Thermally stable green Ba$_3$Y(PO$_4$)$_3$:Ce$^{3+}$,Tb$^{3+}$ and red Ca$_3$Y(AlO)$_3$(BO$_3$)$_4$:Eu$^{3+}$ phosphors for white-light fluorescent lamps

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Abstract: A class of thermal stable of green-emitting phosphors Ba$_3$Y(PO$_4$)$_3$:Ce$^{3+}$,Tb$^{3+}$ (BYP:Ce$^{3+}$,Tb$^{3+}$) and red-emitting phosphors Ca$_3$Y(AlO)$_3$(BO$_3$)$_4$:Eu$^{3+}$ (CYAB:Eu$^{3+}$) for white-light fluorescent lamps were synthesized by high temperature solid-state reaction. We observed a decay of only 3% at 150 °C for BYP:0.25Ce$^{3+}$,0.25Tb$^{3+}$ (3% for LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$), and a decay of 4% for CYAB:0.5Eu$^{3+}$ (7% for Y$_2$O$_3$:Eu$^{3+}$, 24% for Y$_2$O$_2$:S:Eu$^{3+}$). The emission intensity of composition-optimized Ba$_3$(Y$_{0.5}$Eu$_{0.3}$Tb$_{0.2}$)(PO$_4$)$_3$ is 70% of that of commercial LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$ phosphors, and the CIE chromaticity coordinates are found to be (0.323, 0.534). The emission intensity of Ca$_3$(Y$_{0.5}$Eu$_{0.5}$)(AlO)$_3$(BO$_3$)$_4$ is 70% and 83% of those of Y$_2$O$_3$:Eu$^{3+}$ and Y$_2$O$_2$:S:Eu$^{3+}$ phosphors, respectively, and the CIE chromaticity coordinates are redder (0.652, 0.342) than those of Y$_2$O$_3$:Eu$^{3+}$ (0.645, 0.347) and Y$_2$O$_2$:S:Eu$^{3+}$ (0.647, 0.343). A white-light fluorescent lamp is fabricated using composition-optimized Ba$_3$(Y$_{0.5}$Ce$_{0.25}$Tb$_{0.25}$)(PO$_4$)$_3$ and Ca$_3$(Y$_{0.5}$Eu$_{0.5}$)(AlO)$_3$(BO$_3$)$_4$ phosphors and matching blue-emitting phosphors. The results indicate that the quality of the brightness and color reproduction is suitable for application in shortwave UV fluorescent lamps. The white-light fluorescent lamp displays CIE chromaticity coordinates of x = 0.33, y = 0.35, a warm white light with a correlated color temperature of 5646 K, and a color-rendering index of Ra = 70.

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References and links
1. Introduction

In the mid 1970s, fluorescent lamps containing a mixture of triphosphors—the blue-emitting BaMgAl\(_2\)O\(_4\):Eu\(^{2+}\) (BAM) [1,2], the red-emitting \(\text{Y}_2\text{O}_3:\text{Eu}^{3+}\) [3,4] oxides, and the green-emitting \(\text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+}\) [5,6]—became commercially available. These phosphors have been some of the most popular commercialized oxide phosphors. Fluorescent lamps (FLs) employing these oxide phosphors offered luminous output equivalent to that of the lamps employing the common calcium halophosphate phosphor [7]. Although the basics of industrial-scale phosphor synthesis were well-established a decade ago, the development of new phosphors continues because of the importance of phosphor efficiency required for different applications as well as for production cost and hence market share. The following are the basic requirements for an efficient FL phosphor [8]: it should retain its luminescent characteristics at 50 °C, i.e., the operating temperature of the FL; it must be capable of being prepared in a finely divided form (~7 μm) and should retain its luminescent characteristics over long periods of operation in a lamp; and it should be a non-toxic inorganic material of a sufficiently stable nature that will enable it to withstand both processing and operating conditions. A typical FL consists of a glass tube lined on the inside with a coating of phosphor material and filled with a mixture of mercury vapor and argon. As electric current flows through the lamp, the mercury atoms are bombarded by electrons and excited to produce emissions at 254 nm (~65%) and 185 nm (~20%) [9] as well as in the longwave UV and visible light regions (weaker mercury emission lines at 365, 405, 436, 546, and 577 nm) [10]. Therefore, the phosphors must also have strong optical absorption in the shortwave UV region of 254 nm.

