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Reduction of Ce(IV) to Ce(III) induced by structural characteristics and performance characterization of pyrophosphate $MgIn_2P_4O_{14}$-based phosphors

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ABSTRACT

Due to the high sensitivity of the unshielded 5d orbit to the host environment, Ce^{3+} has a wide-spread emission ranging from near ultraviolet to the red light region, making it a favorable choice for being UV-emitting phosphor activator and sensitizer of other co-doped lanthanide ions in luminescent materials. In present work, Ce^{4+}→Ce^{3+} self-reduction phenomenon in the layered phosphate $MgIn_2P_4O_{14}$ was observed. Noting that self-reduction ability is a valuable characteristic of new host materials, a new viewpoint underlying mechanism was put forward. Structure-, composition-, and temperature-dependence of photoluminescence of the new UV-emitting $MgIn_2P_4O_{14}$: Ce_x phosphors were investigated, with the relative mechanism discussed. Moreover, the sensitization of Dy^{3+} by Ce^{3+} was observed in Ce^{3+}/Dy^{3+} co-doped $MgIn_2P_4O_{14}$ phosphors. The excitation region of Dy^{3+} in $MgIn_2P_4O_{14}$: CeDy (220–460 nm) is markedly broadened compared to that of the Dy^{3+} single-doped phosphor (270–460 nm) on account of the Ce^{3+}→Dy^{3+} energy transfer process. Present work shows that the $MgIn_2P_4O_{14}$: CeDy phosphor can be promising phosphor using for fabrication of both light-emitting diodes (LEDs) and fluorescent lamps (FLs).

1. Introduction

In recent years, ultraviolet radiation has been widely applied in a variety of utilization, such as anti-counterfeiting, polymer curing, photolithography, sterilization and disinfection, optical storage, insect traps and biological therapy [1,2]. Depending on wavelength ranges, the UV radiation is usually classified into three types, UVA (380–315 nm), UVB (315–280 nm), and UVC (280–200 nm). UVA can be utilized in those applications of solid-state lighting, bug zappers, and medical imaging of cells etc [3]. As for UVB, light therapy in medicine is one of its prominent usage since the phototherapy lamps in 305–315 nm ranges are effective in treating skin diseases and disorders [4]. UVC, with shorter wavelength and higher energy, can be used for disinfecting water and killing harmful microorganisms on surfaces and in air [5]. The most common way of obtaining UVA and UVB is to use a low-pressure Hg discharge and then convert the 254 nm radiation to the desired wavelength using UV-emitting phosphors [6,7], which is also known as black light phosphor. Among rare earths, Ce^{3+} is a favorable choice for being UV-emitting phosphor activator because it can lead to a wide-spread emission wavelength range from near ultraviolet to the red-light region, due to its high sensitivity of the unshielded 5d orbit to the host environment [8]. Owing to the characteristic of Ce^{3+} ions, it can not only be used in ultraviolet radiation devices, but also in some other lighting areas (FLs and wLEDs *etc.*). In $GdPO_4$: Ce^{3+}, the dominant emission is located at around 350 nm in the UVA region [9], whereas $Y_3Al_5O_{12}$: Ce^{3+} (YAG: Ce) is the most widely used yellow phosphor in white LED along with blue-light-emitting InGaN chips [10]. Besides, since the d-f transition in Ce^{3+} can generate a broad emission band, which is overlapped with the absorption region of many other luminescent ions, Ce^{3+} has also been widely used as the activator or sensitizer of other co-doped lanthanide ions in luminescent materials. For instance, in Ce^{3+}, Tb^{3+}, Eu^{3+}- *co*-doped $Ba_2Y_2(PO_4)_2(SiO_4)$ phosphors, Ce^{3+} is not only the blue-light-component activation center, but also the sensitizer of Tb^{3+}, and Tb^{3+} further sensitizes Eu^{3+} through energy transfer process [11]. When Ce^{3+} functions as sensitizer, the broad-band white emission can be obtained by the energy transfer from Ce^{3+} to Dy^{3+} ions in $Ba_2B_2O_5$ [12]. Moreover, the 5d-4f transition in Ce^{3+} exhibits a short decay time, which is preferable for the application of scintillators - $LaBr_3$: Ce^{3+} [13], Ce^{3+}-activated $MGd(PO_3)_4$ (M = Li, Na, K, Cs) [14] and cerium-activated single crystals Tl_2GdCl_5 [15], for example.

