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Preparation and characterization of γ-La_2S_3 nanoparticles from thermal decomposition

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Abstract: To synthesize pure γ-La_2S_3 at lower temperature, lanthanide complex $La(Et_2S_2CN)_3$·phen, containing La–S bond, was chosen as the precursors to decompose. The obtained samples were characterized by X-ray power diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) with an energy dispersive spectrometer and UV-Vis diffuse reflectance spectra. The decomposition mechanism of the lanthanide complex was studied by thermogravimetric analyses (TGA). The results show that the obtained samples are cubic phase particles with sizes among 20-50 nm and the band gap is 2.97 eV, which is bigger than that of its bulk crystal. TG/DTG results indicate that $La(Et_2S_2CN)_3$·phen decomposed to γ-La_2S_3 *via* $La_4(Et_2S_2CN)_3$ as an intermediate product.

Keywords: chalcogenides; nanoparticles; thermogravimetric analysis; decomposition; optical properties

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1. Introduction

Lanthanum sesquisulfide, having a wide transmission range (0.5-14 mm), possesses a superior combination of low thermal expansion coefficient, high melting point, and sufficient mechanical hardness, making it an attractive alternative for future IR window and dome materials [1-5]. Lanthanum sulfide has three different allotropic forms (α, β, and γ-La_2S_3) in the crystalline state. Although the high-temperature cubic phase γ-La_2S_3 is metastable at room temperature, it shows potential application as a far IR (8-14 mm) window material. So γ-La_2S_3 is focused on by many research groups in last several decades.

Usually, the synthesis routine for γ-La_2S_3 consists of reacting corresponding oxides, chlorides, nitrate and so on with H_2S or CS_2 at above 1000°C for several hours in the absence of oxygen and moisture, while in the presence of oxygen and moisture, β phase is mainly obtained [6-9]. Kumta and Risbud [6] synthesized oxysulfide precursors from metal alkoxides in a wet chemical route. The product crystallites prepared in a high-temperature reaction are usually in the degree of microns. A new approach is searched to prepare γ-La_2S_3 at a lower temperature. Lanthanum chalcogenolate complexes containing La–S bonds, which have been studied by many chemistry researchers [10-11], might provide a chance for precursors to prepare γ-La_2S_3.

In this paper, we presented the results about the preparation of γ-La_2S_3 nanoparticles by the thermal decomposition of lanthanide complex $La(Et_2S_2CN)_3$·phen at a lower temperature. The morphologies and optical properties of γ-La_2S_3 nanoparticles were studied.

2. Experimental procedures

All chemical reagents used in this paper except hydrochloric acid were of analytical grade. Hydrous lanthanum chloride was prepared by the reaction of lanthanum oxide (99.99%) and hydrochloric acid [10]. The as-prepared $LaCl_3·7H_2O$ was placed in vacuum desiccators until its mass was kept constant in several days.

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Lanthanide complex La(Et$_2$S$_2$CN)$_3$·phen was synthesized by the following chemical equation.

$$LaCl_3\cdot nH_2O+3NaEt_2S_2CN\cdot 3H_2O+phen\cdot H_2O= La(Et_2S_2CN)_3\cdot phen+3NaCl+(n+10)H_2O \quad (1)$$

Hydrous lanthanum chlorides, sodium diethyldithiocarbamate (NaEt$_2$S$_2$CN·3H$_2$O), and 1,10-phenanthroline (phen·H$_2$O) in the mole ratio of 1:3:1 were dissolved in a minimal amount of anhydrous ethanol, respectively, and then solutions of phen and NaEt$_2$dtc were mixed together. Subsequently, the lanthanum chloride alcoholic solution was titrated slowly into the mixture with stirring. The final yellow complex La(Et$_2$S$_2$CN)$_3$·phen was obtained after it was washed by anhydrous ethanol many times.