2. Experimental

Polycrystalline \(\text{Ba}_3\text{Y}(\text{PO}_4)_2:\text{Ce}^{3+},\text{Tb}^{3+}\) and \(\text{Ca}_3\text{Y}(\text{AlO})_3(\text{BO}_4)_2:\text{Eu}^{3+}\) phosphors were synthesized by a conventional high-temperature solid-state reaction. For the synthesis of \(\text{Ba}_3\text{Y}(\text{PO}_4)_2:\text{Ce}^{3+},\text{Tb}^{3+}\) phosphors by mixtures of the chemical constituents in stoichiometric molar ratio of \(\text{BaCO}_3: \text{Y}_2\text{O}_3: (\text{NH}_4)_2\text{HPO}_4: \text{CeO}_2: \text{Tb}_2\text{O}_3 = 3: (1/2-x-y/4): 3: x: y/4\) in an agate mortar, pressed into pellets and calcined at 1400°C for 6 h. The obtained samples were reduced at 1000 °C for 6 h under an reducing atmosphere of 15% \(\text{H}_2\) / 85% \(\text{N}_2\) in an alumina boat. For \(\text{Ca}_3\text{Y}(\text{AlO})_3(\text{BO}_4)_2:\text{Eu}^{3+}\) phosphors, \(\text{CaCO}_3: \text{Y}_2\text{O}_3: \text{Al}_2\text{O}_3: \text{H}_2\text{BO}_3: \text{Eu}_{2}\text{O}_3 = 3: (1/2-x): 3/2: 4: 2: x\) were calcined at 1100 °C for 8 h, an excess 5 mole % of \(\text{H}_2\text{BO}_3\) as a flux.

All crystal structure compositions were checked for phase formation by using powder X-ray diffraction analysis with a Bruker AXS D8 advanced automatic diffractometer with Cu Kα radiation. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the samples were analyzed by using a Spex Fluorolog-3 Spectrofluorometer equipped with a 450-W Xe light source. The Commission International de l’Eclairage (CIE) chromaticity coordinates for all samples were measured by a Laiko DT-101 color analyzer equipped with a CCD detector (Laiko Co., Tokyo, Japan). A white-light FL was fabricated by filling a single-U configuration quartz glass with mercury (~1.1 mg) and argon (~6.1 torr). The inner surface of the quartz glass lamp envelope has a luminescent coating—a blend of green-emitting \(\text{BY}:0.25\text{Ce}^{3+},0.25\text{Tb}^{3+}\), red-emitting \(\text{CY}:0.5\text{Eu}^{3+}\) and blue-emitting \(\text{BAM}:\text{Eu}^{2+}\)—which emits visible white-light when excited by UV radiation, and a pair of discharge electrodes each arranged at a respective sealed end of the lamp envelope.
3. Results and discussion

Figure 1 illustrates the X-ray powder diffraction patterns for \( \text{Ba}_3\text{Y(PO}_4\text{)}_3\text{Ce}^{3+}\text{Tb}^{3+} \) (BYP:Ce,Tb) and \( \text{Ca}_3\text{Y(AlO)}_3\text{(BO}_3\text{)}_4\text{Eu}^{3+} \) (CYAB:Eu) phosphors. The results indicate that all samples of BYP and CYAB match well with the XRD patterns for \( \text{Ba}_3\text{Y(PO}_4\text{)}_3 \) (JCPDS:044-0318) [11] and \( \text{Ca}_3\text{Y(AlO)}_3\text{(BO}_3\text{)}_4 \) (ICSD:172154) [12]. In addition doping BYP or CYAB with \( \text{Ce}^{3+} \) and \( \text{Tb}^{3+} \) or \( \text{Eu}^{3+} \) does not produce any significant change in the crystalline structure.

