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Preparation of integrated multifunction $Pb_3B_{10}O_{16}[OH]_4$ whisker by solvothermal method

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ABSTRACT

Elaborate design of multifunction materials is of great scientific and technological significance; but it is a great challenge. Here, a lead borate is successfully prepared via a facile solvothermal method. The results of XRD, SEM and TEM show the product is a kind of whiskers with uniform structure and high length–diameter ratio, which is represented as $Pb_3B_{10}O_{16}[OH]_4$. The whisker is capable of attenuating both γ-rays and neutrons and shows a little difference with that of the equal molar mass of Pb and B in mixture. In addition, the whisker displays good photoluminescence properties, especially for luminescent intensity. These significant results indicate an integrated multifunction whisker that will stimulate new application research.

1. Introduction

Complex radiation field simultaneously containing various high-energy particles, such as γ-rays, neutrons and protons, often exists in numerous places, such as aerospace and nuclear power plants, thereby imposing gravely hazards to life [1,2]. Hence, designing a material to jointly attenuate the radiations is of vital significance, especially for both γ-rays and neutrons [3]. Lead and other high Z (atomic number) matter have been used for the shielding of γ-rays [4]. And low Z matter (e.g. H and B) are good kinds of materials for the shielding of neutrons [5]. Either low Z or high Z matter alone may not always be able to block the complex radiations that require the shielding materials composed of both the matter [6,7]. Notably, the radiation shielding used in the special facilities (manned spacecrafts, for example) demands the materials with lightweight and less volume due to the constraints of space and maneuverability [3,8]. Up to now, composites can be ideal to feed the mentioned dilemma. First, they can be fabricated with both low Z and high Z matter that has the attenuation ability to the complex radiations [9,10]. Second, they are easy to process which that contributes to form special shape [11]. Finally, they are light but effective shielding in favor of saving cost in specific industry, such as the spacecraft [12].

The radiation shielding of composites is significantly influenced by the nature of functional fillers [3,13]. Selecting the mixed fillers composed of both low Z and high Z matter is an usual measure. However, the large difference in the density of fillers is a negative factor for the dispersion in matrices. It would further affect the shielding capacity and other physical properties of composites. To overcome the obstacles, designing compounds that chemically bond low Z and high Z elements as the functional fillers is one of the most practical and effective strategies. In this way, it promotes the homogeneous dispersion of various elements in composites but does not harm its attenuation ability to the complex radiations.

In this work, a lead borate whisker is firstly prepared by a facile solvothermal method, which is used for precise morphology control and nano-structuring of inorganic materials [14,15]. Compared with the mixed fillers, the synthesized whisker as the functional filler has much more advantages for the shielding of complex radiations. Firstly, the whisker composed of Pb, B and H that are chemically bonded is solely filled in composites, resulting in a perfect homogeneous dispersion of various elements. Secondly, the anisotropic characteristics of whisker tend to improve other physical properties of composites, such as mechanical properties [16]. Therefore, the outstanding features of the lead borate whisker facilitate the radiation shielding of composites. Besides, lead borates are provided with other physical properties, such as photoluminescence, nonlinear optics, which have triggered increasing research

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interests in recent years. As a result, the synthesized whisker possesses an amazing integrated performance. Here, the structure of the synthesized product is determined via XRD, SEM and TEM technologies. And the shielding of γ-rays and neutrons as well as photoluminescence property is examined carefully.

2. Material and methods

2.1. Sample preparation

All chemicals reagents were of analytic purity and applied directly without further purification. The synthesis of whisker followed a simple route. First, $Pb(CH_3COO)_2{\cdot}3H_2O$ and H_3BO_3 (mole ratio, 1:12) were dissolved in 6.2 ml deionized water, in which was added with a 22.0 ml pyridine under constant stirring. Afterwards, the pH value of the mixture was adjusted to 7 by dropping $NH_3{\cdot}H_2O$. Second, the final precursor was transferred into a 100 ml Teflon-lined stainless steel autoclave, which was undertaken seal deals and maintained at 230 °C for 10 h, and then naturally cooled down to room temperature. Third, the synthesized product was treated by filtration, washing with distilled water and absolute ethanol and then drying at 60 °C for 10 h under air atmosphere. Then, a white precipitate was obtained, which was the final product.

2.2. Structure characterization

The structure of the as-synthesized products was characterized by X-ray diffraction (XRD, PANalytical X'Pert PRO) with Cu Kα radiation at room temperature. The product morphology was identified by a field launch scanning electron microscope (FSEM, Carl zeiss Ultra55) equipped with the system of energy dispersive X-ray (EDX) analysis. Furthermore, the product was ultrasonically dispersed in ethanol solution and dropped onto a carbon coated copper grid for transmission electron microscopy (TEM, Carl zeiss Libra200FE), high-resolution transmission electron microscopy (HRTEM) and selection area electron diffraction (SAED) studies.

