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A study on the luminescent properties of new green-emitting terbium-activated $\text{CaIn}_2\text{O}_4 : x\text{Tb}$ phosphors

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Abstract

Calcium indate phosphors have been prepared by solid-state reactions at 1400°C. This indate matrix permits photoluminescence when doped with terbium. It was found that under ultraviolet excitation with a wavelength of 254 nm the phosphors revealed yellowish green luminescence that was attributed to the transitions from $^5\text{D}_4$ excited state to $^7\text{F}_j$ multiplet ground states of Tb^{3+} ions. The powder X-ray diffraction, photoluminescence spectra, brightness, fluorescence decay lifetime, and chromatic characteristics of the Tb^{3+} -activated CaIn_2O_4 phosphors were systematically investigated and reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: $\text{CaIn}_2\text{O}_4 : x\text{Tb}$ phosphor; Photoluminescence spectra; CIE coordinates decay lifetime

1. Introduction

In recent years, great efforts have been made to develop efficient phosphor systems. Among these, a number of works have been carried out on investigations of the luminescent properties for borates [1], aluminates [2] and gallates [3]. From the fact that indium belongs to the same group as boron, aluminum and gallium in the periodic table, it was suggested that metal indates might also act as a potential host lattice for luminescence. This consideration prompted us to extend our research to compounds with different compositions in the ternary Ca–In–O system. We have been working with a semiconducting compound

CaIn_2O_4 as a potential host matrix for phosphors since its band gap of 3.9 eV [4] is wide enough to incorporate visible luminescence centers such as rare-earth ions. Moreover, no self-activated photoluminescence was observed for the undoped CaIn_2O_4 samples measured at ambient temperature.

Recently, we have synthesized and characterized a series of Pr^{3+} -doped CaIn_2O_4 that emits orange fluorescence under ultraviolet excitation. Some results obtained from the spectroscopic and luminescence studies have already been reported elsewhere [5]. Since Tb^{3+} -activated green phosphors have been reported in three-band fluorescent lamps (e.g., $(\text{Ce},\text{Gd})\text{MgB}_5\text{O}_{10} : \text{Tb}^{3+}$ [6]), projection television tubes (e.g., $\text{Y}_3\text{Al}_5\text{O}_{12} : \text{Tb}^{3+}$ [7]), and X-ray intensifying screens (e.g., $\text{Gd}_2\text{O}_2\text{S} : \text{Tb}^{3+}$ [8]), our work is essentially motivated by the quest to acquire a deeper insight into the materials nature of CaIn_2O_4 as a potentially

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effective host lattice for green phosphors containing the Tb^{3+} ion as an activator.

The optical properties of Tb^{3+} in different host matrices have been extensively studied [9–11]. In view of its intense luminescence in the visible region, the transitions from $^5\text{D}_3$ and $^5\text{D}_4$ to the $^7\text{F}_J$ multiplet ground states have been proposed. To the best of our knowledge, there has not been any study on Tb^{3+} -activated CaIn_2O_4 host reported in the literature. In the present work, we report in detail the investigation results of the photoluminescent properties, possible radiative relaxation mechanisms and fluorescence decay lifetimes for a series of Tb^{3+} -activated CaIn_2O_4 phosphors.

2. Experimental procedure

Polycrystalline $(\text{Ca}_{1-x}\text{Tb}_x)\text{In}_2\text{O}_4$ (as $\text{CaIn}_2\text{O}_4:x\text{Tb}$) phases with $x = 0.125\%$, 0.5% and 2% were investigated, respectively. The series of samples were synthesized by conventional solid-state reactions. Stoichiometric amounts of constituent materials CaO , In_2O_3 , and Tb_4O_7 with high purity (99.9%, all from Aldrich Chemicals Co., Milwaukee, WI, USA) were finely ground together. Without addition of any flux, the mixtures were then calcined at 550°C for 6 h to avoid the inclusion of carbonate impurities and, subsequently, sintered at 1400°C for 24 h in air.

