

EVIDENCE OF PRESENCE OF Ce^{3+} TRACES IN PRASEODYMIUM DOPED LUTETIUM AND YTTRIUM ORTHOBORATES AND THEIR INFLUENCE ON Pr^{3+} LUMINESCENCE SPECTRA

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Abstract

The luminescence of three compounds: LuBO_3 , with calcite and vaterite structures, and YBO_3 (vaterite structure) doped with Pr^{3+} ions has been investigated. The emission was ascribed to four spin-allowed transitions and one spin-forbidden transition from the $4f5d$ to the $4f^2$ configuration. Two additional broad emission bands with very weak intensity at 440 and 580 nm were studied. Evidence of the presence of Ce^{3+} traces is reported and their influence on Pr^{3+} luminescence is discussed.

1. Introduction

The trivalent praseodymium ion is an attractive optical activator since it offers the potential of laser action (both in the visible and infrared region) along with upconversion processes [1-2]. Furthermore, transitions between the opposite parity configurations $4f5d$ - $4f^2$ yield fast and intense broad emission bands in the near ultraviolet useful for scintillator applications [3] or tunable UV lasers [4]. In most host crystals, Pr^{3+} ion yields under $4f5d$ excitation an emission spectrum that consists of at least four intense bands in the near UV region [5]. These bands can be attributed unequivocally to the emission from the lowest $4f5d$ level of Pr^{3+} to $4f^2$ ground configuration triplets: $^3H_4, ^3H_5, (^3H_6, ^3F_2)$ and $(^3F_3, ^3F_4)$. However, additional broad bands with very weak intensity can be distinguished at longer wavelengths. In this work, we have focused our attention on the investigation of the origin of these weak broad bands.

2. Experimental details

LuBO_3 and YBO_3 powder samples doped with Pr^{3+} (1 at. %) were synthesized by means of a solid state reaction method described elsewhere [6]. LuBO_3 presents both a low-temperature calcite form and a high-temperature vaterite form, while YBO_3 may be obtained in the vaterite type only.

Room temperature excitation and emission spectra were recorded in the 200 - 800 nm range using a Perkin-Elmer LS 55 luminescence spectrometer. A powder holder was placed at a suitable angle with respect to the excitation beam to achieve maximum fluorescence and minimum scattered incident light. The spectra were corrected for wavelength dependent detection efficiency using the correction curve delivered by the supplier.

3. Experimental results and discussion

Figure 1 depicts the emission spectrum of calcite $\text{LuBO}_3:\text{Pr}^{3+}$ under 4f5d excitation (230 nm). The emission spectra of vaterite $\text{LuBO}_3:\text{Pr}^{3+}$ and $\text{YBO}_3:\text{Pr}^{3+}$ present an identical shape to that of calcite $\text{LuBO}_3:\text{Pr}^{3+}$, but are slightly shifted towards longer wavelengths. In each spectrum, at least four intense bands can be distinguished between 250 and 330 nm, numbered 1-4 in Fig. 1. These bands can be attributed, in order of decreasing energy, to the emission from the lowest crystal field component of the 4f5d excited configuration to the following groups of $4f^2$ ground configuration levels: $^3H_4, ^3H_5, (^3H_6, ^3F_2)$ and $(^3F_3, ^3F_4)$.

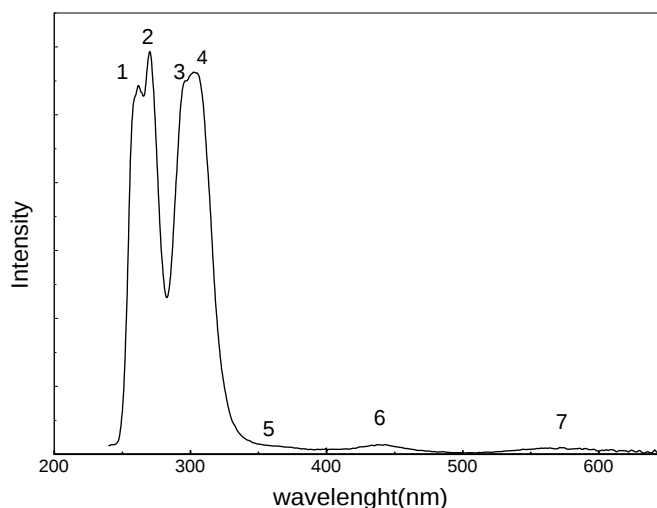


Figure 1. Emission spectrum of $\text{LuBO}_3:\text{Pr}^{3+}$ calcite under 4f5d excitation (230 nm)