The La(Et$_2$S$_2$CN)$_3$·phen was weighed and placed on the surface of a quartz boat in a quartz tube, one of whose ends was sealed and the other was connected with a vacuum system. The crucible's temperature was maintained above 450°C, and the tube was under dynamic vacuum of 1.3 Pa. The other method was that 300 mL/min of high-purity Ar gas was introduced into the quartz tube, and then the tube was heated and maintained above 450°C. The products were washed for many times by carbon disulfides and anhydrous ethanol to expel the carbon and organic compound.

X-ray powder diffraction patterns were obtained using a Rigaku D/max-3C X-ray diffractometer equipped with Cu K$_\alpha$ radiation (λ=0.1548 nm). The accelerating voltage and current were 40 kV and 35 mA, respectively. The FE-SEM images of the products were obtained from a Supera 55 instrument. Energy-dispersed spectroscopy (EDS) characterizations were performed with Supera 55 instrument equipped with an EDS unit. The UV-Vis diffuse reflectance spectrum of the product was obtained from UV-3150. Thermogravimetric analyses (TGA) of the complex were performed on a HI-Res TGA2950 Thermogravimetric Analyzer at 5 K·min^{-1} in a 60 mL·min^{-1} high pure N$_2$ atmosphere.

3. Results and discussion

γ-La$_2$S$_3$ powders were prepared in two different atmospheres of vacuum and Ar, and their XRD patterns are shown in Fig. 1. It is found that both of the samples can be indexed as cubic phase (JCPDS 25-1041). The sample prepared in inert gas Ar atmospheres has more diffraction peaks including (220), (422), (521) than the sample prepared in vacuum condition. While all of the diffraction peaks of the sample prepared in vacuum condition are obviously broader than the peaks of the sample prepared in inert gas Ar atmospheres, indicating that the samples prepared in vacuum condition are smaller.

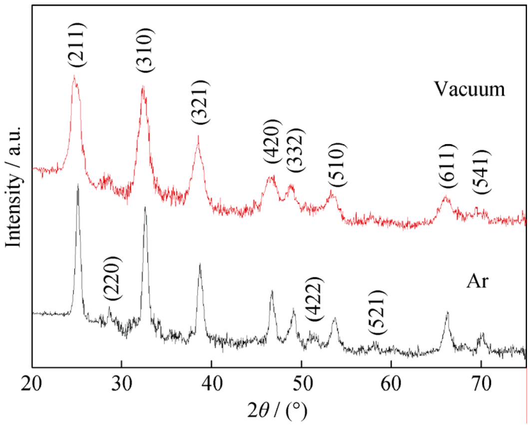

Fig. 1. XRD patterns of γ-La$_2$S$_3$ powders prepared in two different atmospheres.

Based on the above results, vacuum atmosphere was chosen as the better atmosphere condition to investigate the effect of decomposition temperature on the powder preparation. Fig. 2 shows the XRD patterns of the powders prepared by the thermal decomposition of the lanthanide complex at various temperatures. It is found that all of the diffraction patterns consist of pure γ-La$_2$S$_3$ during the whole decomposition temperature of 450-750°C. The sizes of the four samples prepared at various temperatures are calculated by Debby-Scherer's equation.

$$L=K\lambda/(B\cdot\cos\theta) \quad (2)$$

where L is the average size of crystal particles, K a constant taking a value of 0.89, λ the wavelength of X-ray, B the half width of the diffraction peak, and θ the corresponding incidence angle. The results show that the sizes of the four samples prepared at various temperatures are all in the range of 20-30 nm. At 650 and 750°C, the XRD results have similar patterns and more obvious diffraction peaks, which are different from the patterns of the samples prepared at lower temperatures. The results show that the samples have a better crystallization when they are prepared at above 650°C.

