Electrical resistivity, optical and magnetic properties of the layered oxyselenide SmCuOSe

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Abstract

The electrical and magnetic properties of the tetragonal phase SmCuOSe are reported as a function of the temperature. The optical properties were studied by means of diffuse reflectance spectrum in the UV–Vis range. The electrical resistivity measurements as well as diffuse reflectance spectrum show that SmCuOSe is a semiconductor with an optical band gap (E_g) of 2.6 eV. In this phase, Cu is at its monovalent oxidation state and, as such, it does not contribute to the total magnetic moment, whereas Sm is in its 3+ oxidation state, with a large VanVleck contribution due to the admixture of the fundamental state with higher energy levels.
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1. Introduction

Quaternary-layered oxychalcogenides of the general formula $LnCuOQ$ (Ln = lanthanides and Q = S, Se) are known to exhibit interesting structures and physical properties [1–4].

The structure of these phases is built up of $[Ln_2O_2]$ fluorite-like layers normal to the c-axis alternating with $[Cu_2Q_2]$ layers formed by slightly distorted CuQ_4 tetrahedra that shared Q–Q edges. Oxygen and chalcogen atoms have never been found simultaneously on the same crystallographic position, so there is a type of anionic segregation in these compounds. The coordination polyhedra of Ln and Q atoms in the structure are distorted squared antiprism with four O atoms in one base and four Q atoms in another base for each Ln atom, and with four Cu atoms in one base, and four Ln atoms in another base for the chalcogenide [5].

On the other hand, the layered oxychalcogenides $LnCuOQ$ are wide gap semiconductors and exhibit efficient blue photoluminescence. These features make these materials very promising candidates for the active or contact layers of blue or UV LEDs [6–9].

In the present paper, we have undertaken an investigation of the electrical and magnetic properties, as well as the optical band gap determination for the tetragonal phase SmCuOSe. Zhu et al. [5] already described this compound in 1994; however, there is no information about its physical and optical properties.

2. Experimental

2.1. Synthesis

Polycrystalline SmCuOSe was prepared from a thoroughly ground mixture of Sm (Aldrich, 99.9% pure), CuO (Alfa, 99.9 pure) and Se (99.5% pure) in a molar ratio of 1:1:1. The starting materials were loaded

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in a glove box into a quartz ampoule subsequently sealed under vacuum (10^{-4} Pa). The ampoule was heated at 1123 K for a period of 10 days and then cooled to room temperature at 10 K/h. Inspection of the product showed a homogeneous powder of dark green color.

To check phase purity, powder X-ray diffraction data were collected with a Siemens D-5000 diffractometer fitted with a graphite monochromator, using Cu$K\alpha$ radiation ($\lambda = 154.057$ pm). α-quartz was used as internal standard. For qualitative comparison of the experimental powder pattern, theoretical patterns were calculated from structural data using the program Lazy-Pulverix [10].

2.2. Resistivity measurements

The electrical resistivity measurements of the sample have been performed on a pellet of 3 mm diameter pressed at about 5 kbar, using the standard four-probe van der Pauw method [11]. Electrical contacts were made by soldering a gold wire to the pellet with pure indium metal.

2.3. Optical properties

The diffuse reflectance UV–Vis spectrum was recorded using a Perkin–Elmer lambda 20 UV–Vis spectrophotometer equipped with a Labsphere RSA-PE-20 diffuse reflectance accessory. Magnesium oxide was used as reference and the spectrum was recorded in the range of 1.0 and 6.0 eV at room temperature. Reflectance measurement was converted to absorption spectra using the Kubelka–Munk function $F(R_\infty)$.

2.4. Magnetic measurements

The magnetic measurements were performed on a SHE-VTS-906 SQUID magnetometer, at static fields of 1 and 5 kœ, and with increasing temperatures from 5 K up to 300 K. Under these experimental conditions, no difference was detected on the susceptibility values described below with respect to the applied field. The powdered sample was contained in a gelatin capsule. Considering the small amount of sample being used (ca. 40 mg), the sample holder contribution amounted to about 15% of the total signal at room temperature, and it was then subtracted at each temperature point.