In addition, broad bands with very weak intensity can be distinguished around 350 nm (band 5) and 582 nm (band 7) for all the three compounds, 440 nm for calcite LuBO_3 , 460 nm for vaterite LuBO_3 and 455 nm for YBO_3 (band 6). The weak intensity of band 5 relative to bands 1-4 suggests that we are in presence of a spin-forbidden transition. It could be attributed to a transition from the lowest 4f5d level of Pr^{3+} to the $4f^2$ configuration singlet level 1G_4 . It has been assumed before that the lowest 4f5d level is a triplet state in Pr^{3+} doped orthoborates [5]. This assumption could explain the fact that the transitions from the lowest 4f5d level to the spin triplets 3H_J and 3F_J are more intense than those to the spin singlet multiplets. The excitation spectrum of the band situated at 350 nm is identical to those measured for the intense bands 1-4, which indicates that it has a purely 4f5d - 1G_4 nature. However, the situation is more complex for the two bands situated around 440 – 460 nm and 580 nm as shown by figures 2 for the former and 3 for the latter.

3.1. Investigation of the emission band situated around 440-460 nm:

The excitation spectrum of calcite $\text{LuBO}_3:\text{Pr}^{3+}$ for 440 nm monitored emission wavelength exhibits two efficient excitation regions (Fig. 2a). The first region between 200 and 260 nm is characterized by a broad complex band that could be assigned to $4f^2$ –4f5d interconfigurational transitions in Pr^{3+} . The second region situated between 260 and 380 nm consists of a broad band with a maximum at 345 nm. In order to unravel the nature of this

band, we have measured the emission spectrum excited by 350 nm wavelength (Fig. 2b) which consists of two overlapping bands with a splitting around 2000 cm^{-1} .

The band positions and the characteristic value of the splitting are in good agreement with interconfigurational transitions from the lowest $^2T_{2g}$ level of 5d configuration to the $^2F_{5/2}$, $^2F_{7/2}$ spin-orbit components of 4f ground configuration observed previously in these compounds doped with trivalent cerium [6]. Excitation spectrum of these emission bands is displayed in Fig. 2c. The structure and the positions of these excitation bands are also in good agreement with those of trivalent cerium.

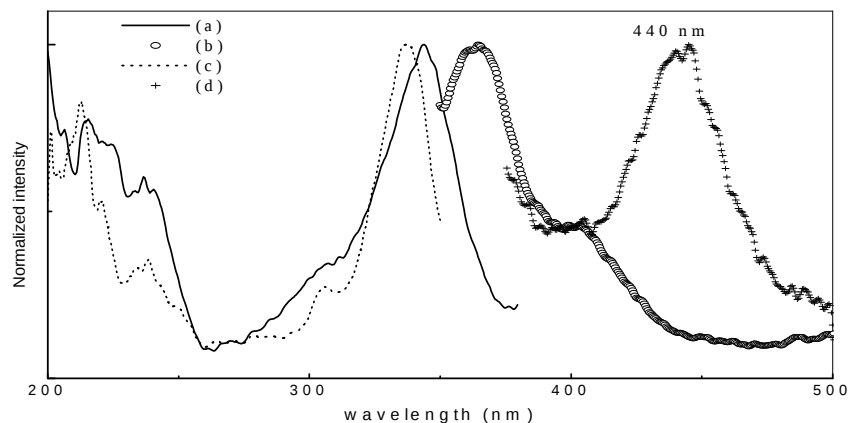


Figure 2. a) Normalized excitation spectrum of calcite LuBO_3 for 440 nm monitored emission wavelength
 b) Normalized emission spectrum of calcite LuBO_3 under 345 nm excitation wavelength
 c) Normalized excitation spectrum of calcite LuBO_3 for 5d - $^2F_{7/2}$ emission in Ce^{3+}
 d) Normalized 440 nm emission band under 230 nm excitation wavelength

