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Luminescence and scintillation properties of $XPO_4:Nd^{3+}$ (X = Y, Lu, Sc, La) crystals

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ABSTRACT

Due to their very fast short-wavelength emission, neodymium-doped materials are a subject of current interest as potential scintillators. Although the initial reports regarding neodymium-doped orthophosphates (in crystalline form) and their scintillation properties appeared almost twenty years ago, they remain an interesting class of materials since there is no in-depth understanding of their fundamental scintillation mechanism. In the present research, we focus on the crystalline systems: $XPO_4:Nd^{3+}$, where X = Y, Lu, La, Sc. The pulse height, optical absorption, radioluminescence and photoluminescence spectra were investigated and are reported here for various temperatures from 10 to 350 K. Additionally, results of both low and high temperature thermoluminescence measurements are reported in this communication.

1. Introduction

Single crystals of neodymium activated YPO_4, $LuPO_4$, $LaPO_4$ and $ScPO_4$ were grown at the Oak Ridge National Laboratory [1] and their luminescence and scintillation properties are investigated here. The d-f emission of wide band-gap crystals peaking at about 190 nm makes such crystals suitable, for example, for use as UV detectors. Density is one of the more important features of scintillation materials and the densities of $YPO_4:Nd^{3+}$, $LuPO_4:Nd^{3+}$, $ScPO_4:Nd^{3+}$, $LaPO_4:Nd^{3+}$ are 4.28, 6.53, 3.71, and 4.12 g/cm^3, respectively [2,3].

It has previously been shown [4] that compounds with a general chemical formula XPO_4 (X - a lanthanide element) can be activated with relatively large concentrations of lanthanide ions without any significant alteration of their crystalline structure. In particular, various concentrations of neodymium ions in yttrium and lutetium orthophosphates have been investigated with respect to their light yield (LY) under ^{137}Cs excitation [5]. This prior research has shown that the LY does not solely depend on the activation level. The structural properties of yttrium, lutetium, scandium and lanthanum orthophosphates have been fully described previously [2,6,7], and $YPO_4:Nd^{3+}$ and $LuPO_4:Nd^{3+}$, in particular, have also already been recognized as promising VUV scintillation materials [5,8].

In this communication, we focus on a comparison of the luminescence properties of $XPO_4:Nd^{3+}$ (X = Y, Lu, La, Sc) crystals (including their pulse height spectra, radio- and photoluminescence spectra) as a function of temperature and thermoluminescence glow curves properties. Attention has been paid to the strong $4f^n{-}^1$5d-$4f^n$ (d-f) transitions important for the scintillation properties and to the $4f^n$-$4f^n$ (f-f) emission bands and lines.

2. Experiment

The crystals of $YPO_4:Nd^{3+}$ (1%), $LuPO_4:Nd^{3+}$ (2%), $LaPO_4:Nd^{3+}$ (1%), $ScPO_4:Nd^{3+}$ (2%) investigated here were grown by a high-temperature flux method [1]. Irregular plate samples about 2 mm in thickness with the two other dimensions not larger than 6 mm were selected for the present studies.

Absorption spectra between 190 and 1100 nm were obtained at room temperature with a Perkin-Elmer Lambda Series double beam spectrophotometer.

Radioluminescence spectra and low temperature thermoluminescence glow curves were recorded with a SpectraPro-500i (Acton

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Research Corporation) monochromator equipped with a Hamamatsu R928 photomultiplier. A LakeShore 330 Temperature Controller and a rotary vacuum pump were used to stabilize and control the thermal conditions inside the sample chamber. As an excitation source an Inel XRG3500 X-ray generator (Cu-anode tube, 45 kV, 10 mA) was used. All of the spectra were measured at temperatures ranging from 10 to 350 K under pressures below 10 mTorr. To separate the low temperature glow curves from afterglow, a long break (1 h) between the X-ray irradiation and the start of linear heating was employed. The heating rate was then 9 K/min.

The high temperature thermoluminescence was measured with a Microlab RA'04 Reader. With this equipment it was possible to obtain glow curves at temperatures from 315 up to 550 K using a heating rate of 2 K/s.

Photoluminescence spectra were obtained with a VM-504 (Acton Research Corporation) monochromator, attached to a turbo molecular pump and a deuterium lamp VO397 source (Princeton Instruments). The emission monochromator was a SpectraPro-300i (Acton Research Corporation), equipped with a Hamamatsu 1P28 photomultiplier. A LakeShore 331S temperature controller and again a rotary pump were used to stabilize and control the ambient conditions inside the sample chamber. This arrangement allowed us to record spectra at temperatures from 10 to 350 K.

The pulse height spectra at room temperature were measured with under gamma irradiation from a ^{137}Cs source using Canberra electronics, a Tukan 8k MCA and a Hamamatsu R2059 photomultiplier.