2.3. Performance testing

γ-rays absorption was carried out at narrow beam transmission geometry with very small sample-detector solid angle. The used γ-rays source was a mixed ^{22}Na and ^{155}Eu at 105.3 keV. Thermal neutrons absorption was examined a Monte Carlo simulation [17]. The MCNPX code calculates low energy ($E = 0.025$ eV) hadronic cross-sections on-the-fly with an intranuclear cascade model. 4 g synthesized whiskers and 6 g polystyrene (PS) was first blended in dimethylbenzene. Then, the blend was casted into a barrel with 5 cm diameter. After vacuum drying, the disc sample for γ-rays and neutrom absorption testing was prepared. The γ-rays and neutrons transmissions (I/I_o) of the whisker were collected with the data of the sample divided by the data of a 6 g PS disc with the same diameter. For comparison, the mixture of PbO and B_2O_3 with equal molar mass of Pb and B to the whisker was prepared by the same solution blending. Besides, photoluminescence was conducted on a Jobin Yvon Fluorolog-3-Tou fluorescence spectrometer (xenon lamp power: 15 W, operating voltage: 400 V) at 250 nm ultraviolet excitation.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-synthesized product. All of the diffraction peaks can be readily indexed to a pure hexagonal phase [space group: P31c(159)] with a lattice constants $a = b = 10.093$ Å, $c = 8.539$ Å, which are in good accordance with

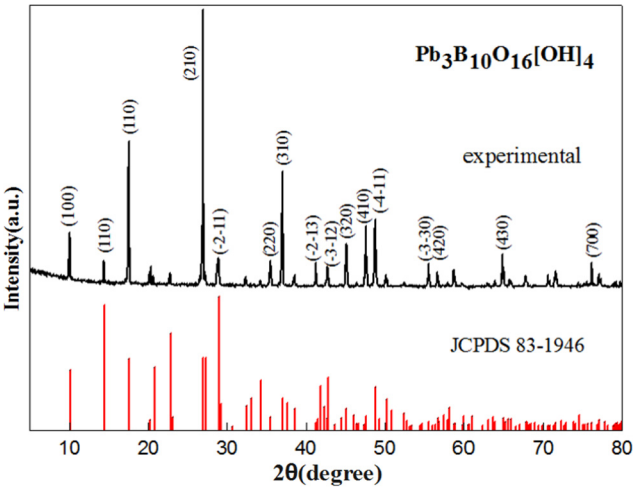

Fig. 1. XRD patterns of the as-synthesized product.

the standard values for the bulk hexagonal $Pb_3B_{10}O_{16}[OH]_4$ (JCPDS 83-1946). No peaks corresponded to impurities can be observed. Besides, it can be seen that peak (210) in the XRD pattern is practically strong in relative intensity. It indicates the preferred growth of the product occurs along the [210] direction. Compared with other methods [18,19], the synthesized product possesses much higher crystallinity due to the intense peaks. It also suggests that the lead, the boron and the oxygen atoms are well chemically bonded and the synthesized product is a kind of high-purity lead borates. It could be used as the good functional materials for the shielding of complex radiations.

Fig. 2 displays the morphological observation and the EDS elemental analysis of the product. Clearly shown is that one-dimensional fibers are tidily stacked with diameter ranging from 100 to 500 nm and length–diameter ratio from 200 to 1000, as represented in Fig. 2(a) and (b). Fig. 2(d) shows the collected EDS results for the positions of the fibers based in Fig. 2(c). Lead, boron, oxygen and carbon are detected at both points. Importantly, the ratio of atoms (Pb:B) in point 1 is roughly the same as that of in point 2. The chemical composition shows the fibers are composed of Pb, B and O, and the Pb:B atomic ratio is about 1:3.37, which closely meets the theoretical ratio of 1:3.33 for $Pb_3B_{10}O_{16}[OH]_4$, the minor deviation may be due to measurement error caused by semi quantitative analysis method. The basic form of the grown crystals is a hexagonal cylinder with pyramidal or truncated pyramidal end faces. $Pb_3B_{10}O_{16}[OH]_4$ might be firstly formed from the nuclei, which is a tip of whisker structure. Then it causes the crystals to grow continuously under the hydrothermal condition [18]. It indicates different positions of the whole root fiber contain same composition. It can be concluded that the uniform and anisotropic structures contribute to improving the integrated physical properties of product as well as its composites, such as mechanical properties.

Fig. 3 shows TEM results of the product. It is clearly displayed that the product is represented as a fibrous structure with a diameter of about 120 nm, which possesses smooth surface and uniform shape in the lengthwise direction, as shown in Fig. 3(a) and Fig. 2(c). In addition, the SAED image of the structure can be indexed as the $Pb_3B_{10}O_{16}[OH]_4$ single crystal, which is in good agreement with the above XRD results. Notably, the SAED tests taken from different positions of the structure are found to be obtained almost identical results. It indicates the entire structure is a single crystal in nature and the synthesized $Pb_3B_{10}O_{16}[OH]_4$ is a kind of whiskers, which have been proved to be equipped with excellent physical properties [14,20,21], especially for composites. Fig. 3(b) shows a typical HRTEM image of the whisker. It can be

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