3. Results and discussion

A description of the crystal structure of LnCuOQ (Ln = Lanthanides and Q = S, Se) can be found in literature and it is briefly recalled here [5,12]. SmCuOSe crystallizes in the tetragonal system with space group
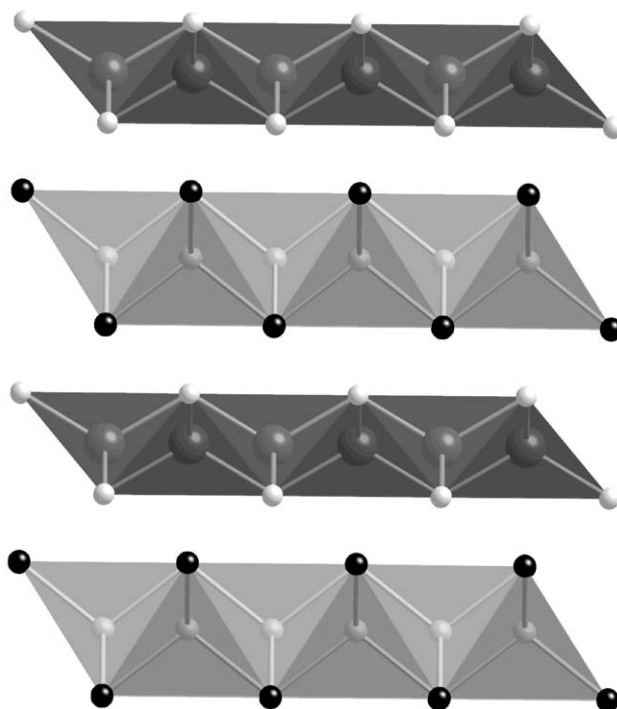

Fig. 1. Polyhedral representation of SmCuOSe along [100]. Black tetrahedra represent the coordination sphere of the [Sm_2O_2] layers, and gray tetrahedra represent the antifluorite-type block [Cu_2Se_2]; the dark spheres represent S atoms.

$P4/nmm$ (No. 129). As shown in Fig. 1, SmCuOSe has a layered structure composed of antifluorite-type block [Cu_2Se_2] where Cu is tetrahedrally coordinated by Se and the fluorite-type block [Sm_2O_2] extended in the plane 0 0 1, forming two different layers piled along the [001] direction [5]. The CuSe layers are formed with edge-sharing sulfur tetrahedral by covalent Cu–Se bonds [13]. The Sm–O layers are composed of ionic Sm–O bonds [3]. The structure is closely related with the well-known ThCr$_2$Si$_2$-type layer structure because the blocks [Sm_2O_2] replace the thorium atoms and the [Cr_2Si_2] sheets are replaced by the layers [Cu_2Se_2] [14].

The resistivity curve ($\rho = f(T)$) illustrated in Fig. 2 for SmCuOSe in the temperature range 77–293 K is typical for semiconducting materials, though it is not possible to estimate the activation energy. The electrical resistivity at 290 K for the title compound is 32 Ω cm and increases to 814 Ω cm at 79 K. This behavior, besides the usual electron counting rules, leading to formal d^{10} Cu centers, are consistent with the semiconductor character of the sample. The curve obtained in this work is quite similar to that given by Takase et al. [3] for LaOCuS.

In order to gain primal information about the nature of the electronic structure of SmCuOSe, its UV–Vis diffuse reflectance spectrum was analyzed. The spectrum plotted after a Kubelka–Munk transformation is given in Fig. 3. The optical band gap (E_g) corresponds to the
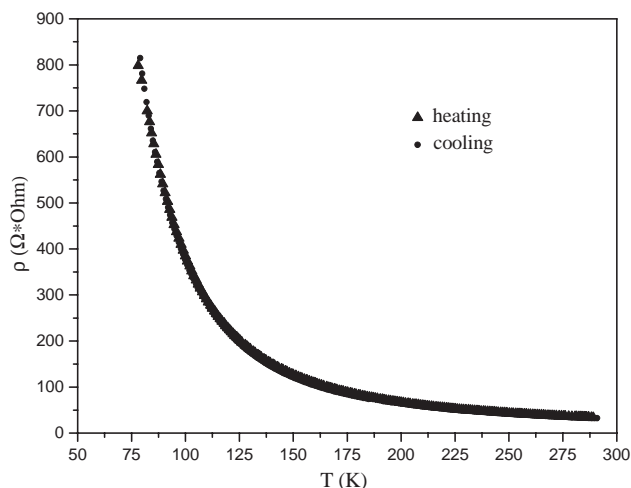
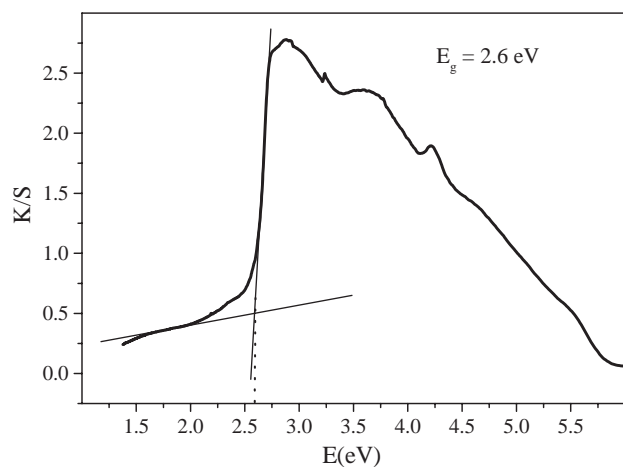Fig. 2. Temperature dependences of electrical resistivity of SmCuOSe.

