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Luminescence study of the $LuBO_3$ and $LuPO_4$ doped with RE^{3+}

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ABSTRACT

Lutetium borates and phosphates doped with RE^{3+} ions are perspective scintillators. In the paper, the results of the luminescence spectroscopy of $LuPO_4$ and $LuBO_3$ doped with Pr^{3+}, Ce^{3+}, Tb^{3+} and Eu^{3+} under synchrotron radiation excitation are presented. The processes of the energy transfer from the host lattice to the luminescence centers are considered. The creation of excitons at the edge of fundamental absorption region is shown. The bandgap values for lutetium borate and phosphate were estimated.

1. Introduction

Borates and phosphates doped with rare-earth ions are considered as perspective materials for scintillating detectors, X-ray imaging and as plasma display panel phosphors (Balcerzyk et al., 2000; Rao and Devine, 2000). Incorporation of lutetium as a cation benefits in the increasing of material density and in high light yield in comparison to that with yttrium, gadolinium or lanthanum cations (Mansuy et al., 2004). The luminescence properties of $LuPO_4$ and $LuBO_3$ doped with RE^{3+} were widely investigated at the direct excitation of RE ions and at the high-energy excitation (X-rays). However, the luminescence properties at the excitation in the fundamental absorption region were poorly studied. Excitation spectra measured in this energy region contains information about the processes of energy transfer from the host lattice to the luminescence centers. This stage of relaxation is important for the efficient conversion of high-energy radiation into scintillations. The bandgap values (E_g) and information about excitons creation are also derived from the excitation spectra. Available data on the values of E_g are presented in Table 1. The results of the luminescence study of $LuPO_4$ and $LuBO_3$ doped with RE^{3+} ions (RE = Ce, Tb, Eu and Pr) are presented in the paper. Attention was focused on the processes of energy transfer from the host lattice to the luminescence centers as well as to the exciton creation on the edge of the fundamental absorption region.

2. Experimental details

$LuPO_4$ and $LuBO_3$ were synthesized by sol-gel method and characterized by the X-ray diffraction and scanning electron microscopy. X-ray phase analysis showed that the measured sample of $LuBO_3$ was crystallized in the vaterite structure. $LuPO_4$ crystallized in xenotime structure. Concentration of RE ions was 5 mol % for Tb, Eu and Pr and 0.5 mol% for Ce. Predominant size of the obtained crystalline particles varies in the range 250–1000 nm.

Spectroscopic study of the samples was carried out using synchrotron radiation in the energy region 3.7–22 eV at the SUPERLUMI station, DESY (Zimmerer, 2007). Synchrotron radiation is an ideal light source for the luminescence spectroscopy in VUV region due to its continuous spectrum, high intensity and temporal structure.

3. Results and discussion

Luminescence spectra of $LuPO_4$ doped with Tb, Eu and Pr as well as of $LuBO_3$ doped with Ce and Tb are presented in Fig. 1. Radiative transitions in RE ions determine the structure of luminescence spectra. Doublet in $LuBO_3$:Ce with maxima at 390 and 420 nm is due to the $5d–{}^2F_{5/2,7/2}$ transitions in Ce^{3+}. In $LuPO_4$:Tb and $LuBO_3$:Tb, four intensive groups of peaks at 480–500, 535–560, 580–595 and 615–635 nm are due to the ${}^5D_3–{}^7F_J$ (J = 3-6) transitions in Tb^{3+}. Three prominent groups of peaks were observed in $LuPO_4$:Eu at 585–600, 610–625 and 690–710 nm. These peaks are caused by ${}^5D_0–{}^7F_{1,2,4}$ transitions in Eu^{3+}. Peaks in $LuPO_4$:Pr are related to Pr^{3+} $4f5d–4f^2$ [3H, 3F] transitions in the range

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Table 1
Physical properties of $LuPO_4$ and $LuBO_3$.

	$LuPO_4$	$LuBO_3$
Structural type	Xenotime	Vaterite (V)/Calcite (C)
ρ, g/cm^3	6.53	7.42 (V) 6.87 (C)
Bandgap value, eV	8.7[a] 8.6[b] 8.85[c]	7.0[b] (V) 6.4[b] (C)

[a] Data on the bandgap values were taken from Lempicki and Wojtowicz, 1994.
[b] Data on the bandgap values were taken from Balcerzyk et al., 2000.
[c] Data on the bandgap values were taken from van Pieterson et al., 2002.