The chemical purity and phase homogeneity of the as-prepared polycrystalline $\text{CaIn}_2\text{O}_4:x\text{Tb}$ phosphors were examined by powder X-ray diffraction (XRD) profiles. The XRD data were collected in the range of $5^\circ < 2\theta < 80^\circ$ by using a MAC Science MXP-3 automatic diffractometer (MAC Science Co., Tokyo, Japan) equipped with graphite-monochromatized and Ni-filtered $\text{CuK}\alpha$ radiation operating at 40 kV and 20 mA. Only single-phased samples were used for further studies.

The measurements of photoluminescence (PL) emission and excitation (PLE) spectra were carried out at room temperature by means of a Spex Fluorolog-3 spectrofluorometer (Instruments S.A., Inc., Edison, NJ, USA) equipped with a 450 W Xe lamp as an excitation source. The spectral

response of the measurement system was calibrated automatically on start-up. The samples were excited under 45° incidence and the emitted fluorescence was recorded by a Hamamatsu R-928 type photomultiplier (Hamamatsu Photonics, Hamamatsu, Japan) positioned perpendicular to the incident beam. To eliminate the second-order emission of the source radiation, a cut-off filter was used in the measurements. The reflectance spectra for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ samples were measured with a Shimadzu UV-2501PC double-beam UV-VIS spectrometer (Shimadzu Co., Tokyo, Japan) with Al_2O_3 used as a standard.

The fluorescence decay lifetimes (τ) were measured by exciting the samples with UV of 248 nm by using a Lamda Physik LPX150 T excimer laser (Spectra-Physics Co., Mountain View, CA, USA) and pulse duration of 0.1 s. The CIE chromaticity coordinates and relative brightness were determined by using a Minolta CS-100 chromameter (Minolta Co., Tokyo, Japan).

3. Results and discussions

The XRD profiles for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ phases with $x = 0.125\%$, 0.5% , and 2% are shown in Fig. 1. As a result, a typical CaIn_2O_4 pattern [12] was observed in the XRD profiles for all the samples investigated. No peak corresponding to any of the source materials or allotropic forms was found, suggesting that a pure crystalline compound with the same structure as CaIn_2O_4 exists. As expected, no obvious shifting of the diffraction peaks was observed as x increases, since the variation of unit cell dimension as a result of a small amount of replacement of Tb^{3+} is beyond the detection limit of the XRD technique.

The ambient temperature PL emission spectra of $\text{CaIn}_2\text{O}_4:x\text{Tb}$ ($x = 0.125\%$, 0.5% and 2%) phosphors excited with 254 nm UV excitation are shown in Fig. 2. These phosphors exhibited a typical, characteristic Tb^{3+} emission. The photoluminescent properties of the three phosphors with different levels of Tb^{3+} doping do not differ greatly from each other and no obvious red or blue shift in wavelength was observed.

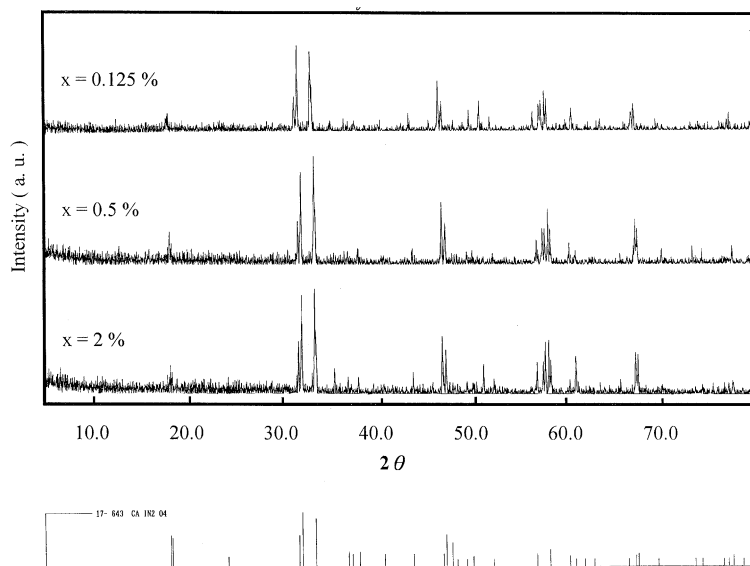


Fig. 1. The XRPD patterns for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ phases with $x = 0.125\%$, 0.5% and 2% , respectively.