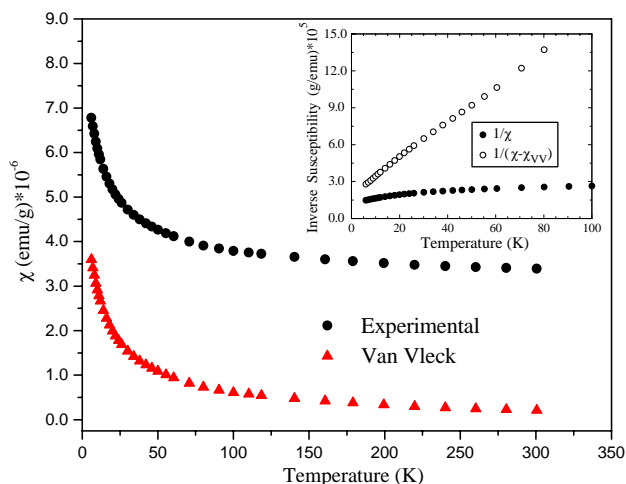Fig. 3. Diffuse reflectance spectrum of SmCuOSe after a Kubelka–Munk transformation ($T = 298$ K).

Fig. 4. Magnetic susceptibility of SmCuSeO measured under 5 kœ. Curve (a) represents the experimental results; curve (b) was obtained after subtraction of the VanVleck term ($\chi_{VV} = 3.18 \times 10^{-6}$ emu/g). Insert: Inverse magnetic susceptibility at low temperatures. The tangent to curve (a), fitted between 5 and 12 K, gives a magnetic moment of $0.79 \pm 0.07 \mu_B$. A linear fit to curve (b), between 5 and 100 K, gives a magnetic moment of $0.41 \pm 0.02 \mu_B$ ($\mu_{Sm^{3+}} = 0.85 \mu_B$) (see text).

intersection point between the base line along the energy axis and the extrapolated line from the linear portion of the threshold. Thus E_g can be assessed to be 2.6 eV a typical value for semiconducting materials. Typical Ln^{3+} absorption spectrum with f–f transition was observed. This absorption proves that the $4f$ electrons are strongly localized and do not affect optical properties such as energy gaps [15].

These results compared with previous works published by Takase et al. [3] and Ueda et al. [15] suggest that SmCuOSe shows wide-gap p-type semiconductive properties.

Fig. 4 shows the thermal dependence of the experimental magnetic susceptibility (curve a), and the one obtained after subtraction of a paramagnetic term (χ_{VV}) due to the admixture between the $^6H_{5/2}$ and the $^6H_{7/2}$ multiplets of the Sm^{3+} ion. This temperature-independent term, known as the VanVleck contribution [16] was

estimated from an $\chi \cdot T$-versus-T diagram in the region [$100\,K \leqslant T \leqslant 300\,K$], to be about 3.18×10^{-6} emu/g $= 982 \times 10^{-6}$ emu/mol (for $H_{app} = 5$ kœ), and then subtracted from the experimental results (Fig. 4). Under a 1 kœ external field, the VanVleck term was estimated to $\chi_{VV} = 1038 \times 10^{-6}$ emu/mol.

Due to the large VanVleck contribution to the total susceptibility, it becomes difficult to evaluate the magnetic moment over the whole range of temperature. The inset of Fig. 4 shows a diagram $(\chi_{exp} - \chi_{VV})^{-1}$-versus-$T$, in which the VanVleck term was subtracted from the experimental values. The Curie–Weiss law thus obtained yields a magnetic moment close to $0.41 \mu_B$. An alternative way to evaluate the magnetic moment is to use the experimental data at very low temperatures, since the $^6H_{5/2}$ level is then situated far from the higher energy states. From the slope of the inverse susceptibility at very low temperatures, it is then possible to give a rough estimation of the magnetic moment as shown also in the insert of Fig. 4. Such estimation gives a magnetic moment of about $0.79 \pm 0.07 \mu_B$ ($0.82 \pm 0.1 \mu_B$, for $H_{app} = 1$ kœ), which corresponds quite reasonably to the expected moment for an independent Sm^{3+} ion ($\mu^{theo} = g\sqrt{J(J+1)} = 0.85 \mu_B$; $g = \frac{2}{7}$). Since the Van Vleck contribution is quite large compared to the experimental values (ca. 93% of the value at room temperature), we do not expect to obtain a good reproducibility of the effective moment evaluated from both methods. However, since the Sm^{2+} free ion ($^7F_0$ state) has a null magnetic moment (g and J are both equal to zero), it becomes quite obvious that the experimental moment corresponds to the contribution

of the samarium ion in its $3+$ oxidation state, presenting in addition, a large VanVleck contribution due to the admixture of the fundamental state with higher energy levels. Cu is in its monovalent oxidation state and, as such, it does not contribute to the total magnetic moment.

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