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Synthesis of pure AlON: Eu^{2+}, Mg^{2+} phosphors by a mechanochemical activation route

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Abstract

Pure AlON: Eu^{2+}, Mg^{2+} phosphors have been synthesized by a novel mechanochemical activation route. In the process of mechanical milling, the starting powder mixtures are mostly transformed into an amorphous phase with homogeneous elemental distribution at the atomic level, which significantly promotes the synthesis of AlON phase at a low reaction temperature. The firing temperature higher than 1500 °C would lead to the appearance of $EuMgAl_{10}O_{17}$ impurity phase. This is why pure AlON: Eu^{2+}, Mg^{2+} phosphors could not be obtained by the traditional solid state reaction method, which requires higher firing temperature. The pure AlON: Eu^{2+}, Mg^{2+} phosphors show comparable luminescence intensity, compared with that synthesized by the solid-state reaction method.

Keywords: C. Optical properties; Amorphous materials; Luminescence; Mechanochemical processing

1. Introduction

Aluminum oxynitride (hereafter AlON), as a solid solution of Al_2O_3–AlN binary system, is transparent in the visible light range and has superior mechanical properties both at room and high temperatures [1]. It is successfully applied for a new armor material and thermal-mechanically stable infrared viewport. Based on its excellent physical and chemical stability, AlON based phosphors have attracted significant attention in recent years. Green Mn^{2+}–Mg^{2+} co-doped γ-AlON phosphor, Tb^{3+} and Ce^{3+} co-doped γ-AlON phosphor and some upconversion Er^{3+} or Tb^{3+}, Tm^{3+} doped γ-AlON phosphors were prepared [2–5]. Eu doped AlON phosphor showed double emission peaks at 475 and 520 nm, which are ascribed to the presence of divalent europium in the $EuAl_{12}O_{19}$ magnetoplumbite-like aluminum oxynitride impurity [6]. In our previous study, it was found that Mg co-doping could favor Eu^{2+} dissolution into the host lattice of AlON by the solid state reaction (SSR) and exhibited a strong broad emission band at about 490 nm [7]. Unfortunately, pure spinel AlON phase was still not obtained. The formation of AlON grains in hand-milled powders by SSR was through a surface diffusion process, leading to an inhomogeneous distribution of Eu^{2+} ions in the host phase and unavoidable segregation. Part of Eu formed $EuMgAl_{10}O_{17}$ impurity together with the major AlON phase. Furthermore high soaking temperature of 1800 °C made the process energy-intensive, and some hard agglomerates existed in the obtained powders. Pulverization of hard agglomerates would cause defects, which drastically reduced their luminescence efficiency. Therefore it is necessary to try another low temperature synthesis method to achieve pure Eu^{2+}, Mg^{2+} co-doped phosphor, such as high-energy ball milling.

High-energy ball milling, (HEBM for short later) is a solid-state powder processing technique involving repeated welding, fracturing and rewelding of powder particles in a high-speed ball mill. This method has been widely applied into the homogeneous metal alloy [8–10]. HEBM can efficiently transform the starting powders into an amorphous phase with homogeneity of elements at the atomic

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level, reduces the particle size and largely lower the reaction temperature [11–15]. For example, in the process of high-energy ball mill of the starting powder Al_2O_3 in N_2 atmosphere, some cubic AlN phase has generated [16].

HEBM method also exhibits big potential application in the preparation of oxynitride phosphors [17]. We have reported the synthesis of Ca–α-SiAlON: Eu^{2+} phosphors by a mechanochemical activation route [18], which significantly promoted the Eu^{2+} ions incorporation into Ca–α-SiAlON crystal lattice and improved the luminescence property. With the help of HEBM method, the Si–N substitutional values for Al–O bond in $BaMgAl_{10-x}Si_xO_{17-x}N_x$: Eu^{2+} phosphors were greatly increased from $x=0.03$ to $x=0.25$, but didnot destroy the crystal structure of BAM. The obtained phosphors showed excellent thermal degradation. The present work was to study the effect of HEBM method on crystallinity and photoluminescence of the prepared Eu^{2+}, Mg^{2+} co-doped AlON phosphors.

2. Experimental procedure

AlON ($Al_{23}O_{27}N_5$)-based powders with the formula of $Eu_{3/2y}Mg_{2.4}Al_{21.4-y}O_{27}N_5$ were synthesized by the conventional solid-state reaction after mechanical milling. Eu concentration is in the range 0.5–1 mol%. A total amount of 4 g was weighed out from Al_2O_3 (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), AlN (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), MgO (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), and Eu_2O_3 (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) starting powders and was well mixed in ethanol using Si_3N_4 balls for 12 h. The as-received powder mixture was then high energy mechanically milled (Seishin planetary ball mill, PM-1200, Japan) using silicon nitride balls 5 mm in diameter and a silicon nitride pot 350 ml in volume. The ball-to-powder weight ratio was 10:1, the milling speed was 1000 rpm and the milling time was 4 h. All powders were fired in BN crucibles under N_2 atmosphere for 2–6 h. The samples were heated and cooled at a constant rate of 300 °C/h.