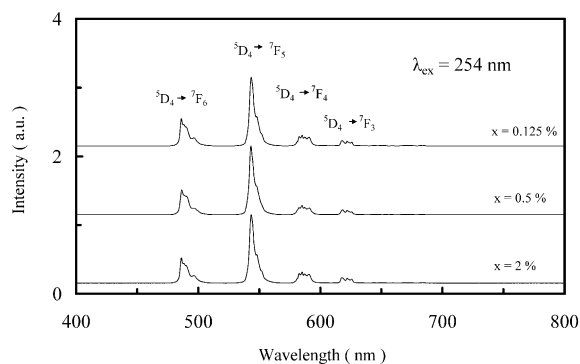


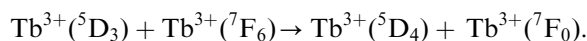
Fig. 2. The PL emission spectra for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ phosphors with $x = 0.125\%$, 0.5% and 2% , respectively.

The fluorescence of Tb^{3+} mainly originated from the transitions from $^5\text{D}_3$ to $^7\text{F}_J$ and/or $^5\text{D}_4$ to $^7\text{F}_J$ (where $J = 1, 2, 3, 4, 5, 6$, respectively). When the Tb^{3+} -activated phosphors are excited by ultraviolet excitation of 254 nm, the Tb^{3+} ions ($4f^8$) would be excited to higher $4f^7 5d^1$ levels and feed afterward, nonradiatively, the $^5\text{D}_3$ or/and $^5\text{D}_4$ excited states. Due to the relatively wide energy gap (i.e., at least $13,000\text{ cm}^{-1}$) between these excited states and the $^7\text{F}_J$ multiplet ground state, the relaxation process occurs only radiatively,

namely, through the emissions in the visible spectral region.

In general, for systems with homogeneously distributed Tb^{3+} activator, a blue emission attributed to the transition from $^5\text{D}_3$ excited state to $^7\text{F}_J$ ground states occurring at wavelength below 485 nm was observed at low Tb^{3+} concentrations [13]. This blue emission was generally found to vanish while the Tb^{3+} concentration is increased beyond the critical concentration for cross-relaxation to occur [14]. On the other hand, there exists another category of Tb^{3+} -activated phosphors such as $\text{CsCdBr}_3:\text{Tb}$ [15] and $\text{LnBO}:\text{Tb}$ [16], exhibiting no blue emissions even at very low Tb^{3+} concentration. The Tb^{3+} ions doped in the CsCdBr_3 matrix were reported to incorporate in pairs or clusters by Lammers et al. [15] and the formation of pairs or clusters of Tb^{3+} implies that the energy transfer between Tb^{3+} ions may occur even for very low concentrations. Therefore, the so-called cross-relaxation can be dominant and, thus, nonradiative relaxation from $^5\text{D}_3$ state to lower $^5\text{D}_4$ level occurs, as proposed by Fordster [17] and Blasse [18] and, consequently, the absence of $^5\text{D}_3$ emission in the PL spectra for $\text{CaIn}_2\text{O}_4:x\text{Tb}^{3+}$ is expected and only the $^5\text{D}_4$ emission with relatively high intensity was observed.

As shown in Fig. 2, it was noted that the blue emission from 5D_3 level to 7F_J multiplets is absent in all three $\text{CaIn}_2\text{O}_4:x\text{Tb}^{3+}$ phases. The observation can be rationalized by the fact that the emission derived from 5D_3 emissions may be quenched by two types of nonradiative relaxation process [19], viz., cross-relaxation mechanism and multiphonon mechanism that result in the rapid population of the 5D_4 level at the expense of 5D_3 . The cross-relaxation occurs only above a certain concentration of Tb^{3+} [19] and is induced by the resonance between the excited states and the ground states of two Tb^{3+} ions described in the following equation [17,18]:



The occurrence of this process depends on the interaction between two adjacent Tb^{3+} ions. For the very low concentration of Tb^{3+} in $\text{CaIn}_2\text{O}_4:x\text{Tb}$ ($x = 0.125\%$), the Tb^{3+} ions are postulated to incorporate in pairs or clusters as in CsCdBr_3 [15] for the relaxation to occur.

