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Tunable transmission light in nanocrystalline $La_{1-x}Eu_xB_6$

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ABSTRACT

Cubic-shaped ternary $La_{1-x}Eu_xB_6$ nanopowders have been synthesized via a solid-state reaction and their optical properties are investigated for the first time. $La_{1-x}Eu_xB_6$ nanopowders have a high crystallinity with a grain size of 40 nm and HAADF–STEM images fully confirm that the Eu element has been successfully doped into the lattice of LaB_6. The optical absorption results indicate that the transmission light wavelength of LaB_6 shifts from 590 nm to 1070 nm with increasing Eu doping content, indicating a “redshift” phenomenon of transmission light. Thus, this novel tunable characteristic of $La_{1-x}Eu_xB_6$ transmission light will open a new way to extend the optical applications of LaB_6 nanopowder.

1. Introduction

Lanthanum hexaboride (LaB_6), known to be an excellent thermionic electron emitter, is characterized by low work function, high emission density and high brightness [1,2]. Recently much attention has been drawn to its another excellent optical property of strong light absorption in near infrared region (NIR) and transparency to visible light (VL), which is resulted from the free electron plasmon resonance [3]. Takeda et al. [4], Schelm et al. [5] and Yuan et al. [6] dispersed the LaB_6 nanopowder into the various polymer materials and obtained the composites with light transmittance around 580–600 nm and the light absorption at 950–1000 nm. This absorption characteristic is well satisfied the demand for reducing solar heat through the windows of automotive and buildings [7]. Theoretically, Xiao et al. [8] studied the optical properties of LaB_6 using first-principles calculations to explain the origins of coexistence of strong NIR absorption with high optical transparency. Based on the above mentioned studies, the optical properties of LaB_6 nanopowder have become a hot research topic [9].

However, up to now the optical properties and synthesis of ternary rare-earth hexaborides have been very rarely reported in the literatures. In addition, if the light transparency wavelength is tunable for LaB_6 nanopowder, it should have important effects for extending the optical applications such as improving the efficiency of organic photovoltaics replacing the expensive gold and silver nanoparticles [10]. On the other hand, the tunable light transparency wavelength should have a good usage of optical filters [11]. In this paper, the ternary $La_{1-x}Eu_xB_6$ nanopowder is synthesized by the solid-state reaction and its optical properties are investigated for the first time. Interestingly, it is found that the light transparency wavelength can be effectively redshift with increasing Eu doping content. Thus, the present approach will open a new way to extend the optical applications of LaB_6 nanopowder [10,11].

2. Experimental

The lanthanum oxide (99.99% purity), uranium oxide (99.99% purity) and sodium borohydride (99.0% purity) powders in a fixed molar ratio were mixed in an agate mortar. Then the mixtures were pressed into slice shape and placed in the resistance furnace at a reaction temperature of 1150 °C for 2 h. The entire reaction was carried out in a vacuum of 2×10^{-2} bar. The phase identification was examined by X-ray diffraction (Cu K_α radiation, Philips PW1830). The crystal morphology was characterized by field emission scanning electron microscopy (FESEM: Hitachi SU-8010). The microstructure and EDS analysis are characterized by transmission electron microscopy (TEM: FEI-Tecnai F20 S-Twin 200 kV).

3. Results and discussion

Fig. 1 shows the XRD patterns of $La_{1-x}Eu_xB_6$ nanopowder with different Eu doping contents. It can be seen that all diffraction patterns can be identified to a CaB_6-type single phase with space

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group *Pm*-3*m*, without any extra impurity peaks of La_2O_3, $LaBO_3$ and $NaBH_4$ in the patterns, confirming the purity of the synthesized products. The diffraction peaks are well indexed and assigned to the parallel crystal planes of (100), (110), (111), (210) and (211), which indicates that the Eu atoms randomly substitute the La atoms.

In order to further study the detailed microstructure of $La_{1-x}Eu_xB_6$ nanopowder, the TEM as an effective characterization method to be used to observe the grain morphology and crystallinity. Herein, as an example the $La_{0.6}Eu_{0.4}B_6$ nanopowder is analyzed in Fig. 2 with the HRTEM image. Fig. 2(a) fully confirms that the synthesized hexaborides have a cubic morphology with a mean size of 40 nm. The single-crystalline nature of $La_{0.6}Eu_{0.4}B_6$ crystal is demonstrated by the HRTEM presented in Fig. 2(b) and the lattice fringes $d=0.42$ nm and $d=0.29$ nm observed in this HRTEM image agree well with the (100) and (110) crystal planes, respectively, shown in Fig. 3(c).

Fig. 3 shows the HAADF–STEM image and its corresponding EDS analysis of $La_{0.6}Eu_{0.4}B_6$ nanopowder. The crystal morphology and crystal size observed under STEM model are in good agreement with the observation of TEM. The EDS analysis shown in Fig. 3(b) confirms the presence of La, Eu and B in the selected particles of the red frame of Fig. 3(a). In order to clarify whether the doping element Eu occupied in the crystal site of ternary $La_{0.6}Eu_{0.4}B_6$ crystal or formed as an individual EuB_6 crystal, we have completed an EDS mapping for a single crystal with grain size of 50 nm shown in right top of Fig. 3(a). It can be clearly seen that the La, Eu and B elements are uniformly distributed in this single crystal, which fully confirmed that the Eu element has been successfully doped into the lattice of LaB_6.