Figure 2 shows the concentration effect of \( \text{BYP:0.15Ce}^{3+},x\text{Tb}^{3+} \) and \( \text{CYAB:xEu}^{3+} \) with various concentrations of \( \text{Tb}^{3+} \) and \( \text{Eu}^{3+} \). For \( \text{BYP:0.15Ce}^{3+},x\text{Tb}^{3+} \) phosphors, the photoluminescence (PL) intensity increases with \( \text{Tb}^{3+} \) content until a maximum \( x \) value of about 0.25 mol, after which it decreases due to interactions between \( \text{Tb}^{3+} \) ions. For \( \text{CYAB:xEu}^{3+} \) phosphors, the optimal doping concentration was observed at 0.50 mol, and the PL intensity was found to decline dramatically as the content of \( \text{Eu}^{3+} \) exceeded 0.50 mol due to concentration quenching. The PL spectra for \( \text{BYP:Ce}^{3+} \) phosphors show the parity- and spin-allowed \( 5d^1 \rightarrow 4f^1 \) band emission of \( \text{Ce}^{3+} \) centered at 367 nm [13]. The BYP co-doped \( \text{Ce}^{3+}, \text{Tb}^{3+} \) phosphor shows the broad band emission of \( \text{Ce}^{3+} \) and sharp characteristic emissions of \( \text{Tb}^{3+} \), i.e., several bands centered at 485, 540, 580, and 619 nm corresponding to transitions from the \( 5D_4 \) level to the \( 7F_6, 7F_5, 7F_4, \) and \( 7F_3 \) levels [14], respectively. Results for the \( \text{CYAB:Eu}^{3+} \) phosphors reveal that the absorption is mainly attributed to an \( \text{O}^{2-} \rightarrow \text{Eu}^{3+} \) charge transfer at about 254 nm, and that the emission spectrum under 254 nm excitation consists of four groups of emission lines located at about 596, 620, 645 and 691 nm. These four groups are due to the \( 5D_0 \rightarrow 7F_J (J = 1, 2, 3, 4) \) transitions [15]. The strong line at 620 nm corresponds to the electric dipole \( 5D_0 \rightarrow 7F_2 \) transition.
Figure 3 shows the optimal-emission intensity of the green-emitting phosphor BYP:0.25Ce\(^{3+}\),0.25Tb\(^{3+}\) compared to that of a commercial LaPO\(_4\):Ce\(^{3+}\),Tb\(^{3+}\) phosphor, and the optimal-emission intensity of the red-emitting phosphor CYAB:0.5Eu\(^{3+}\) compared to those of phosphors Y\(_2\)O\(_2\)S:Eu\(^{3+}\) and Y\(_2\)O\(_3\)S:Eu\(^{3+}\) under excitation at 254 nm. The PL spectrum of the BYP:Ce\(^{3+}\), Tb\(^{3+}\) phosphor shows sharp, characteristic green emission bands centered at 540 nm corresponding to the \(^5\)D\(_4\) \rightarrow \(^7\)F\(_3\) transition of Tb\(^{3+}\) [14], and the emission intensity of BYP:0.25Ce\(^{3+}\),0.25Tb\(^{3+}\) is 70% of that of a commercial LaPO\(_4\):Ce\(^{3+}\),Tb\(^{3+}\) phosphor. The CYAB:Eu\(^{3+}\) phosphor shows sharp red emissions centered at 620 nm attributed to the electric dipole \(^5\)D\(_0\) \rightarrow \(^7\)F\(_2\) transitions of Eu\(^{3+}\) [15], and the emission intensity of CYAB:0.5Eu\(^{3+}\) is 70% and 83% of those of the Y\(_2\)O\(_2\)S:Eu\(^{3+}\) and Y\(_2\)O\(_3\)S:Eu\(^{3+}\) phosphors, respectively.

Temperature dependence is highly important for FL applications. The temperature-dependent relative emission intensities of BYP:0.25Ce\(^{3+}\),0.25Tb\(^{3+}\) and CYAB:0.5Eu\(^{3+}\) phosphors and of commercial phosphors under excitation at 254 nm are compared in Fig. 4. As seen from the insets, the relative emission intensity decreases as the temperature increases. We observed a decay of only 3% at 150 °C for BYP:0.25Ce\(^{3+}\),0.25Tb\(^{3+}\) (3% for LaPO\(_4\):Ce\(^{3+}\),Tb\(^{3+}\)), and a decay of 6% at 200 °C for CYAB:0.5Eu\(^{3+}\) (10% for Y\(_2\)O\(_3\):Eu\(^{3+}\), 35% for Y\(_2\)O\(_3\)S:Eu\(^{3+}\)). The results indicated that the thermal stability of BYP:0.25Ce\(^{3+}\),0.25Tb\(^{3+}\) above 150 °C is higher than that of the commercially available LaPO\(_4\):Ce\(^{3+}\),Tb\(^{3+}\), and that...
CYAB:0.5Eu$^{3+}$ above 200 °C showed less serious thermal quenching than Y$_2$O$_3$:Eu$^{3+}$ or Y$_2$O$_2$S:Eu$^{3+}$, respectively.

Fig. 4. Temperature dependence of relative emission intensities for (a) BYP:0.25Ce$^{3+}$,0.25Tb$^{3+}$; (b) CYAB:0.5Eu$^{3+}$ ($\lambda_{\text{ex}} = 254$ nm). The insets show comparisons of thermal stability between (a) BYP:Ce$^{3+}$,Tb$^{3+}$ and LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$; (b) CYAB:Eu$^{3+}$, Y$_2$O$_3$:Eu$^{3+}$ and Y$_2$O$_2$S:Eu$^{3+}$ ($\lambda_{\text{ex}} = 254$ nm).