220–300 nm and $^3P_{0,1}$–$^3H_{4,6}$, $^3F_{2,4}$ transitions in the range 350–750 nm. For the latter sample, the additional peak at 313 nm was also observed that is the evidence of the presence of Gd^{3+} traces in this sample.

The excitation energy (10.8 eV) definitely exceeds the bandgap values of the crystals providing an opportunity for energy transfer to the intrinsic or defect-related luminescence centers. Actually for the $LuBO_3$ and $LuPO_4$ intrinsic luminescence is observed as broad bands with maxima at 360 nm and 280–300 nm, respectively (Duan et al., 2005; Wisniewski et al., 2002). These bands are not observed in Fig. 1 implying efficient energy transfer to the dopant luminescence centers even via interband excitation of the crystals.

The luminescence intensity was compared by integrating of the luminescence signal overall the spectral region of the measurements (see the inset to Fig. 1). The highest luminescence intensity was detected for the $LuBO_3$:Tb. For phosphates Tb-doped sample also demonstrates the highest luminescence intensity.

The excitation spectra of RE-luminescence for $LuPO_4$ crystals are presented in Fig. 2. Sharp lines with low intensity in the region 3–5 eV are ascribed to the parity-forbidden f-f transitions in RE ion (Mansuy et al., 2006). With further increase of excitation energy up to 8.5 eV, intensive groups of peaks ascribed to f–d parity-allowed transitions in Tb^{3+} and Pr^{3+} are observed (van Pieterson et al., 2002). For Eu^{3+}, the charge-transfer state lies at lower energies than $4f^55d$ state thus the broad peak at 5.8 eV corresponds to the luminescence excitation via charge-transfer state (Dorenbos, 2005). Parity-allowed f-d transitions in $LuPO_4$:Eu^{3+} are manifested at higher energies as a complex peak at 8.15 eV (van Pieterson et al., 2002).

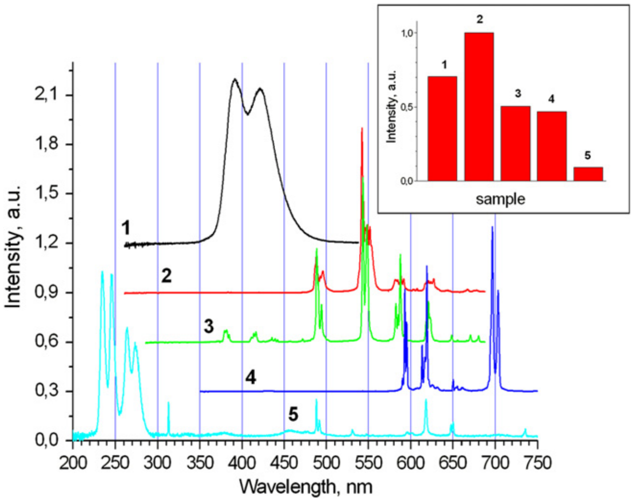

Fig. 1. Luminescence spectra of $LuBO_3$:Ce (1); $LuBO_3$:Tb (2); $LuPO_4$:Tb (3); $LuPO_4$:Eu (4) and $LuPO_4$:Pr (5) at $E_{ex} = 10.8$ eV, $T = 300$ K. In the inset: integrated intensity of the luminescence spectra.

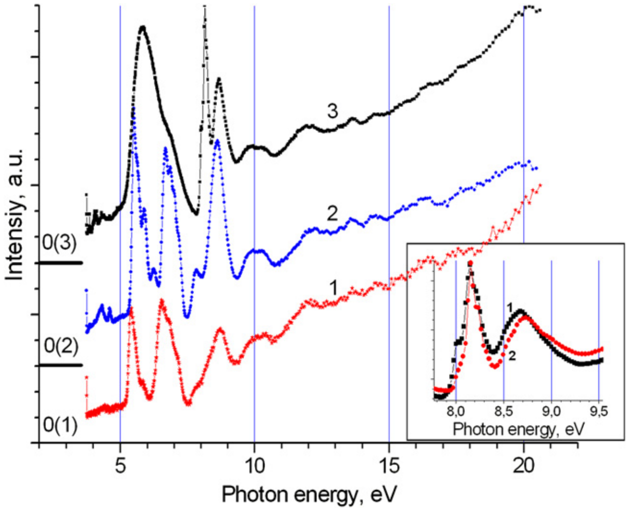

Fig. 2. Luminescence excitation spectra of $LuPO_4$:Eu ($\lambda_{em} = 595$ nm, curve (1), $LuPO_4$:Tb ($\lambda_{em} = 545$ nm, curve 2) and $LuPO_4$:Pr ($\lambda_{em} = 4\ 95$ nm, curve 3), $T = 300$ K. In the inset – excitation of $LuPO_4$:Eu in the exciton region at $T = 300$ K (curve 1) and $T = 10$ K (curve 2).

