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Synthesis of one-dimensional rare earth hexaborides nanostructures and their optical absorption properties

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ABSTRACT

We developed a general solid state reaction to synthesize both single and dual rare earth hexaborides (REB_6) under autogenic pressure. Through a series of nearly similar experiments, one-dimensional (1-D) single crystalline REB_6 (RE = La, Ce, Pr, Nd and Sm) nanostructures can be formed. Detailed structures, morphology and chemical composition of the synthesized samples were studied by XRD, SEM, TEM, EDS and elemental mapping techniques. As a rarely reported solid state reaction for especially 1-D nanostructures growth, the formation mechanism was explored and discussed here. Gaseous species containing boron and rare earth under high pressure was deemed to be important. Optical absorption tests were carried out for all the synthesized samples at the first time. Results indicate a tunable VL transmittance can be achieved in $La_xSm_{1-x}B_6$ nanostructures upon x variation.

1. Introduction

Transparent conductive (TC) materials have aroused interests in last several decades. Specifically, materials with high optical absorption coefficient in near-infrared rays (NIR) region and transmittance in visible light (VL) region can be used as heat-insulating glass, transparent electrodes of various displays and solar cells [1]. Many disadvantages in daily life such as skin burn or environmental contamination can also be avoid without losing brightness by filtering NIR [2]. These outstanding characteristics stimulate the research of materials such as indium tin oxides (ITO) [3], titanium nitride (TiN) [4] and nearly transparent plasmonic compounds (NTPC) [5]. Recently, the traditionally thermionic electron emission sources and field emitters of rare earth hexaborides (REB_6) [6] have been studied in solar control glazing application which reveals their versatile potential [7–11]. Researchers also explored the origin of these interesting characteristics for REB_6 in last several years. Free electron plasma resonance was generally considered as the reason triggered the particular property [7]. Kimura et al. thoroughly investigated the electronic structure of REB_6 through reflectivity spectra and suggested that various interband and intra-atomic transitions were responsible for the optical peculiarity [8]. Localized surface plasmon resonance (LSPR) of conduction electrons and particle size relationship with optical parameters of LaB_6 through Mie theory was discussed to explain NIR absorption phenomenon by Adachi et al. [9]. Different absorption intensity of REB_6 and NIR variation upon particle size was studied by Takeda et al. based on the free electron plasmon resonance derived NIR absorption mechanism [10]. Sato et al. used high energy-resolution electron energy-loss spectroscopy to investigate the dielectric properties of LaB_6 crystals and the plasmonic oscillation excitation in the NIR region of LaB_6 nanoparticles. The dipole oscillation excitation peak was deemed to be responsible for the solar heat-shielding filters [11]. According to present literatures, particle-sized REB_6 and the size-dependent optical absorption have already been explored comprehensively. While the optical absorption study of 1-D REB_6 is still open and need to be addressed. Theoretically calculations of REB_6 nanowires by Cheung et al. revealed the chemical element-specificity, size-dependence, and boundary effects on the electronic structures, which affect the optical absorption according to the 4f and 5d states of the lanthanide metal atoms [12]. Thus the optical absorption of REB_6 nanowires is the object of great interest here.

In this paper, a simple low temperature synthesis approach for REB_6 nanostructures is introduced. On account of the totally sealed circumstance during reaction, the pressure in the sealed autoclave was determined by the quantity of gaseous species formed through the occurred reaction. Similar experiments for successful formation of single (LaB_6, CeB_6, PrB_6, NdB_6 and SmB_6) and dual REB_6 ($La_xSm_{1-x}B_6$) nanostructures manifested the general synthesis method. A series of characterizations were carried out to study the detailed information of the obtained products. For the first time, we investigated the optical absorption properties of all synthesized single and dual REB_6 1-D

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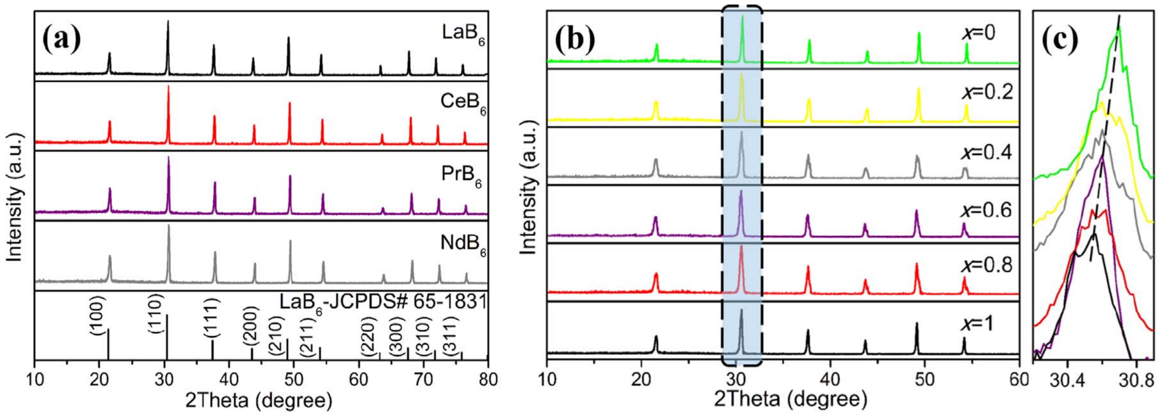

Fig. 1. XRD patterns of REB_6 (RE=La, Ce, Pr, Nd) (a) and $La_xSm_{1-x}B_6$ (b). (c) The magnification of the highest peaks in (b).

nanostructures. The especially tunable absorption range upon doping content is interesting and useful for future application of REB_6.