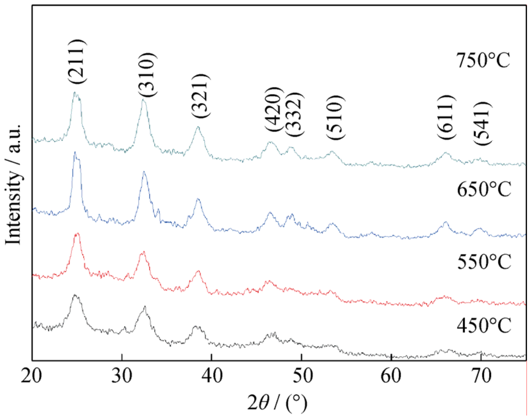

Fig. 2. XRD patterns of γ-La$_2$S$_3$ powders prepared at various temperatures.

The morphologies of nanoparticles prepared at various temperatures are shown in Fig. 3. It can be seen that the powders are roughly spherical and uniform and their sizes slightly increases with the temperature increase. Fig. 3 also shows that the powders have some extents of interconnected necks, which results from a higher activity of the nanoparticles than bulk materials. Another possible reason is that phen lost from the complex is liquid and increases the contact area of the particles before phen is vaporized.

The S/La ratios of the as-prepared samples are measured by the EDS spectrum, and they are shown in Fig. 4. The results shows that the samples have stoichiometric composition of S/La close to 1.5, and the S/La mole ratios of the samples slightly decrease with the increase of decomposition temperature. It might be explained by the serious sulfur loss with the increase of decomposition temperature. The sulfur saturated vapor pressure can be calculated by the following expression [12]. It can be seen that the sulfur saturated vapor pressure increases with the temperature increase.

$$\lg[p(\mathrm{S}_2)/\mathrm{atm}] = (6.31 \pm 0.15) - (12720 \pm 310)T^{-1} \tag{3}$$

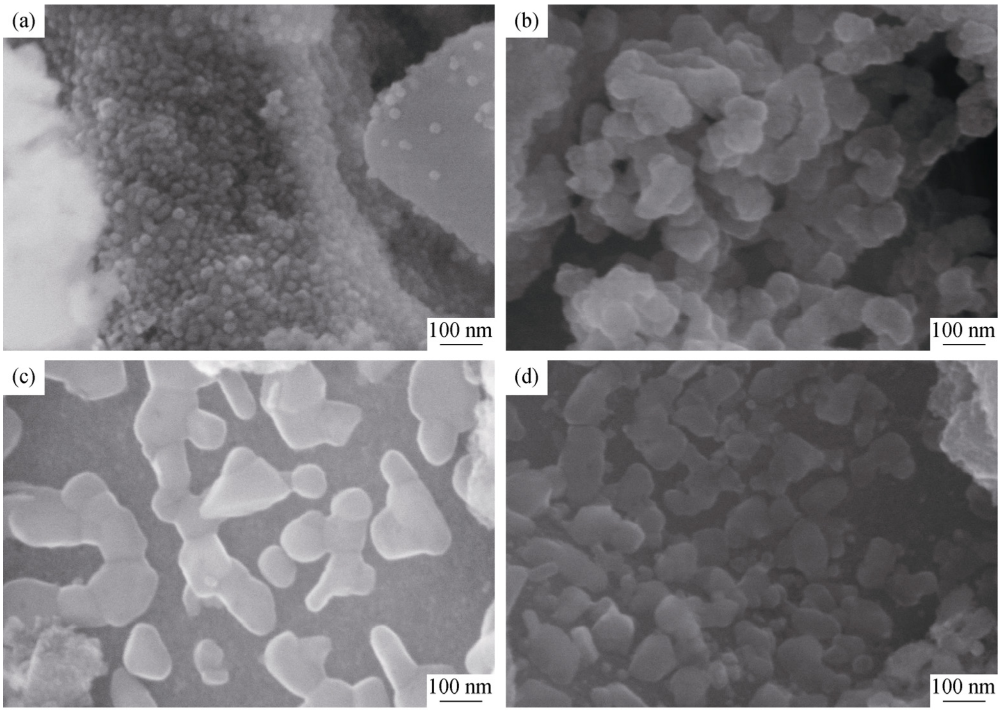

Fig. 3. FE-SEM micrographs of the samples prepared at various temperatures: (a) 450°C; (b) 550°C; (c) 650°C; (d) 750°C.

