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Fabrication of BN nanosheets-coated $SrAl_2O_4:Eu^{2+}$ as a new water-resistant phosphor by a one-pot method

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Abstract

BN nanosheets-coated $SrAl_2O_4:Eu^{2+}$ was fabricated by a simple one-pot method. The BN nanosheets formed into a compact layer coating on the surface of $SrAl_2O_4:Eu^{2+}$ completely. X-ray diffraction, X-ray photoelectron spectroscopy and various microscopy techniques were used to analysis the composite structure of the phosphor. BN layer obstructed H_2O molecule entering into the channels of $SrAl_2O_4$, and restrain $SrAl_2O_4$ from hydrolyzing effectively. The coated phosphor shows a strong green band at about 510 nm which corresponds to the $4f^7$–$4f^65d$ transition in Eu^{2+} ion.

Keywords: Luminescence; Coating; One-pot; Phosphor

1. Introduction

Recent years, strontium aluminate ($SrAl_2O_4$) has been proved to be one of the most efficient host materials for long-lasting phosphorescence [1–4]. The low-temperature phase of $SrAl_2O_4$ adopts a monoclinic structure (space group $P2_1$, $a = 8.447$ Å, $b = 8.816$ Å, $c = 5.163$ Å, $\beta = 93.42°$). Eu^{2+} (1.20 Å) can be readily substituted for Sr^{2+} (1.21 Å) with minor local distortion of the crystal lattice because of their same valence and a similar radius. Therefore, Eu^{2+} activated strontium aluminate ($SrAl_2O_4:Eu^{2+}$) is considered to be a useful phosphor with excellent properties, such as high brightness, no radiation, safety and long duration. Up to now, monoclinic $SrAl_2O_4:Eu^{2+}$ has been prepared in the form of a thin layer [5] or a crystal [6,7], by solid-state reactions at 1300 °C [8], a sol–gel route at 1150 °C [9], a microwave route [10] and a combustion method [11].

However, the structure of monoclinic $SrAl_2O_4$ phase has a three-dimensional network of corner-sharing AlO_4 tetrahedron, which as channels in the a- and c- directions where the Sr^{2+} ions are located [2]. These channels have relatively bigger radius and H_2O molecule can enter easily. Then the strong polarity of H_2O molecule breaks the bond of O–Sr–O and destroys the crystal structure of $SrAl_2O_4$. So the $SrAl_2O_4:Eu^{2+}$ phosphor can easily hydrolyze in humid environment, especially in water solution. The hydrolyze reaction equations are

$$3SrAl_2O_4 + 6H_2O \rightarrow Sr_3Al_2(OH)_{12} + 2Al_2O_3$$

$$Sr_3Al_2(OH)_{12} \leftrightarrow [Sr_3Al_2(OH)_{11}]^+ + OH^-$$

Therefore, how to improve the water-resistance property of $SrAl_2O_4:Eu^{2+}$ phosphors is becoming a key issue in their applications.

Up to now, there are various methods used to synthesis of several kinds of water-resistant strontium aluminate-based phosphors by coating them with different materials. Silica is used to coating of the phosphor by sol–gel method and chemical precipitation method [12–15]. Silicon dioxide, silicon and alumina have been also reported as the coating materials [16–18]. However, all of the reported methods are based on two steps: synthesize $SrAl_2O_4:Eu^{2+}$ phosphor firstly and then coat various materials on the surface of the phosphor. To widen the application areas of this phosphor, it is significant to find a simple method from which we can obtain water-resistant $SrAl_2O_4:Eu^{2+}$ phosphor directly. From the idea that BN has unique chemical and physical properties such as low density, high melting point, chemical inertness, and high thermal conductivity in a

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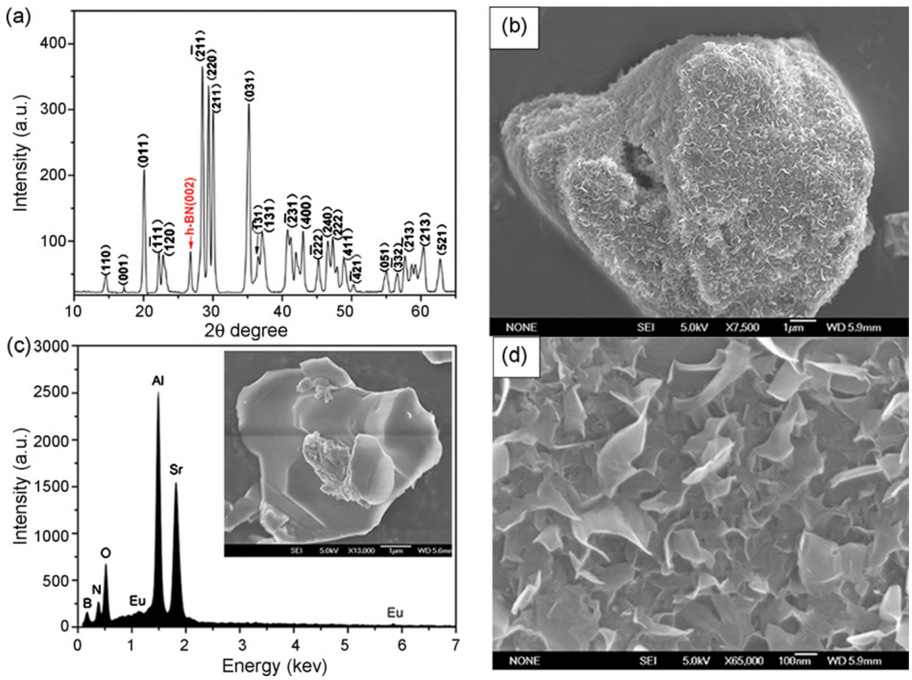