On the other hand, the multiphonon mechanism is intrinsically a thermal relaxation process, i.e., the relaxation of energy into lattice vibration [20]. For Tb^{3+} , the relaxation starts from the pure electronic state A of 5D_3 to the electron–phonon-coupled state of 5D_4 with phonons occurring at A and followed by the instantaneous transfer to C and, subsequently, relaxation to B [20], as indicated in the following configurational coordinate diagram.

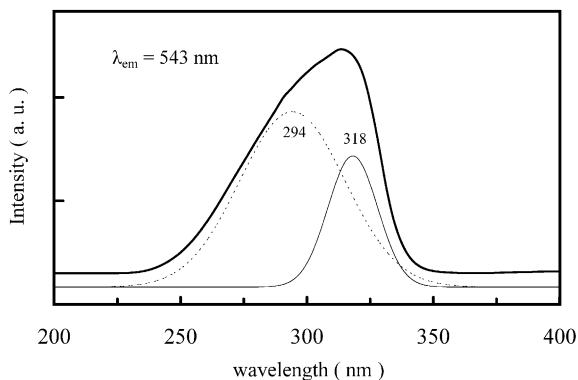
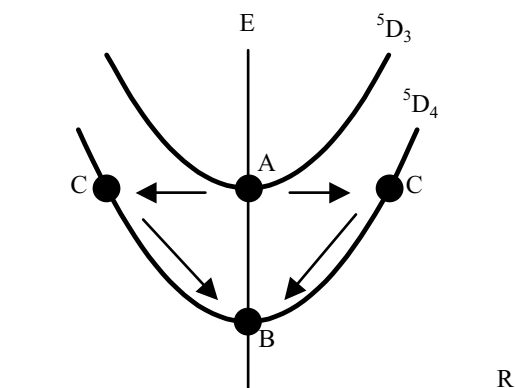


Fig. 3. The PL excitation spectra for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ phosphors with $x = 0.125\%$ (see also text).

Hence, the green to red emissions at 486, 543, 585, and 618 nm that correspond to transitions from 5D_4 to 7F_6 , 7F_5 , 7F_4 and 7F_3 multiplet ground states of Tb^{3+} , respectively, are remarkably enhanced. Since the J values of the 7F_J ground states are high, the crystal field splits the levels into many sublevels and gives the spectrum its complicated appearance and fine structures. The phosphor of $\text{CaIn}_2\text{O}_4:x\text{Tb}$ exhibiting no blue emissions belongs to the same category as $\text{CsCdBr}_3:\text{Tb}$ and $\text{LnBO}_3:\text{Tb}$ phosphors.

The excitation spectrum for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ ($x = 0.125\%$) measured with an emission wavelength (λ_{em}) of 543 nm is shown in Fig. 3. The spectrum was characterized by an asymmetrical broad band with wavelength ranging from 250 to 350 nm. This broad band could be deconvoluted into two Gaussian-shaped bands centered at 294 and 318 nm, represented as a dashed line and a thin solid line in Fig 3, respectively. As indicated by the comparison of Figs. 2 and 3, the excitation spectrum is comparable to the absorption spectrum and the two bands can be reasonably referred to two different absorption mechanisms.