From the $E > 8.5$ eV, the excitation spectra demonstrate similar features that are independent to the dopant. The peaks at 8.7, 9.8, 12.0 eV, and the dips at 9.3, 10.7 eV perfectly coincide for all samples of $LuPO_4$. Similar behavior indicates that at energies $E > 8.5$ eV the luminescence is excited via the fundamental absorption region of the crystal. Several factors affect on the structure of spectra in this region. It is the peculiarities of electron transitions in the host lattice that are determined by the origin and density of electronic states of the valence and conduction bands of the crystal. Furthermore the observed spectra may be modulated with the losses on reflectivity and near-surface losses. Also the creation of exciton is possible at the edge of fundamental absorption region.

Time-resolved spectroscopy allows to separate the slow processes of luminescence excitation connected with sequentional capture of separated charge carriers on the RE ion and the fast processes connected with direct excitation of the luminescence center or via exciton creation. In Fig. 3, the luminescence excitation spectra of $LuPO_4$:Pr measured in “fast” (3–16 ns after the excitation pulse of synchrotron radiation) and “slow” (120–155 ns) time windows are presented. The time windows values were taken assuming the decay time of Pr luminescence at the intracenter f-d excitation of Pr ion (the decay is fitted with two exponentials with $\tau_1 = 3.4$ ns and $\tau_2 = 12$ ns). Obviously, the peaks that were attributed to the parity-allowed f-d transitions within Pr ion are observed in the spectrum measured with “fast” time windows. However, the peak at 8.7 eV preliminary attributed to the excitation of the host lattice is also observed in the “fast” time windows. We suppose that the peak is of exciton origin that provides fast transfer of correlated electron-hole pair to the luminescence centers. Another indication on the exciton origin of the peak at 8.7 eV is its temperature dependence studied for $LuPO_4$:Eu. Its maximum shifts to the high-energies of 0.15 eV with the temperature decrease from 300 to 10 K (see the inset Fig. 2) obeying Urbach rule. At the same time the shift of the peak 8.15 eV that is due to f-d excitation in Eu^{3+} is negligible.

Noticeable rise of luminescence in excitation spectrum measured in the “slow” time windows starts at energies exceeding the exciton peak – 8.8 eV. The rise of slow component is connected

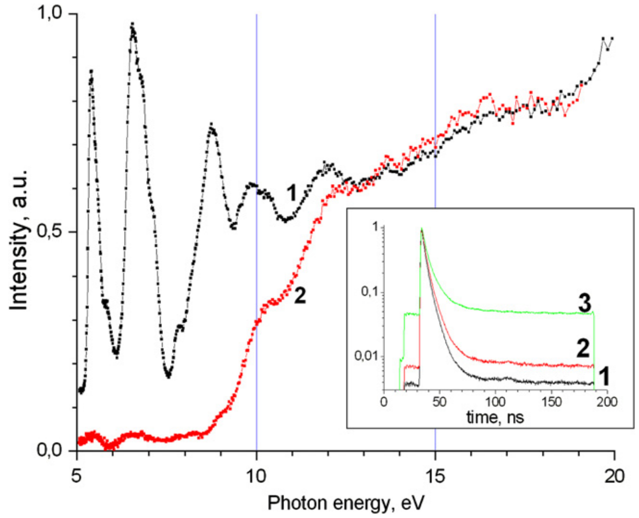

Fig. 3. Time-resolved luminescence excitation spectra of $LuPO_4$:Pr ($\lambda_{em} = 265$ nm) measured in the "fast" (3–16 ns, curve 1) and "slow" (120–155 ns, curve 2) time windows. The intensity of the spectra is normalized. In the inset – luminescence decay curves at $E_{ex} = 5.4–6.7$ eV (curve 1), 8.85 eV (curve 2) and 10.8 eV (curve 3).

with the creation of separated electrons and holes in the conduction and valence bands of $LuPO_4$. The relative contribution of separated charge carriers into the luminescence excitation gradually increases up to 12 eV demonstrating competition of this mechanism with the excitation via exciton creation. The rise at 8.8 eV can be used for the estimation of the bandgap value of $LuPO_4$. This value agrees with that available from the literature (see Table 1, reference c).