Fig. 1. (a) XRD patterns of BN-coated $SrAl_2O_4:Eu^{2+}$ phosphor, (b) typical SEM image of BN nanosheets-coated $SrAl_2O_4:Eu^{2+}$ phosphor, (c)EDS spectrum of the coated phosphor (inset) typical SEM image of uncoated $SrAl_2O_4:Eu^{2+}$ phosphor and (d) high-magnification image of the coated phosphor.

wide range of temperature, coating BN layer on $SrAl_2O_4:Eu^{2+}$ is assumed to effectively improve water-resistance property of the phosphor. In this paper, using the fluxing agent B_2O_3 as reactant, we synthesized BN nanosheets-coated $SrAl_2O_4:Eu^{2+}$ as a composite phosphor by a one-pot method directly. The BN-coated phosphor shows great water-resistance property and may be particularly useful for future commercial applications.

2. Experimental

BN nanosheets-coated $SrAl_2O_4:Eu^{2+}$ powder was synthesized by a one-pot method. The starting materials were commercially available alumina powder (Al_2O_3, 99.0% purity), strontium carbonate ($SrCO_3$, 99.0% purity), boron oxide (B_2O_3, 99.5% purity) and europium oxide (Eu_2O_3, 99.0% purity). The mixtures of Al_2O_3, $SrCO_3$, B_2O_3 and Eu_2O_3 with a molar ratio of 1:1:0.4:0.02 were homogenized in an agate pestle and mortar and used as the initial reaction constituents. The reactants were placed in an alumina crucible located in an alumina tube, which was mounted in a traditional resistance-heating furnace. The system was first purged with a high purity of N_2 gas for 10 min. Then the N_2 gas was replaced by a N_2/NH_3 flow (1:4). The furnace was heated to 1300 °C and held for 3 h. After reaction, a green powder was obtained. For comparing, we also synthesized $SrAl_2O_4:Eu^{2+}$ phosphor without BN coating. The whole process was the same as above except using H_2 instead of NH_3 as reducing gas.

The crystal structures of the products were examined by X-ray diffraction (XRD, D/MAX-rB, Cu Kα radiation) analysis. The morphology and chemical stoichiometry of the sample was checked by scanning electron microscopy (SEM, JEM-6700F, JEOL), transmission electron microscopy (TEM, JEM-2100F, JEOL), energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (ESCALAB MK Π). Photoluminescence studies were carried out at room temperature using Perkin-Elmer LS55 fluorescence spectrometer.

3. Results and discussion

Fig. 1a shows XRD pattern of the product, which can be well indexed as the mixed phase of $SrAl_2O_4$ and hexagonal BN. The measured pattern is in agreement with the reported XRD patterns (JCPDS 34-0379 for $SrAl_2O_4$ and JCPDS 34-0421 for

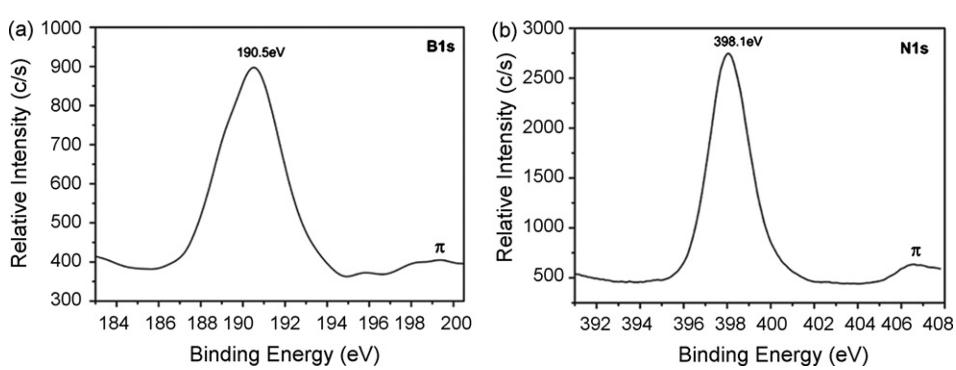

Fig. 2. XPS survey scan of BN nanosheets-coated phosphor: B 1s and N 1s. The B 1s and N 1s spectrum show the binding energies of 190.5 eV and 398.1 eV. Both of them are in good agreement with values of h-BN.