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Optical property and band structure of layered sulfide $La_{1-x}Y_xCuS_2$

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Abstract

The system $La_{1-x}Y_xCuS_2$ has been prepared by a stoichiometric solid-state reaction of La_2S_3, Y_2S_3, Cu, and S at 1223 K. $La_{1-x}Y_xCuS_2$ in the range of x from 0 to 0.25 crystallizes in the $LaCuS_2$ structure type, which is a layered structure. The optical band gap for $La_{1-x}Y_xCuS_2$ changes slightly between 2.23 eV and 2.26 eV, deduced from their absorption spectra. From a band structure calculation, the optical transitions for $La_{1-x}Y_xCuS_2$ mainly arise from the valence orbits of Cu and S atoms.

Keywords: B. Optical property; Sulfide; Solid state reaction

1. Introduction

Layered lanthanide copper oxides have been numerously studied [1–4], since the high temperature superconductivity was discovered in 1986. The unusual electrical transport properties were ascribed to the layer structure and the copper atoms [1]. In contrast to the oxides, lanthanide copper chalcogenides have received little attention and no systematic study is available in the literatures. Based on this, researchers have extended their interest to explore new chalcogenides including the compound synthesis and crystal structure determining, such as $LaCuS_2$ [5], $YCuS_2$ [6], $NdCuS_2$ [7], and $TbCuS_2$ [8]. With respect to the physical property characterization, however, little result was reported yet. Taking $LaCuS_2$ for an example, no optical or electrical property investigations have been performed besides its derivative LaCuOS [9,10], since the compound has been synthesized.

In this paper, the layered compound $LaCuS_2$ is used as a template structure, Y atoms substitute some La atoms in $LaCuS_2$. Because $YCuS_2$ has a different structure type from $LaCuS_2$, the structure of $La_{1-x}Y_xCuS_2$ is expected to change from the $LaCuS_2$-like to the $YCuS_2$-like when x increases from 0 to 1. In order to understand the substitution effect for $La_{1-x}Y_xCuS_2$, the optical band gap is chosen as the index, and $La_{1-x}Y_xCuS_2$ is studied within a $LaCuS_2$-like structure.

2. Experimental

The following reagents were used as obtained: Cu (Sinoreagent, 99.999%) and S (Sinoreagent, 99.999%). La_2S_3 and Y_2S_3 employed in the synthesis were prepared by the reactions of the stoichiometric elements. Each sample $La_{1-x}Y_xCuS_2$ was prepared by a stoichiometric solid-state reaction of La_2S_3, Y_2S_3, Cu, and S. A reaction mixture was loaded into a fused silica tube under an argon atmosphere in a glove box. This tube was sealed under a 10^{-2} Pa atmosphere and then placed in a computer-controlled furnace. The sample was heated to 1223 K at 1 K/min, kept at that temperature for 3 days, then the furnace was turned off and cooled to ambient temperature.

The powder X-ray diffraction measurements were carried out with a Rigaku D/max 2550V diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) monochromatized with graphite. The X-ray reflection was measured from $2\theta = 10^\circ$ to 80° by continuous scanning with an interval of 0.02°. A Shimadzu UV-3101 UV–vis–NIR scanning spectrophotometer with a diffuse reflectance accessory was used to measure the diffuse reflectance spectra of the compounds over the wavelength range from 400 nm to 800 nm at 293 K.

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The electronic structures of $LaCuS_2$ and $YCuS_2$ were performed with the use of the tight-binding (TB) linear muffin-tin orbital (LMTO) method in the atomic sphere approximation, including the combining correction [11,12]. In the calculations on $LaCuS_2$, the La atoms were replaced by Y atoms because of program limitation.

3. Result and discussion

The crystal structure of $LaCuS_2$ has already been reported by X-ray diffraction on a single crystal [5]. $LaCuS_2$ crystallizes in monoclinic system (space group $P2_1/c$). It can be considered as a layered structure, consisting of the ${}^{2}_{\infty}[\mathrm{LaS}]$ layers and the ${}^{2}_{\infty}[\mathrm{CuS}]$ tetrahedral layers. Compared with $LaCuS_2$, $YCuS_2$ crystallizes in orthorhombic system (space group *Pnma*). The structure comprised one-dimensional chains ${}^{1}_{\infty}[\mathrm{CuS_2}]$ along [0 1 0] direction and a network ${}^{3}_{\infty}[\mathrm{YS_3}]$ by sharing vertices and edges [6]. The coordination numbers of rare-earth atoms are reduced from 7 in $LaCuS_2$ to 6 in $YCuS_2$. The average distances of Cu–S and Ln–S are 2.417 Å as well as 2.738 Å in $YCuS_2$ respectively, compared with 2.432 Å and 2.947 Å in $LaCuS_2$.