Fig. 5. CIE chromaticity diagram of BYP:0.25Ce$^{3+}$,0.25Tb$^{3+}$ and CYAB:0.5Eu$^{3+}$ phosphors mixed with different weight ratios and excited at 254 nm. (1) 1:0; (2) 4:1; (3) 3:1; (4) 3:2; (5) 3:3; (6) 2:3; (7) 1:3; (8) 0:1; and commercial phosphors (9) Y$_2$O$_2$S:Eu$^{3+}$; (10) Y$_2$O$_3$:Eu$^{3+}$; (11) LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$; (12) BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$; (13) white-light phosphors (mixing of BYP:0.25Ce$^{3+}$,0.25Tb$^{3+}$, CYAB:0.5Eu$^{3+}$, BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$); (14) white-light Fluorescent Lamp.

Figure 5 illustrates the CIE chromaticity diagram of BYP:0.25Ce$^{3+}$,0.25Tb$^{3+}$ and CYAB:0.5Eu$^{3+}$ phosphors mixed at different weight ratios of 1:0, 4:1, 3:1, 3:2, 3:3, 2:3, 1:3, and 0:1. The CIE chromaticity diagram is found to be tunable from green through yellow to red in the visible spectral region, with chromaticity coordinates ($x$, $y$) correspondingly varying from (0.323, 0.534) to (0.652, 0.342), by controlling the weights of the BYP:0.25Ce$^{3+}$,0.25Tb$^{3+}$ and CYAB:0.5Eu$^{3+}$ phosphors. White-light phosphors were fabricated by using a phosphor blend of composition-optimized green-emitting BYP:0.25Ce$^{3+}$,0.25Tb$^{3+}$, red-emitting CYAB:0.5Eu$^{3+}$ and blue-emitting BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$, which the CIE color coordinates $x = 0.324$ and $y = 0.317$. 
Fig. 6. PL spectrum of a fluorescent lamp fabricated using mercury vapor and mixture of BAM:Eu$^{2+}$, BYP:0.25Ce$^{3+}$,0.25Tb$^{3+}$, and CYAB:0.5Eu$^{3+}$ phosphors. The insets show the 8 W white-light fluorescent lamps.

Figure 6 is the EL spectrum of a white-light FL under a power of 8 watts. The radiation emitted by the gas discharge is mostly in the UV region of the spectrum, with only a small portion in the visible spectrum. The excited fluorescent layer efficiently emits a white light having three main peaks at around the 445 nm emission of BAM:Eu$^{2+}$, the 540 nm emission of BYP:0.25Ce$^{3+}$,0.25Tb$^{3+}$ and the 620 nm emission of CYAB:0.5Eu$^{3+}$. The white-light FL shows CIE chromaticity coordinates of x = 0.33, y = 0.35, a warm white light with a correlated color temperature (CCT) of 5646 K, and an average color-rendering index (CRI) of Ra = 70.

4. Conclusion
In summary, we have analyzed and demonstrated the creation of a warm white-light FL. The emission intensity for the composition-optimized green-emitting phosphor Ba$_3$(Y$_{0.5}$Ce$_{0.25}$Tb$_{0.25}$)(PO$_4$)$_3$ is 70% that of commercial LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$, and the emission intensity for the red-emitting phosphor Ca$_3$(Y$_{0.5}$Eu$_{0.5}$)(AlO)$_3$(BO$_3$)$_4$ is 70% and 83% of those of Y$_2$O$_3$:Eu$^{3+}$ and Y$_2$O$_2$:Eu$^{3+}$ phosphors, respectively. The Ba$_3$(Y$_{0.5}$Ce$_{0.25}$Tb$_{0.25}$)(PO$_4$)$_3$ and Ca$_3$(Y$_{0.5}$Eu$_{0.5}$)(AlO)$_3$(BO$_3$)$_4$ phosphors show high thermal stability compared to commercial LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$, Y$_2$O$_3$:Eu$^{3+}$ and Y$_2$O$_2$:Eu$^{3+}$, and matching blue-emitting phosphors show that the quality of the brightness and color reproduction is suitable for application to short UV FLs. These results indicate that the white-light FL has CIE = (0.33, 0.35), CCT = 5646 K, and CRI = 70.

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