As noted in the diffuse reflectance spectrum for the undoped CaIn_2O_4 sample shown in Fig. 4, the optical band gap of the compound was roughly estimated to be 3.86 eV that amounts to ca. 318 nm observed in the reflectance spectrum (similar to that reported in Ref. [4]). The absorption band observed at 318 nm in the excitation spectrum was then inferred to be the absorption of the host

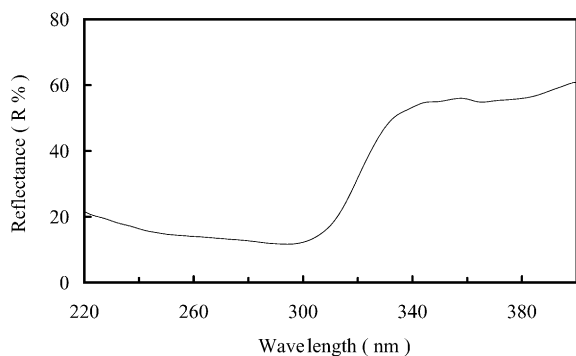


Fig. 4. The diffuse reflectance spectrum of CaIn_2O_4 .

lattice itself. On the other hand, the absorption band at 294 nm was essentially attributed to the absorption of the Tb^{3+} ions.

The allowed transitions of rare-earth ions are interconfigurational and consist of two different types, viz., charge-transfer transitions and $4f^n \rightarrow 4f^{n-1} 5d$ transitions. The charge-transfer transitions were found for rare-earth ions, which are likely to be reduced, such as Eu^{3+} and Sm^{3+} . For trivalent ions having a tendency to become tetravalent, the $4f \rightarrow 5d$ absorption band in the ultraviolet was often observed, for instance, Pr^{3+} and Tb^{3+} [21]. From these arguments, the absorption band at 294 nm, being well above the host absorption edge, can be ascribed to the $4f \rightarrow 5d$ transitions of Tb^{3+} in CaIn_2O_4 matrix.

Considering the large area ratio of band at 318 nm/band at 294 nm (i.e., 0.53), the band centered at 318 nm at the absorption edge of the host that gives rise to significant emission indicates that the energy transfer from the host to the activator ions is efficient in this condition. Furthermore, no obvious $4f \rightarrow 4f$ absorption features were observed in the excitation spectrum, since the parity-selection rule forbids these transitions.

To examine the quenching effect on the brightness due to activator concentration, a number of samples were prepared with terbium content varying from 0.125 to 2 at%. The relative brightness is displayed as a function of Tb^{3+} concentration and represented in Fig. 5. The activator concentration dependence of brightness can be

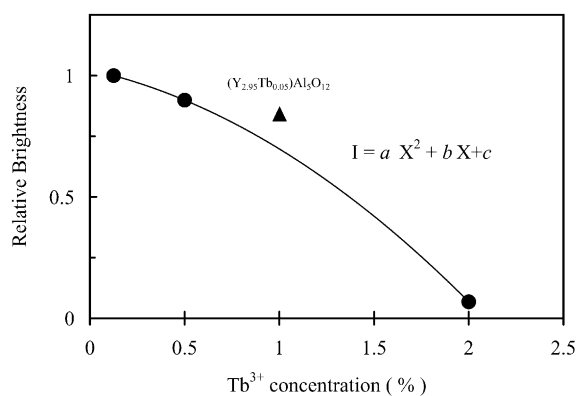


Fig. 5. The relative brightness as a function of Tb^{3+} contents for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ phosphors. The solid line indicates the activator concentration dependence of brightness.

well fitted with a solid line in Fig. 5 according to the following equation:

$$I = ax^2 + bx + c,$$

where I is the relative brightness, a , b and c are constants and x is Tb^{3+} concentration (at%). The values of a , b , c and deviation (R^2) were found to be -0.152 , -0.175 , 1.024 and 1 , respectively. From these results, it was concluded that the maximal brightness was obtained for the sample with a terbium concentration of 0.125% and the brightness decreased by more than one order of magnitude while Tb^{3+} concentration was increased from 0.125% up to 2%. The decrease in brightness with increasing activator concentration was presumably due to the well-established theory of concentration quenching [22]. Moreover, $\text{CaIn}_2\text{O}_4:x\text{Tb}$ ($x = 0.125\%$) was found to be much brighter than $(\text{Y}_{2.95}\text{Tb}_{0.05})\text{Al}_5\text{O}_{12}$ under 254 nm UV excitation, as indicated by brightness measurements.