X-ray diffraction (XRD) patterns of the $La_{1-x}Y_xCuS_2$ samples from $x = 0$ to 0.25 as well as $La_{0.5}Y_{0.5}CuS_2$ are shown in Fig. 1. The trial and error search for each sample was made with the aid of the XRD software package of JADE 5. All reflection peaks of solid-solution $La_{1-x}Y_xCuS_2$ can be indexed on the pattern of $LaCuS_2$ up to $x = 0.25$. As dopant level x increases to 0.50, there is a tendency to have the impurity phase, which may be assigned to the orthorhombic $YCuS_2$ phase.

To determine the effect of Y dopant on the structure of $La_{1-x}Y_xCuS_2$, Rietveld refinements on lattice constants, using XRD patterns with silicon powder as an internal standard, were carried out. The refined lattice constants are listed in Table 1. As shown, all the lattice constants (a, b, and c) of $La_{1-x}Y_xCuS_2$ decrease with Y (x) increasing. The cell volume as a function of Y (x) is plotted in Fig. 2, which decreases linearly followed by a reduced volume of 5.5 Å^3 from $x = 0$ to 0.25. It might be considered that smaller ion (Y) substituting for larger one (La) will lead to contract accordingly. More details about phase transformation are still under investigation.

Table 1
Lattice constants refined by the least-squares method

Content (%)	a (Å)	b (Å)	c (Å)	γ (°)
$LaCuS_2$[a]	6.646(0)	6.938(2)	7.325(2)	98.73(2)
$LaCuS_2$	6.6360(1)	6.9309(9)	7.3236(9)	98.70(1)
$La_{0.95}Y_{0.05}CuS_2$	6.6319(5)	6.9303(6)	7.3197(7)	98.73(7)
$La_{0.85}Y_{0.15}CuS_2$	6.6265(3)	6.9216(5)	7.3053(4)	98.70(1)
$La_{0.75}Y_{0.25}CuS_2$	6.623(2)	6.899(3)	7.270(3)	98.77(5)

[a] Data as reported in ref. [5].

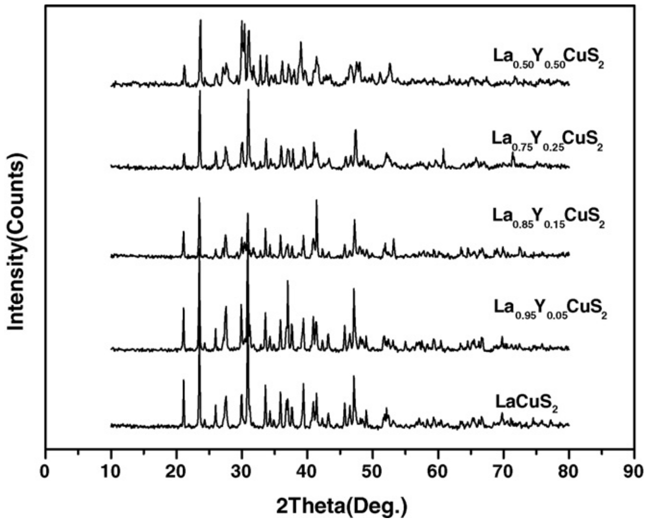

Fig. 1. X-ray diffraction patters for $La_{1-x}Y_xCuS_2$ $(0 \leq x \leq 0.25)$ and $La_{0.5}Y_{0.5}CuS_2$.

Optical properties of the compounds were then studied. The results with different Y levels ($x = 0$, 0.05, 0.15, and 0.25) are plotted in Fig. 3. All the absorption spectra have analogous shape and start to increase rapidly in the same region. It can be concluded that a fine gap-modulation arose with increasing Y (x). To distinguish the effect in gap-modulation, extrapolation lines of the spectra for energy band-gap (E_g) determining were plotted accordingly (not shown), and their E_g values are listed in the inset. Obviously, the band gap increases as Y (x) increases. The E_g values are also well consistent with the observed red-yellow color.

In order to explain the results stated above, we have calculated electronic structure of "$LaCuS_2$" and $YCuS_2$. The band structure of $LaCuS_2$ is closely similar to that of $YCuS_2$. Most of the contributions around the Fermi level are from the density of states (DOS) of Cu and S, as shown in Fig. 4, and the Y electrons contribute minimally. Note that electrons of different size lanthanides contribute little to DOS, and hence the band gap is mainly determined by the building-layer ${}^{2}_{\infty}[\mathrm{CuS}]$ of template structure of $LaCuS_2$. The analysis of DOS also shows the Cu 3d and S 3p orbits hybridize strongly near the Fermi level, and form a hybridized (Cu 3d)–(S 3p) band at the top of the valence band as most lanthanide copper sulfides [13]. A band gap of about 2.2 eV is calculated, well close to those deduced from the absorption spectra. These results could