Syntheses of compounds containing lanthanide ions with reduced

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valence state, such as Ce^{3+} and Eu^{2+}, usually require a reducing atmosphere [16–19], because these ions are generally more stable at fully oxidized states than their reduced states in the air. Nevertheless, researchers have found that the self-reduction phenomenon appears in some compounds, where the lanthanide ion dopants can automatically reduce themselves to a lower valence state even when synthesized in the air. For example, Eu^{2+}/Tm^{2+}/Yb^{2+}-doped $BaZnSiO_4$ [20], Eu^{2+}-doped α- $Ca_3(PO_4)_2$ [21], Ce^{3+}-doped $Sr_3Y(PO_4)_3$ [22] and Eu^{2+}-doped SrB_6O_{10} [23] have been synthesized by solid-state reaction in air atmosphere. On one hand, the conventional synthesis in the air is suitable for large-scale production at a low cost. On the other hand, the compounds with the self-reduction ability are resistant to the oxygen in air and thus do not require inert atmosphere protection in their practical use. Therefore, self-reduction ability is a valuable characteristic in the exploration of new host materials.

In terms of luminescent materials, phosphate is always regarded as one of the promising source for the exploration of new host materials [24], due to their outstanding properties, such as high chemical and thermal stability, structural diversity, and proper raw material price. Till now, plenty of studies related to rare-earth-doped phosphate phosphors have been carried out, such as color-tunable $KNaCa_2(PO_4)_2$: A (A = Ce^{3+}, Eu^{2+}, Tb^{3+}, Mn^{2+}, Sm^{3+}) [25], white light-emitting $NaLa(PO_3)_4$: Dy^{3+} [26], green-yellow-red-tunable $Mg_3In_4P_6O_{24}$: Eu^{3+}, Tb^{3+} [27], yellow super long-lasting $Ca_6BaP_4O_{17}$: Eu^{2+},Ho^{3+} [19], and promising green-emitting VUV-excited phosphors $Na_3Gd(BO_3)_2$: Tb^{3+} [28].

Recently, during our investigation of MgO-In_2O_3-P_2O_5 ternary system a new phosphate $MgIn_2P_4O_{14}$ was found and confirmed for the first time [29]. The three-dimensional framework of $MgIn_2P_4O_{14}$ can be regarded as built of anionic and cationic layers arranged alternatively. Very recently, the Ce^{4+}→Ce^{3+} self-reduction phenomenon in phosphate $MgIn_2P_4O_{14}$ was observed with cerium doped in. In this contribution, we made a detailed analysis of the mechanism of the self-reduction behavior. Relative luminescence properties of the UV-emitting $MgIn_2P_4O_{14}$: Ce_x phosphors have been investigated. Moreover, brief discussion of luminescence properties of Ce/Dy co-doped $MgIn_2P_4O_{14}$ phosphors was conducted.

2. Experimental

2.1. Sample preparations

A series of Ce-doped and Ce/Dy co-doped powder samples $MgIn_2P_4O_{14}$: Ce_xDy_y (x = 0, 0.01, 0.03, 0.04, 0.05, 0.07, 0.09, 0.11; y = 0, 0.04) were synthesized via conventional high-temperature solid-state reaction method. The reactants used in the preparation were MgO (Aladdin, 99.99%), In_2O_3 (Aladdin, 99.99%), $NH_4H_2PO_4$ (Xilong Scientific Co., LTD., 99.5%), CeO_2 (Alfa Aesar, 99.99%) and Dy_2O_3 (Aladdin, 99.99%). Stoichiometric reactants with an approximate molar ratio of Mg: In: P: Ce: Dy = 1: 2(1-x-y): 4: 2 × : 2y were ground for 30 min to mix uniformly in an agate mortar. The mixtures were preheated at 600 °C for 12 h in an alumina crucible. Then, the mixtures were re-ground and calcined at 1000 °C for 24 h with a heating rate of 5 °C/min in air or using carbon reduction method. Finally, the samples were naturally cooled to room temperature and ground again for the following analysis.