The phase was analyzed by an X-ray diffractometer (XRD, Philips PW 1700) using Cu $K_{\alpha 1}$ radiation at a scanning rate of 0.5°/min. The photoluminescence spectra were measured at room temperature by a fluorescent spectrophotometer (F-4600, Hitachi Ltd., Japan) with a 200 W Xe lamp as an excitation source. The emission spectrum was corrected for the spectral response of a monochromater and Hamamatsu R928P photomultiplier tube (Hamamatsu Photonics K.K., Hamamatsu, Japan) by a light diffuser and tungsten lamp (Noma Electric Corp., NY; 10 V, 4 A). The excitation spectrum was also corrected for the spectral distribution of the xenon lamp intensity by measuring Rhodamine-B as reference.

3. Results and discussions

As seen in Fig. 1, with the help of high-energy ball milling, the XRD peaks of starting powders are significantly weakened, and a highly diffuse background structure is observed. This indicates that the milled powders have mostly been transformed into an amorphous state, indicating the powders are mixed well at an atomic scale. Only little amount of AlN crystal could be detected due to its strong covalent Al–N bond for AlN atomic crystal.

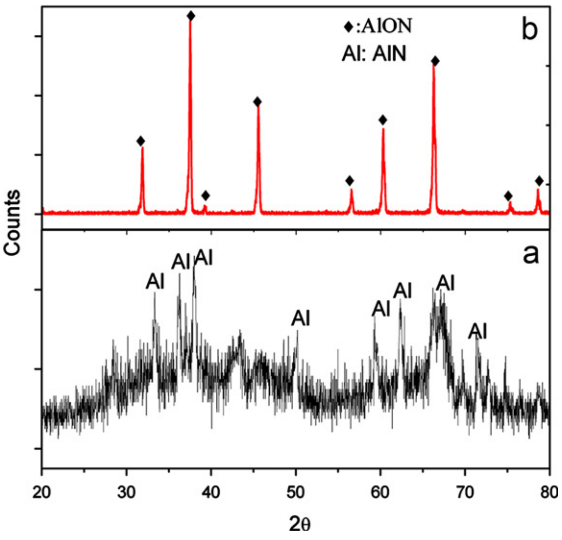

Fig. 1. XRD patterns of (a) raw materials after HEBM and (b) powders after thermal treatment at 1400 °C for 2 h.

As seen in Fig. 1, the pure Mg–AlON phase can be obtained from the amorphous powders at the firing temperature of 1400 °C for 2 h. This synthesis temperature is obviously lower than reported 1700 °C for the products by solid state reaction [19]. This result indicates that HEBM method is useful to produce materials at a subtle condition. In the process of high-energy ball milling, each element mutually diffuses and homogeneous metastable amorphous phase is achieved, which significantly promotes powder reaction activity. For direct solid-state reaction method, elements show a character of an inhomogeneous distribution. Reactions can happen only by solid-state diffusion, which needs large activation energy. Especially for AlN crystal, Al–N bond is very strong and difficult to destroy. So high firing temperature is necessary for the synthesis of Mg–AlON powder by solid-state reaction.

Following, the effect of HEBM on rare-earth doped Mg–AlON phosphor is also studied. The starting powders of 0.5 mol% Eu doped Mg–AlON are also milled in the same way. The obtained precursors are fired at 1300–1550 °C for 2 h. As seen in Fig. 2, a single AlON phase can be obtained under the firing temperature of 1450 °C. Due to the low diffusion coefficient of N^{3-} ions, the products show residual reactant, such as Al_2O_3 and AlN under the low temperature. As temperature increases, Al_2O_3 and AlN are gradually incorporated into AlON crystal lattice. But with further increase of temperature to 1550 °C, the impurity $EuMgAl_{10}O_{17}$ phase appears, which is always detected in AlON: Eu^{2+}, Mg^{2+} phosphors synthesized by solid-state reaction at high temperature. It seems that the

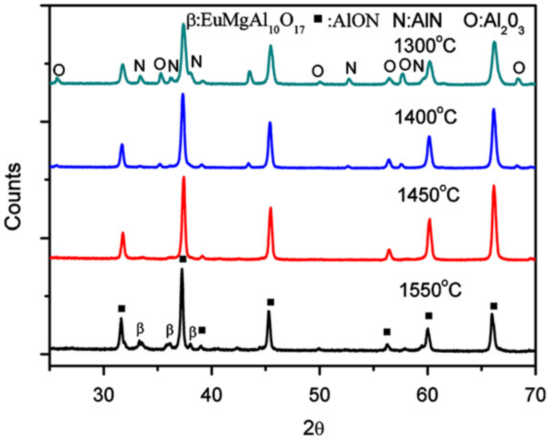

Fig. 2. XRD patterns of the fired powders under different firing temperatures.