It is important to note that emission and excitation spectra attributed to Ce^{3+} ions exhibit a very weak intensity relatively to those of Pr^{3+} , thus it is reasonable to assume that in our samples doped with trivalent praseodymium, some traces of trivalent cerium are present. It is well known that rare earths are often found in the same ores and are difficult to separate because of their similar chemical properties. The presence of traces of Ce^{3+} ions may be prejudicial for Pr^{3+} UV emission as excitation energy may be transferred from Pr^{3+} 4f5d levels to 5d levels of neighboring Ce^{3+} ions. In our case, despite the overlapping of Pr^{3+} UV emission bands and Ce^{3+} excitation bands, we did not observe clearly the characteristic emission of trivalent cerium under 4f5d excitation of Pr^{3+} . This excitation yields, in addition to bands 1-5, the emission band under study situated around 440-460 nm. Instead, the excitation at 345 nm yields clearly the characteristic Ce^{3+} emission spectrum, but with a very weak intensity. The band peaking at 345 nm overlaps with the low energy bands of Ce^{3+} excitation spectrum. Thus, it could be concluded that the 440-460 nm emission band stems from two distinct contributions: (i) a spin-forbidden transition from the lowest crystal field component of Pr^{3+} 4f5d configuration to the 4f² configuration singlet level 1D_2 , as its excitation spectrum shows clearly the 4f² (3H_4) – 4f5d excitation band of Pr^{3+} in the near UV region, (ii) the tail of Ce^{3+} emission spectrum, as its excitation spectrum contains also the band peaking at 345 nm which overlaps strongly with Ce^{3+} excitation bands. The band peaking at 345 nm could be related to some structure defect or impurity center present in these orthoborates. It is responsible for the transfer of a small amount of excitation energy

from Pr^{3+} to Ce^{3+} . Because of the small portion of Ce^{3+} ions existing in the samples, only a small amount of excitation energy can be transferred to them from Pr^{3+} .

3.2. Investigation of the emission band situated at 580 nm:

We have measured the excitation spectra for the three compounds by monitoring the emission wavelength corresponding to the maximum of the broad band with very weak intensity situated around 582 nm. The spectrum of calcite LuBO_3 is shown in Fig. 3a, in which two regions of efficient excitation may be clearly distinguished. The first region situated in the near UV between 200 and 300 nm, consists of one intense broad complex band, identical in shape and position to the excitation bands measured for the intense emission bands 1-4 and even 5 (figure 1) and consequently could be assigned to $4f^2(^3\text{H}_4) - 4f5d$ interconfigurational transitions in Pr^{3+} .

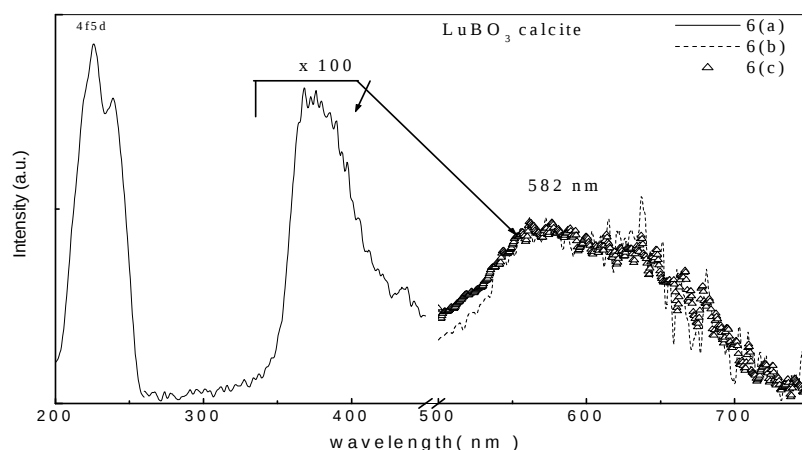


Figure 3. a) Excitation spectrum of calcite LuBO_3 for 582 nm monitored emission wavelength with enlarged intensity between 300 and 450 nm
b) 582 nm emission band of calcite LuBO_3 under 4f5d excitation (230 nm) with enlarged intensity
c) 582 nm emission band of calcite LuBO_3 under 375 nm wavelength excitation with enlarged intensity

The second region appears as a broad band with very weak intensity relative to the former (enlarged in Fig.3) peaking at around 375 nm for all the three orthoborates. Excitation upon 4f5d wavelength (230-240 nm) yields the 582 nm emission band observed in figure 1 and reproduced in Fig.3b with enlarged intensity. It is important to note that 375 nm excitation wavelength leads to a similar broad weak intensity emission band (Fig. 3c). The origin of the 375 nm excitation band is unclear, it could be related to an unknown defect level that is present in all the three compounds. The fact that both 4f5d and 375 nm excitations yield the same emission band peaking at 582 nm indicates that an energy transfer from Pr^{3+} to this unknown center occurs. The radiative decay of this center gives rise to the 582 nm emission band. Its weak intensity suggests the transfer rate from Pr^{3+} to this unknown center is very low.

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