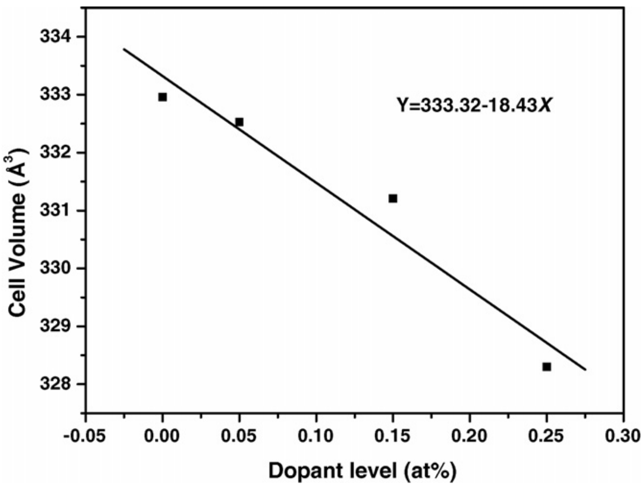

Fig. 2. Cell volume as a function of the content of Y (x).

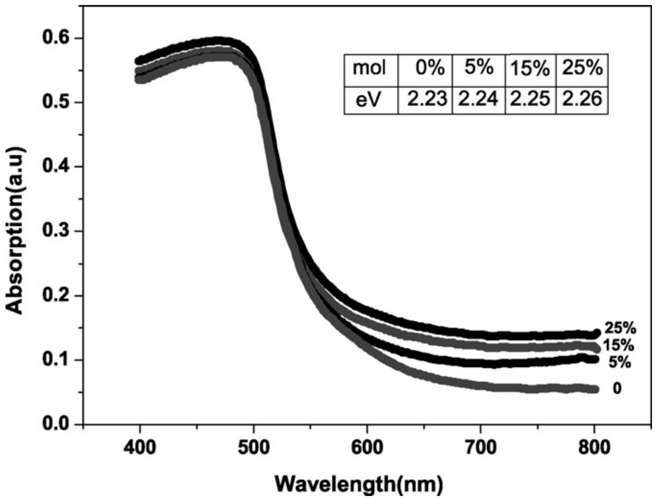

Fig. 3. Optical absorption spectra of $La_{1-x}Y_xCuS_2$ ($0 \leq x \leq 0.25$). The inset shows the band gap by extrapolation line accordingly.

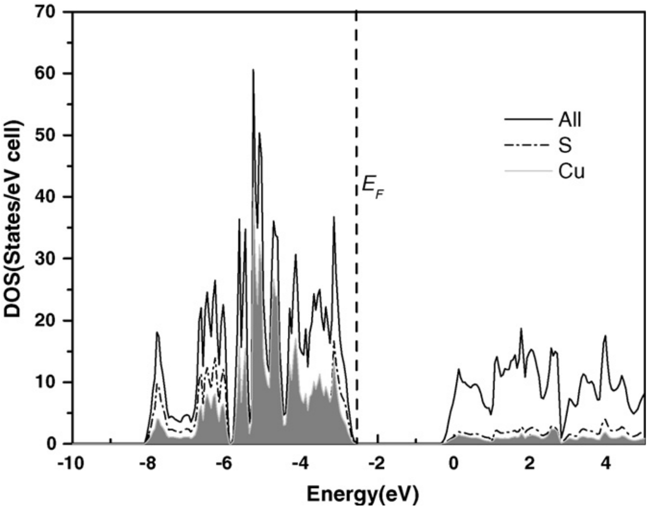

Fig. 4. Total density of state (DOS) and the partial DOS for S and Cu.

explain the reason, why $La_{1-x}Y_xCuS_2$ ($0 < x \leq 0.25$) shows similar optical property as $LaCuS_2$ but fine gap-modulation.

4. Conclusion

A single phase of a sulfide with $^{2}_{\infty}$[CuS] layers, $La_{1-x}Y_xCuS_2$ ($x \leq 0.25$), was successfully prepared to examine its optical property. The non-doped $LaCuS_2$ shows similar optical property as $La_{1-x}Y_xCuS_2$ on the whole, and the band gaps of $La_{1-x}Y_xCuS_2$ change from 2.23 eV ($x = 0$) to 2.26 eV ($x = 0.25$) over the selected solid-solutions, demonstrating a linear trend with different Y (x). $La_{1-x}Y_xCuS_2$ also shows a linear correlation between cell volume and different Y levels (x). Considering the fact in achieving fine gap-modulation, the $LaCuS_2$ type materials may present a good template for continuing study and exploitation as a candidate material for transparent p-type conductors.

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