed in Table 1. From the X-ray diffraction profile for $EuGdBiS_4$, the crystallographic site of Gd^{3+} cannot be distinguished from that of Eu^{2+} because these ions have the same number of electrons. However, on the assumption that the divalent Eu and trivalent Gd sites in the $EuGdBiS_4$ correspond to the the Eu(1) and Eu(2) sites in the Eu_2BiS_4, respectively, the positional parameters for $EuGdBiS_4$ should be well refined, as will be discussed later. Some selected interatomic distances for Eu_2BiS_4 and $EuGdBiS_4$ are listed in Table 2.

Fig. 3(a) and (b) illustrate the polyhedral representation of the Eu_2BiS_4 structure. The Eu ions occupy two crystallographically independent sites. The Eu(1) and Eu(2) ions are coordinated by eight and seven sulfide ions, respectively. The $Eu(1)S_8$ and $Eu(2)S_7$ polyhedra are connected to each other by face sharing as shown in Fig. 3(a). The Bi ions are coordinated by six sulfide ions and the BiS_6 octahedra share edges, forming double chains along the *b*-axis as shown in Fig. 3(b).

The valences of the cations are calculated by the bond valence sum (V_i) [16]:

$$v_{ij} = \exp\left(\frac{R_0 - d_{ij}}{b}\right), \tag{1}$$

$$V_i = \sum_j v_{ij}, \tag{2}$$

where R_0 and b are known as the bond valence parameters of various cations and a constant value (0.37 Å), respectively, and d_{ij} means the