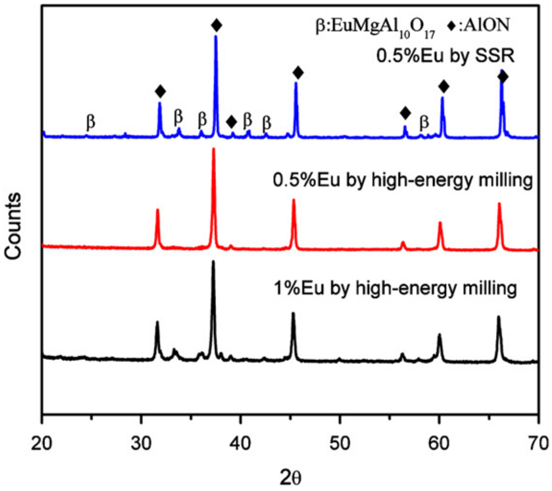

Fig. 3. XRD patterns of powders synthesized by the SSR and HEBM method.

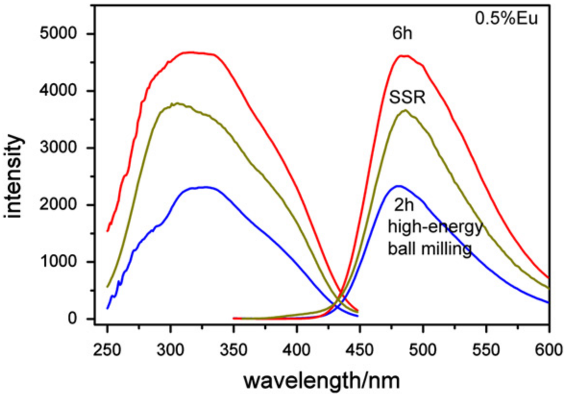

Fig. 4. Excitation and emission spectra of powders synthesized by HEBM under the firing temperature of 1450 °C for 2–6 h. The spectra of SSR phosphors are given as a comparison.

AlON phase is thermodynamically accompanied by impurity $EuMgAl_{10}O_{17}$ phase at temperature higher than 1500 °C, so pure AlON: Eu^{2+}, Mg^{2+} phosphor could not be obtained by a simple solid state reaction without mechanical activation, because this method requires higher temperature to achieve complete reactions.

As mentioned above, the HEBM method can effectively accelerate homogeneity of elements at the atomic level, which significantly promotes the reaction and Eu dissolution in AlON crystal lattice at a relatively low temperature, resulting in single AlON phase. From the view of X-ray diffraction peaks in the powders through the HEBM method in Fig. 3, it shifts to lower angle, indicating the expanded lattice parameter. Based on XRD peaks, the cubic lattice parameter increases from $a=7.96$ Å to $a=8.01$ Å calculated by UnitCell software, which is larger than the literature value of AlON. The lattice parameter of Mg–AlON can be expressed by $a=0.7900+0.0160x+0.0206y$ by Willems et al. [20] or $a=0.7900+0.0150x+0.0375y$ by Granon et al. [21], where a is the lattice parameter in nm and x and y are the mol fractions of AlN and MgO respectively. The total content of AlN and MgO in the starting materials is impossibly increased in the process of high-energy ball milling. So the increased lattice parameter should be contributed to more Eu, AlN and MgO dissolution into AlON crystal lattice. With 1% Eu concentration, some impurities are detected in the product. The XRD peaks of AlON still shift to lower angle, indicating that the solid solubility of Eu in Mg–AlON is larger than 0.5%. So higher speed or longer milling time in the process of HEBM will favor more Eu dissolution in Mg–AlON, which needs more studies.

Excitation and emission spectra are shown in Fig. 4. All samples display blue-green luminescence upon 330 nm excitation. The emission band shows a broad band character in the wavelength range of 430–620 nm centered at about 490 nm, which is attributed to the allowed $4f^65d$–$4f^7$ transition of Eu^{2+}. Compared with the phosphors with weak luminescence intensity under the soaking time of 2 h, the phosphors under long soaking time of 6 h show much higher intensity due to better crystallinity. The intensity is 1.3 times of that of phosphor synthesized by the conventional solid-state reaction method.

4. Conclusion

Single phase Eu^{2+}, Mg^{2+} co-doped AlON phosphors were prepared by a mechanochemical activation route. Mechanical milling can effectively accelerate homogeneity of elements at the atomic level, which significantly promotes the reaction and Eu dissolution in AlON crystal lattice. Pure Eu^{2+}, Mg^{2+} co-doped AlON phosphors with high photoluminescence property could be achieved at a relatively low firing temperature.

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