The fluorescence decay lifetime (τ) for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ is defined as the time required for the fluorescence intensity to decay down to $1/e$ of its initial value [23] and the measured lifetimes are summarized in Table 1. The fluorescence decay lifetimes for the phosphors were found to be in the range of microseconds and appear to meet the application requirements for CRT color televisions.

Table 1
The fluorescence decay lifetime (τ) for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ phosphors

X (%)	τ (μs)
0.125	195
0.5	150
2	102

Table 2
The relative brightness and CIE coordinates for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ phosphors

Compound	Relative brightness	Chromaticity coordinates
$\text{CaIn}_2\text{O}_4:0.125\% \text{ Tb}$	1	(0.36, 0.49)
$\text{CaIn}_2\text{O}_4:0.5\% \text{ Tb}$	0.91	(0.35, 0.50)
$\text{CaIn}_2\text{O}_4:2\% \text{ Tb}$	0.07	(0.33, 0.53)
$(\text{Y}_{2.95}\text{Tb}_{0.05})\text{Al}_5\text{O}_{12}$	0.75	(0.31, 0.51)

The PL emission spectra shown in Fig. 2 confirm the fact that the $\text{CaIn}_2\text{O}_4:x\text{Tb}$ phosphors emit in both the green and red spectral regions and the green emission was found to dominate the red. Consequently, the emission color for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ would shift slightly from pure green toward red and results in yellowish green. The emission color was analyzed and confirmed with the help of CIE chromaticity coordinates. The measured color coordinates for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ denoted by (x, y) are shown in Table 2. The coordinates were found to fall into the yellowish green region of the CIE chromaticity diagram and the hue of the phosphor becomes a deeper green with increasing terbium concentration, as shown in Fig. 6. Furthermore, as comparing to $(\text{Y}_{2.95}\text{Tb}_{0.05})\text{Al}_5\text{O}_{12}$, $(\text{Y}_{2.95}\text{Tb}_{0.05})\text{Al}_5\text{O}_{12}$ exhibits deeper green emission than $\text{CaIn}_2\text{O}_4:x\text{Tb}$ ($x = 0.125\%$) under the UV excitation of 254 nm.

4. Conclusions

A series of unprecedented yellowish green emitting $\text{CaIn}_2\text{O}_4:x\text{Tb}$ ($x = 0.125\%$, 0.5% and 2%) phosphors were synthesized at 1400°C. The PL emission spectra of these phosphors are

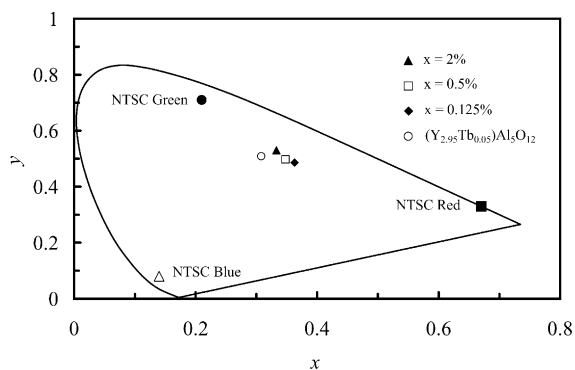


Fig. 6. Chromaticity diagram indicating the difference of hues for $\text{CaIn}_2\text{O}_4:x\text{Tb}$ phosphors, NTSC green, NTSC red and NTSC blue phosphors. (NTSC: National Television Standard Committee).

composed of four sharp bands with maxima at 486, 543, 585 and 618 nm which resulted from the $^5\text{D}_4$ transitions to $^7\text{F}_6$, $^7\text{F}_5$, $^7\text{F}_4$ and $^7\text{F}_3$ ground states of Tb^{3+} , respectively. The brightness was found to decrease with increasing activator concentration and the fluorescence decay lifetimes were determined in microsecond range and meet the requirements for CRT applications.

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