2. Experimental section

All reagents are of analytical grade and are used without further purification. Synthesis of single and dual rare earth hexaborides nanostructures were carried out through a low temperature solid state reaction. In a typical process, 3 mmol rare earth powders, 18 mmol H_3BO_3, 60 mmol Mg, and 8 mmol I_2 were uniformly mixed and grinded in an argon-filled glovebox. Then the homogeneous mixture were tightly sealed in an autoclave with 25 mL capacity followed by heat treatment at 280 °C for 12 h. After being cooled down to room temperature, dark-colored products can be obtained. While on account of complicated reactions occurred, byproducts such as MgO, $MgCl_2$, $REBO_3$ and other unwanted impurities were also existed and should be removed. Thus the samples were immersed into hydrochloric acid solution for 2 h and then washed with double distilled water several times. After vacuum-dried in a 90 °C oven overnight, the final pure products can be obtained. All procedures above were conducted in constant pressure.

The obtained products were characterized by using x-ray powder diffraction (XRD, TD3500, Cu Kα radiation, China), field emission scanning electron microscope (FE-SEM, Nova NanoSEM 430, FEI, USA) and high-resolution transmission electron microscope (HRTEM, Tecnai™ G^2 F30, FEI, USA). The chemical compositions were analyzed by energy dispersive spectrometer (EDS, Oxford instrument, UK) attached to the SEM. The optical absorption properties were acquired from an ultraviolet-visible-near infrared spectrophotometer (Lambda950, P-E, USA). In detail, we dilute the samples into ethanol to get REB_6 suspension for measurement. Optical absorption of pure ethanol is also tested for calibration. Incident light passed through REB_6 suspension and pure ethanol are collected, respectively. As for basic principle, the incident light would be mainly presented as three parts including scattering, reflectance and absorption after interaction with the REB_6 suspensions. The directly reflected and directly transmitted light together with scattered components of transmitted and reflected light would be detected in the measurement. Thus the optical absorption value (%) should be obtained by 100 minus the above obtained results.

3. Results and discussion

This general synthesis method is based on the reaction process which can be described as the equation below:

$$RE + 24Mg + 6I_2 + 6B(OH)_3 = REB_6 + 18MgO + 6MgI_2 + 9H_2$$

We used magnesium and iodine to provide sufficient reductive atmosphere and high pressure to stimulate the reaction by lowering the reaction barrier which go against the reaction itself. Literatures had already reported this kind of solid state reactions under autogenic pressure at elevated temperature (SRAPET) [13]. The intermediates and other assistants are of great importance for providing sufficient pressure to accelerate reaction rates and improve the completeness of transformation in SRAPET. Qian's group found that two-fold amount of Mg served as both co-reductant and in-situ heat provider while the I_2 could form MgI_2 availing the crystallization of REB_6 nanoparticles [14]. Detailed comparison of SRAPET with chemical vapor deposition (CVD) process had also been drawn by them for a judicious choice of precursors. They think that the role of Mg and I_2 can be analogized to catalyst in CVD method. On the basis of the enlightenment mentioned above, we chose highly active rare earth metal powders as precursor in term of the higher vapor phase and pressure during reaction to avail one-dimensional nanostructures growth.

XRD technique was applied to determine the purity and crystallinity of the as-synthesized samples. Patterns of the as-synthesized REB_6 (RE=La, Ce, Pr, Nd) and standard LaB_6 (JCPDS#65-1831) are located in Fig. 1(a). All the curves present their single-phase nature and can be perfectly indexed to simple cubic LaB_6 (space group: *Pm*-3*m*) with the lattice constant about 0.41 nm. Specific indices of crystal planes are labelled above the corresponding peaks as well. Dual rare earth hexaborides were fabricated through a totally same process with that of the single ones. We chose $La_xSm_{1-x}B_6$ on behalf of dual-REB_6 for detailed study. As shown in Fig. 1(b) and (c), all the sharp peaks with gradually shifted locations for the series of $La_xSm_{1-x}B_6$ (x=0, 0.2, 0.4, 0.6, 0.8, 1) can be attributed to the cubic LaB_6-type symmetry with the space group of *Pm*-3*m*, indicating the forming of solid solution of $La_xSm_{1-x}B_6$ according to Vegard's law [15].

Representative FE-SEM images of the as-synthesized single REB_6 (LaB_6, CeB_6, PrB_6 and NdB_6) nanostructures are illustrated in Fig. 2(a). The overview image under medium-magnification unambiguously shows the homogeneous and flexible nanowires/nanorods (Left in Fig. 2(a)). None adherent impurities or particles can be seen from the surface of every single nanowire/nanorod. From the Fig. 2(b) of the TEM images of an individual LaB_6 nanowire, one can see a straight uniform nanowire with round corner angle at the wire tip. The wire surface is highly smooth and the tip is clean without any attached droplets derived small particles, which is in consistence with the catalyst-free process. Crystal lattice stripes with vertically connected feature acquired from HRTEM can also be clearly seen under high-magnification mode. The d-spacings of both directions are equal to 0.41 nm, conforming the (100) plane of LaB_6 with cubic symmetry. Spots from the selected area electron diffraction (SAED) further affirms the single crystal nature of the individual LaB_6 nanowire.

In the dual-rare earth hexaborides series of $La_xSm_{1-x}B_6$ (x=0.2, 0.4, 0.6, 0.8), $La_{0.4}Sm_{0.6}B_6$ (x=0.4) sample was selected for TEM detection.