3. Results and discussion

The room temperature absorption spectra of the examined orthophosphates are compared in Fig. 1. In order to calculate the neodymium energy levels splitting (with the crystalline field included), we have assumed D_{2d} symmetry [2] for all of the compounds (in fact, it is C_1 for the La^{3+} site in $LaPO_4$ [9], nevertheless, since D_{2d} is a higher symmetry, this still is a good practical choice). We have employed the available energy parameters from Ref. [10] and performed similar calculations to those described in Ref. [11]. Correspondingly, all of the peaks characteristic of neodymium ions have been identified (see Table 1 and the vertical lines in Fig. 1). The broad band extending from 190 to 500 nm in the spectrum of

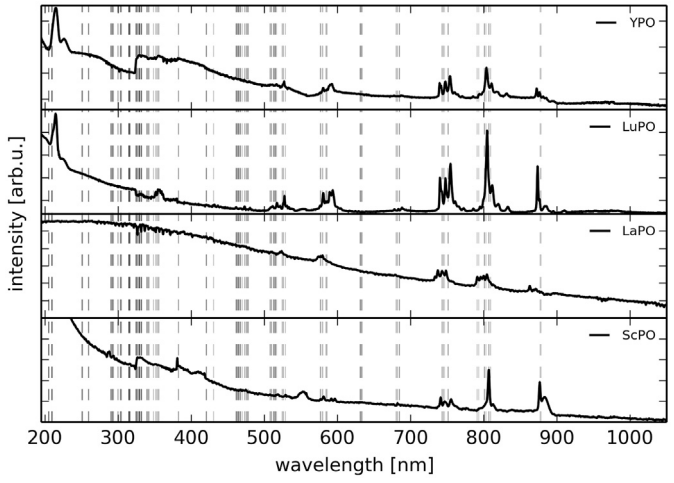

Fig. 1. Comparison of the optical absorption spectra at room temperature (the step features at about 325 nm are caused by switching between two light sources, dedicated to the UV and visible range, respectively).

Table 1
Identification of f-f transitions from $^4I_{9/2}$.

Lp.	Position [nm]	Energy level(s)	YPO_4	$LuPO_4$	$LaPO_4$	$ScPO_4$
1	215	$[^2G(2)_{9/2},^2G_{9/2}]$	+	+	–	–
2	270	$[^2F(2)_{5/2},^2F_{5/2}]$	+	–	–	+
3	330	$[^2L_{15/2},^2K_{15/2}]$	+	+	–	+
4	360	$[^4D_{3/2},^2D(2)_{3/2}]$	+	+	–	+
5	380	$[^2P_{3/2},^2D_{3/2}]$	+	+	–	+
6	420	$[^2D_{5/2},^4F_{5/2}]$	–	–	–	+
7	470	$[^2G_{9/2},^2G(2)_{9/2}]$	–	+	–	+
8	530	$[^4G_{7/2},^2G_{7/2}]$	+	+	+	+
9	580	$[^4G_{5/2}]$	+	+	+	+
10	680	$[^4F_{9/2},^2H(2)_{9/2}]$	+	+	+	+
11	750	$[^4F_{7/2},^2G_{7/2}]$	+	+	+	+
12	800	$[^2H(2)_{9/2},^4F_{9/2}]$	+	+	+	+
13	880	$[^4F_{3/2},^2D_{3/2}]$	+	+	+	+

$LaPO_4$:Nd^{3+} occurs due to the sample size and the presence of color center [1].

For each of the examined orthophosphates both radio- and photoluminescence spectra were measured, and spectral maps have been computed based on the sets of recorded spectra.

In Fig. 2a, b the radioluminescence of yttrium orthophosphate is presented. Strong d-f emission lines are observed from 200 to 320 nm. Additionally, a few f-f emission lines from the excited state $[^2L_{15/2},^2K_{15/2}]$ are detected. Below 150 K these lines are imposed on a broad band ranging from about 300 to 600 nm and peaking close to 420 nm. Such a band has been reported previously by Makhov et al. [8] and attributed to a self-trapped exciton (STE). In Fig. 2c the photoluminescence of YPO_4:Nd^{3+} is shown. Only two broad d-f bands are observed at 190 nm excitation - with the longer wavelength band strongly increasing in intensity towards low temperatures.

Fig. 3 shows the radio- and photoluminescence spectra of lutetium orthophosphate. These spectra have significantly less complicated structures than those observed for YPO_4:Nd^{3+}. They are clearly dominated by the d-f emission bands, with a slight addition of the f-f lines and, at lower temperatures, the STE-related band is observed.

Lanthanum orthophosphate shows the simplest structure of the spectra (see Fig. 4) among all of the examined samples. At room temperature only d-f bands below 380 nm and a few f-f lines from $[^2P_{3/2},^2D_{3/2}]$ are observed. The intensity of the f-f emission decreases with temperature. Below 100 K the longer wavelength d-f band weakens in favor of the STE luminescence. Potentially, this behavior may be due to some type of a radiative or nonradiative energy transfer that will require further investigation.

Fig. 5 displays the radio- and photoluminescence of scandium orthophosphate. Here the d-f emission appears as a broad band centered at 215 nm, while the remaining lines are identified as f-f transitions - respectively from $[^2H_{11/2},^2I_{11/2}]$, $[^2P_{3/2},^2D_{3/2}]$ and $[^2P_{1/2},^4D_{1/2}]$. Unlike the case of yttrium and lutetium orthophosphates, the STE emission has not been detected.

Fig. 6 shows the 662 keV gamma ray pulse height spectra taken at a shaping time of 2 μs. Due to the irregular sample shapes it has been difficult to ensure optimal conditions for the light collection - hence the full energy peaks are broad, which deteriorates the energy resolution. Moreover, the evaluated scintillation light yields are definitely underestimated, and comparing the present accumulated data with previously reported information is presently not warranted [12]. However, the spectra are sufficient to carry out a comparison of the sample characteristic with each other. With respect to both yield and resolution YPO_4:Nd^{3+} seems to provide the best choice, since it offers a light yield that is more than twice higher that of $LuPO_4$:Nd^{3+} or $LaPO_4$:Nd^{3+}, at an acceptable