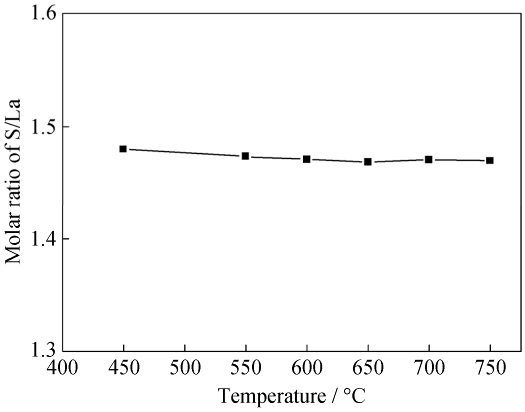

Fig. 4. Mole ratios of S/La at various temperatures.

The band gap of the sample can be measured by diffuse reflectance spectra. Fig. 5(a) displays the UV-Vis diffuse reflectance spectra of the as-prepared sample at room temperature. According to the Kubelka-Munk relationship expressed by Eq. (4), the value between the absorption coefficient (α) and the scattering coefficient (s) can be calculated by use of diffuse reflectance spectra (R_∞).

$$f(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{\alpha}{s} \tag{4}$$

where R_∞ is the absolute reflectance of the sample. In the meanwhile, its band gap can be expressed as the following equation for direct gap materials.

$$\alpha = s\frac{(h\upsilon - E_\mathrm{g})^{\frac{1}{2}}}{h\upsilon} \tag{5}$$

where E_g is the energy of the band gap, h the Planks constant, and υ the optical frequency. So the band gap E_g can

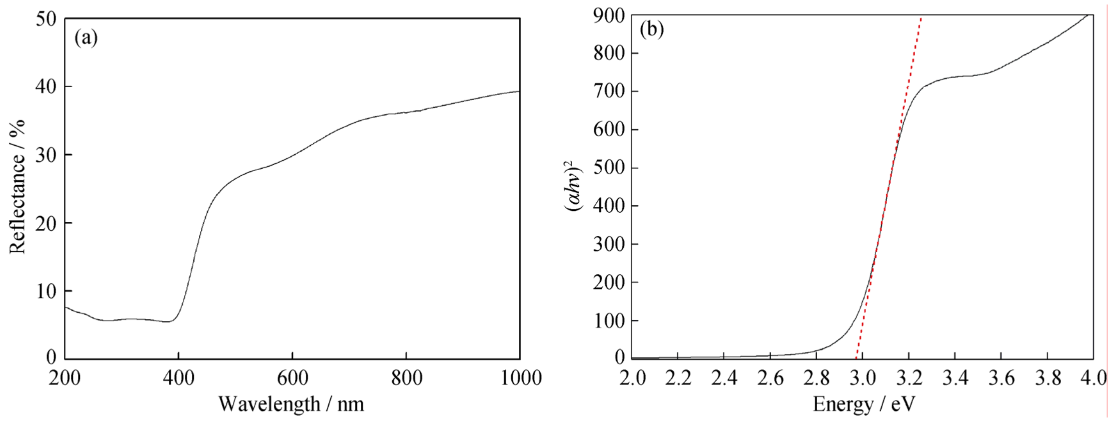

Fig. 5. Diffuse reflectance spectrum (a) of the as-prepared sample and its transformed spectrum (b).

be calculated from Fig. 5(b), which is plotted by Eqs. (4) and (5). The band gap of the as-prepared sample is estimated at 2.97 eV, which is blue shift comparing to the bulk crystal, such as 2.9 eV [13], 2.85 eV [14], and 2.8±0.25 eV [15] by optical gap. Such a phenomenon may be due to the pronounced quantum confinement effect of nanoparticles.