2.2. Characterization

2.2.1. X-Ray diffraction

Powder XRD patterns for phase analyses were collected on an X-ray Rigaku diffractometer D/MAX-2500 with Cu Kα radiation and graphite monochromator operated at 40 kV, 150 mA.

2.2.2. X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) measurement was conducted using a Thermo Fisher- VG Scientific (ESCALAB 250Xi) photoelectron spectrometer.

2.2.3. Photoluminescence excitation and emission spectra

Photoluminescence excitation (PLE) and Photoluminescence emission (PL) spectra at room temperature were recorded on a fluorescence spectrophotometer (Hitachi, F-7000) equipped with a 150 W Xe lamp as the excitation source. Temperature-dependent luminescence spectra (25–300 °C) were detected by applying a heating apparatus (Tianjin Orient KOJI Co., LTD., TAP-02). The powder sample was placed in a sample cavity and then heated to a different temperature adjusted by the temperature controller. The sample was kept at the target temperature for 2–3 min before each measurement was taken, in order to achieve a uniform temperature of the sample and cavity.

2.2.4. Vacuum ultraviolet excitation and emission spectroscopy

The luminescence spectra in the VUV region was measured at Beam line 3B1B in Beijing Synchrotron Radiation Facilities (BSRF) under normal operating conditions (220 mA).

2.2.5. Time-resolved decay measurement

Time-resolved emission decay behaviors were measured on an Edinburgh Instruments Ltd. spectrometer (FLS920, UK) with μF900 Lamp as the excitation source and a R928-PA photo multiplier for signal detection.

2.2.6. Ultraviolet-visible diffuse reflectance spectra

UV- visual diffuse reflectance (UV-DR) spectra were measured on a UV-visible spectrophotometer (Shimadzu, UV-2600) equipped with an integration sphere using $BaSO_4$ as a reference.

3. Results and discussion

3.1. Phase identification of Ce-doped $MgIn_2P_4O_{14}$

Fig. 1 shows representative patterns of the Ce doped $MgIn_2P_4O_{14}$ phosphors with different doping concentrations or fabricated in different annealing atmospheres. As can be seen from Fig. 1, XRD patterns of the representative phosphors of $MgIn_2P_4O_{14}$: $Ce_{0.01}$ (a) and $MgIn_2P_4O_{14}$: $Ce_{0.04}$ (b and c) show good consistency with the pattern of $MgIn_2P_4O_{14}$ and no impurities are detected, implying that the doped RE ions are completely dissolved into the host lattice of $MgIn_2P_4O_{14}$ without inducing any significant changes in the crystal structure. Peaks before 50° of sample (c) are identified as belonging to $MgIn_2P_4O_{14}$, which is shown on the enlarged pattern of Fig. 1.

3.2. Characteristics of Ce-doped $MgIn_2P_4O_{14}$

3.2.1. Self-reduction of Ce^{4+}→Ce^{3+} in $MgIn_2P_4O_{14}$

The excitation and emission spectra of $MgIn_2P_4O_{14}$: $Ce_{0.04}$ prepared in air and carbon reduction atmosphere are depicted in Fig. 2. The two samples exhibited similar band profiles and peak positions, except for that the intensity of the sample sintered in air is a little bit weaker than the one obtained under carbon reduction condition. As is known to all, Ce^{4+} is not optically active. Thus, it is probably that self-reduction reaction of Ce^{4+}→Ce^{3+} occurs in the unique structure of the host $MgIn_2P_4O_{14}$.

To further verify the presence of trivalent cerium, X-ray photoelectron spectroscopy (XPS) technique was employed. Binding energy of Ce 3d is within the range of 870–925 eV [30–32]. In Fig. 3, two broad bands located around 885 eV and 905 eV can be assigned to Ce(III, IV) $3d_{5/2}$ and Ce(III, IV) $3d_{3/2}$, and the weak peak centered at about 921 eV is the fingerprint of Ce^{4+} species. All the XPS spectra were fitted after a Tougaard background correction and detailed data for binding energy are listed in Table 1. The percentages of two Ce species in $MgIn_2P_4O_{14}$: $Ce_{0.04}$ synthesized in air are calculated to be Ce(III) 69.5% and Ce(IV)