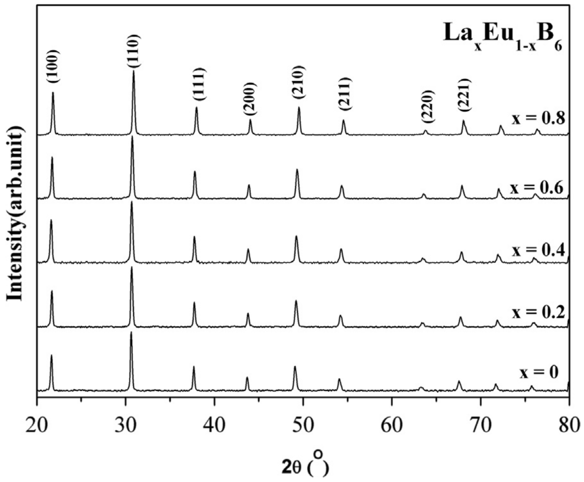

Fig. 1. XRD patterns of $La_{1-x}Eu_xB_6$ nanopowder obtained from the reaction at 1150 °C.

Fig. 4 shows the absorption spectrum for $La_{1-x}Eu_xB_6$ nanopowder measured by diffuse reflectance spectroscopy using an ultraviolet–visible–near infrared spectrometer. The interference peak at 860 nm marked by arrow is owing to the switching light source in the moment of measurement. It is notable from the absorption curve of LaB_6 nanopowder that an absorption valley is located at a wavelength of 590 nm; it is accurately in agreement with the previous experimental results of minimum reflectivity [12] and maximum transmission positions of LaB_6 [5,6]. Meanwhile, it is interestingly found that the wavelength of transmission light increases from 590 to 642 nm obviously when the Eu doping content increase to $x=0.2$, which means that the Eu doping leads to redshift of transmission light wavelength. Further increasing the doping content to $x=0.4$, 0.6 and 0.8, the wavelength of transmission light increases to 720, 821 and 1070 nm linearly. It is well known that when the incident light energy is close to the plasma frequency of nano-materials, the materials should exhibit weak reflectivity and absorption. As to the increasing trend of $La_{1-x}Eu_xB_6$ absorption valley, it is also considered as the plasma frequency moving toward lower band with increasing the Eu doping content. Sato et al. [13] have measured the plasma frequency of LaB_6 located at excitation energy of 2.0 eV, which is theoretically explained by Xiao et al. that the high optical transparency occurred at this plasmon frequency. According to the works of Kimura et al. [14], as to the number of conduction electrons of EuB_6 is much smaller than that of LaB_6, it reduces the plasma energy of EuB_6 to 1.0 eV. This indicates that the wavelength of transmission light of EuB_6 should move toward higher band than that of LaB_6. As shown in Fig. 4, the weak absorption valley locates at around 1100 nm of EuB_6 which is much larger than 590 nm of LaB_6, which is in good agreement with the results of Kimura et al. Based on the above analysis it is easy to explain the tunable characteristic of $La_{1-x}Eu_xB_6$ transmission light wavelength, which is due to the plasmon frequency of $La_{1-x}Eu_xB_6$ locating in the scope of 1–2.0 eV.

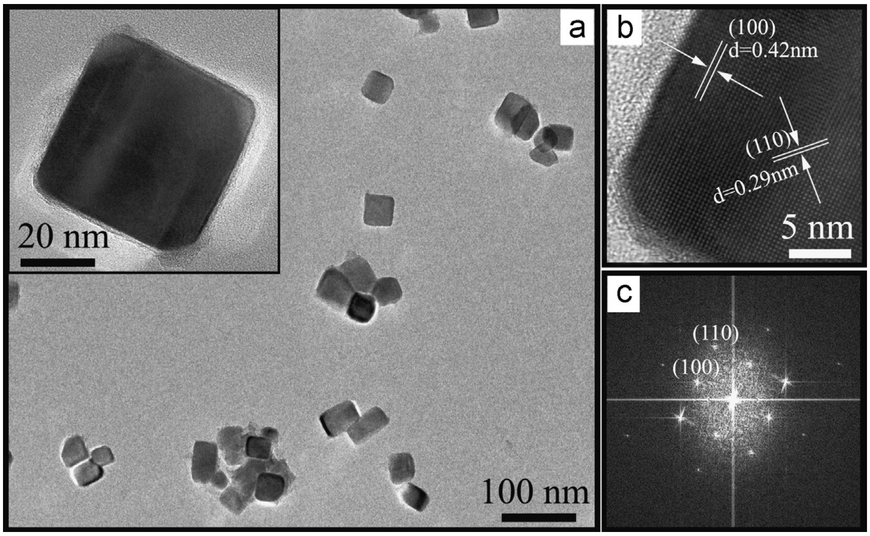

Fig. 2. (a) TEM analyses of $La_{0.6}Eu_{0.4}B_6$ nanopowder, (b) the HRTEM image (top right), and (c) the indexing FFT patterns (down left).