Thermal analyses were carried out for lanthanide complex $\mathrm{La(Et_2S_2CN)_3}$·phen to study the possible decompose mechanism of the γ-$\mathrm{La_2S_3}$ formation. The TG/DTG curves (Fig. 6(a)) show that the complex $\mathrm{La(Et_2S_2CN)_3}$·phen decomposes to $\mathrm{La_2S_3}$ at 200-445°C. The weight loss below 100°C is ascribed to the evaporation of the absorbed water. There are two main steps for the weight loss at 200-445°C in the TG, which are corresponding to the endothermic peaks in the DSC curve. So the decomposition of the complex $\mathrm{La(Et_2S_2CN)_3}$·phen might go through two processes to γ-$\mathrm{La_2S_3}$. The possible decomposition processes are listed in Table 1. First, the complex $\mathrm{La(Et_2S_2CN)_3}$·phen restructures and gradually expulses parts of the diethyldithiocarbamate groups after it lost the phen groups at 200-279.31°C. The residual weight decreases to 49.13%. Further, the intermediate is decomposed to be γ-$\mathrm{La_2S_3}$ and the weight of the final product is 40.4%. Carbon is deposited on γ-$\mathrm{La_2S_3}$ because of the decomposition of the organic groups.

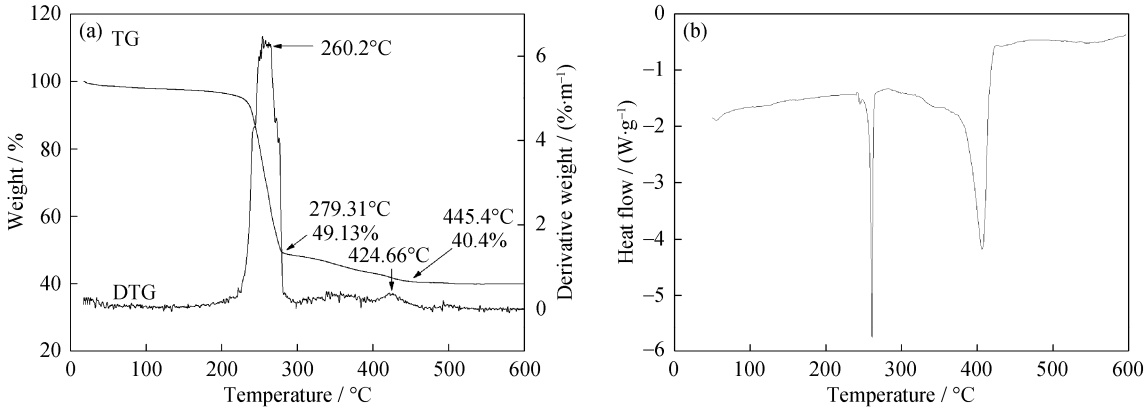

Fig. 6. TG-DTG (a) and DSC (b) curves of $\mathrm{La(Et_2S_2CN)_3}$·phen.

Table 1. Decomposition mechanism of $\mathrm{La(Et_2S_2CN)_3}$·phen

Step	Possible residues	Temperature / °C	Residual weight (calculated) / %
1	$\mathrm{0.25La_4(Et_2S_2CN)_3+10.5C}$	200-279.31	49.13 (49.50)
2	$\mathrm{0.5La_2S_3+10.5C}$	279.31-445	40.40 (40.97)

4. Conclusions

(1) γ-$\mathrm{La_2S_3}$ nanoparticles can be prepared in different atmospheres by means of a simple and convenient thermal decomposition route from single-source precursor $\mathrm{La(Et_2S_2CN)_3}$·phen at a relative lower temperature of 750°C or even below this.

(2) XRD and EDS studies indicate clearly that the precursors decompose completely to prepare pure γ-$\mathrm{La_2S_3}$ nanoparticles in a vacuum of 1.3 Pa. The γ-$\mathrm{La_2S_3}$ nanoparticles are thermally stable and do not result in phase transition from γ to β or α.

(3) TG/DTG results show that the lanthanide complex

$La(Et_2S_2CN)_3$·phen decomposes to γ-La_2S_3 by $La_4(Et_2S_2CN)_3$ as an intermediate product.

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