Luminescence excitation spectra of $LuBO_3$:RE (RE = Tb, Ce) are presented in Fig. 4. The structure in the energy region up to 7.2 eV is connected with excitation via f-d parity-allowed transitions. From the peak at 7.85 eV the main features in structure in the excitation spectra of $LuBO_3$ doped with Tb and Ce ions are the same. Analogously to phosphates the exciton is detected at the edge of the fundamental absorption region using time-resolved spectroscopy.

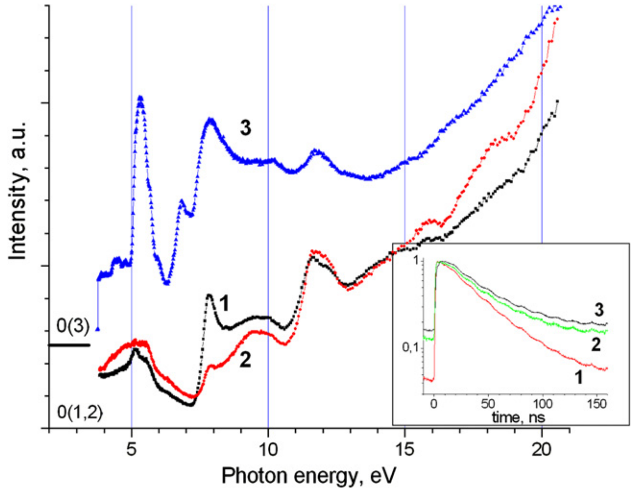

Fig. 4. Time-resolved luminescence excitation spectra of $LuBO_3$:Ce ($\lambda_{em} = 425$ nm) measured in the "fast" (3–20 ns, curve 1) and "slow" (90–155 ns, curve 2) time windows as well as luminescence excitation spectrum of $LuBO_3$:Tb ($\lambda_{em} = 545$ nm, curve 3). In the inset – luminescence decay curves at the $E_{ex} = 7.75$ eV (curve 1), 5.16 eV (curve 2) and 10.8 eV (curve 3).

The separation between the slow and fast processes is worse for $LuBO_3$:Ce than for $LuPO_4$:Pr due to slower decay time of Ce^{3+} luminescence. At excitation in exciton peak (7.75 eV), decay time was 55 ns. Slow decay components appear at the lower (5.16 eV) and higher (10.8 eV) excitation energies. In the latter case, luminescence rise-on is also observed. Presence of the slow decay component at excitation in the region of f-d transition within Ce^{3+} is not clear. Overlapping of cerium states with some defect states may be the reason of decay slowing, however, this supposition requires further approvement.

Relatively slow decay time of $LuBO_3$ complicates the determination of the separated charge carriers creation edge in $LuBO_3$. However, the bandgap value of $LuBO_3$ estimated from the presented results ($E > 7.75$ eV) significantly exceeds the values available from the literature (see Table 1).

From the luminescence excitation spectra follows that the energy transfer from the host material to RE^{3+} ions is efficient both in lutetium borates and phosphates. The intensity of the luminescence at the interband excitation stays approximately at the same level for the borates from the exciton peak up to the edge of photon multiplication process 17 eV (Zhang et al., 1999). For $LuBO_3$:Tb, the intensity is only slightly lower to that at the direct excitation of Tb^{3+} ion. In the case of phosphates, the decrease of the luminescence intensity was observed at the energies exceeding the exciton peak. It allows to suppose the existence of other (non-radiative) relaxation channel. In our measurements, it appeared in lower values of intensity for Tb-doped phosphate in comparison to borate (inset to Fig. 1) at the interband excitation. Moreover, it may be the one of the reasons for the lower value of light output from the lutetium phosphates in comparison with borates (Balcerzyk et al., 2000; Mansuy et al., 2004).

4. Conclusions

Luminescence properties of $LuPO_4$ and $LuBO_3$ doped with RE^{3+} (RE = Ce, Tb, Eu, Pr) were studied. Luminescence is related to the RE^{3+} emission without noticeable contribution of the intrinsic luminescence. The highest luminescence intensity was detected for $LuBO_3$:Tb at the interband excitation. Exciton creation in $LuPO_4$ and $LuBO_3$ at the edge of fundamental absorption region is demonstrated. Bandgap values were estimated using time-resolved spectroscopy. Efficient energy transfer from the host lattice to luminescence centers is one of the reasons for the superior scintillating properties of Lu-based borates and phosphates.

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