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Optical properties and thermal stability of Poly(vinyl butyral) films embedded with $LaB_6@SiO_2$ core–shell nanoparticles

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ABSTRACT

In this work, $LaB_6@SiO_2$ nanoparticle with a core–shell structure was synthesized and doped into Poly(vinyl butyral) (PVB) matrix to prepare $LaB_6@SiO_2$–PVB nanocomposite film. Field emission scanning electron microscopy (FE-SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and ultraviolet–visible–near infrared spectroscopy (UV–vis–NIR) were employed to characterize these materials. The TGA and UV–vis–NIR results show that $LaB_6@SiO_2$ nanoparticle contributed to improving thermal stability of PVB in $LaB_6@SiO_2$–PVB film, with an increase of almost 60 °C from the initial decomposition temperature in the case of the neat PVB film; additionally, maximum transmittance in visible region red-shifted from 605 to 645 nm and maximum absorption in near-infrared region moved slightly from 1466 to 1472 nm. In short, the $LaB_6@SiO_2$ NPs could be a potential candidate for transparent and heat insulation materials.

1. Introduction

Lanthanum hexaboride (LaB_6) was an excellent thermionic electron emitter material characterized by excellent thermal stability, high emission density, creep resistance and low work function. This

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material which is usually prepared by a high-temperature reaction procedure owns the highest electronic emissivity among all known materials. All these brilliant properties enable LaB_6 to be used in a wide range of applications, such as high-energy optical system, electron lithography, and coating for resistor [1–4]. The LaB_6 nanoparticles (NPs) with a diameter less than 120 nm exhibit excellent light absorbing properties in the near infrared region of 650–1600 nm [5,6] due to surface plasmon resonance effect. Hence, they are used commercially in laminated windows and car windscreens to reduce heat transmission [7]. Moreover, these nanoparticles have been successfully applied to solar control filters in automotive and architectural windows as a coating [8] or as an inclusion in polymer layers [9].

In the late 1980s, researchers found that heterogeneous, composite or sandwich colloidal semiconductor particles have better efficiency than the separate particles, they even showed some new properties in various areas [10–13]. During the early 1990s, researchers synthesized concentric multilayer semiconductor NPs with the purpose of improving properties of the materials. Hence, more and more attention has been paid to the research and application of the materials with a core–shell structure [14–16].

A silica coating endows substrate materials with not only the reduction in bulk conductivity but also the improvement in the suspension stability. In addition, silica is the most chemically inert material available, thus preventing the core from being involved in a redox reaction at the surface. Silica coating can also be used to modulate the position and intensity of the surface plasmon absorbance band since silica is optically transparent. As a result, the coating of silica on different objects, such as metal, binary inorganic composite, metal oxide and metal salt, has attracted more attention than other combinations [17]. In the present work, effect of the $LaB_6@SiO_2$ NPs on optical and thermal properties of the nanocomposite film based on PVB was investigated.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS), Ammonium hydroxide (28–30 wt.%), silane coupling agent KH570, PVB (average molecular weight = 35,000–45,000 g/mol), ethanol, dodecylbenzenesulfonic acid (DBS) were purchased from Aladdin Chemical Co., China. LaB_6 particles with an average diameter of 20–50 nm were purchased from Ronghua technology Co. Ltd., China. Deionized water was used throughout.

2.2. Preparation of $LaB_6@SiO_2$ core–shell NPs

First of all, surface of the LaB_6 particles was pretreated by anionic surfactant DBS. Briefly, the solid powder was dispersed in ethanol containing 0.05 wt.% of DBS, and the solid content was adjusted to 1 wt.%. After several minutes of stirring, color of the suspension changed to navy blue, and then it was transferred into a planetary ball mill for better homogenization.

Secondly, $LaB_6@SiO_2$ NPs were prepared via a sol–gel process mentioned elsewhere [18]. In a typical procedure, 20 mL of the above navy blue suspension, 2 mL of ammonium hydroxide and 2 mL of TEOS were sequentially added into a mixture composed of 80 mL of ethanol and 20 mL of water. The mixture was vigorously stirred in a water bath at 40 °C for 6 h. Finally the precipitate was collected and washed with ethanol and water for several times, waiting for the next experimental step.

2.3. Preparation of $LaB_6@SiO_2$/PVB nanocomposite films

$LaB_6@SiO_2$ powders and silane coupling agent KH570 were simultaneously dispersed in anhydrous ethanol with the assistance of ultrasonics. Then PVB powder was dissolved in 50 ml of ethanol at 65 °C for at least 60 min under continuous stirring. After full dispersion of the $LaB_6@SiO_2$ particles was completed, ethanol solution of PVB (10 wt.%) was mixed with the suspensions. The consequent mixture was stirred for 6 h at 65 °C with 30 min of sonication. The final suspension was casted onto glass Petri dishes, followed by drying at 40 °C in oven for 24 h. Then, fully dried films were separated from Petri dishes. Thickness of the nanocomposite films was controlled in the range of 0.15–0.3 mm. The synthesis process of $LaB_6@SiO_2$ NPs and $LaB_6@SiO_2$–PVB films is illustrated in Fig. 1.