Fast UV luminescence in Pr$^{3+}$-doped eulytite double phosphates

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Abstract

The paper presents the synthetic procedure and the structural characterisation of Pr$^{3+}$-doped eulytite double phosphates Sr$_3$La(PO$_4$)$_3$ and Ba$_3$Lu(PO$_4$)$_3$. The luminescence properties of these materials were studied employing time-resolved VUV spectroscopy upon excitation with synchrotron radiation. The 5d-4f emission of Pr$^{3+}$ ions was detected and assigned. It was shown that energy transfer from host to Pr$^{3+}$ 5d states is quite inefficient. At the same time the materials demonstrate unwanted defect-related emission that presents main path for relaxation of host relaxation excitations.

1. Introduction

Luminescent inorganic materials doped with trivalent lanthanide ions and showing 5d-4f electric dipole allowed transitions located in the blue-UV region find numerous applications in important technological fields, such as scintillators, converting ionising radiation (X- and γ-rays) to UV and visible emission, and are very useful for applications in medicinal imaging and high energy physics. The Pr$^{3+}$ ion can give rise to 4f$^5$5d $\rightarrow$ 4f$^2$ luminescence located at shorter wavelengths than Ce$^{3+}$, and characterized by shorter decay times (less than 30 ns), allowing for higher count rates and superior spatial resolution [1]. Our search for new materials showing efficient 5d-4f emission of the Pr$^{3+}$ ion [2] has led us to the synthesis and study of double phosphates, namely Sr$_3$La(PO$_4$)$_3$ and Ba$_3$Lu(PO$_4$)$_3$, doped with this ion. In particular, we have found it interesting to investigate phosphate hosts belonging to the eulytite family. These materials are expected to be suitably
transparent in the VUV region [3] and have been proved to show efficient 5d-4f emission when doped with Ce$^{3+}$ [4]. To our knowledge, the spectroscopic investigation of Pr$^{3+}$ 5d-4f emission in these hosts has not been reported so far. Moreover, the phosphates having the eulytite structure are lacking time-resolved spectroscopic investigation that will contribute to a better understanding of energy dissipating mechanisms in this family of compounds. Obviously, a new achievement on this way would be helpful to revive a stronger technological interest in eulytite double phosphates.

In this contribution we will focus our attention to the Pr$^{3+}$ doped hosts Sr$_3$La(PO$_4$)$_3$ and Ba$_3$Lu(PO$_4$)$_3$. The synthetic procedure and structural characterization of these doped materials are described in detail. Time-resolved emission and excitation spectra as well as luminescence decay curves measured upon selective excitation with synchrotron radiation (SR) in the UV-VUV region are presented and analysed. The prospective applications of these luminescent materials are discussed.

2. Experimental

Polycrystalline samples of Sr$_3$La(PO$_4$)$_3$ and Ba$_3$Lu(PO$_4$)$_3$, doped with 1 mol% of Pr$^{3+}$ substituting La$^{3+}$ and Lu$^{3+}$, respectively, were obtained by a solid state reaction at high temperature (1250 °C, 48 h) starting from SrCO$_3$ or BaCO$_3$, NH$_4$H$_2$PO$_4$ (all reagent grade), Lu$_2$O$_3$ (99.99%) or La$_2$O$_3$ (99.99%) and Pr$_6$O$_{11}$ (99.999%), following the method described in [5].

All the materials obtained are single phase with a eulytite-type structure, as confirmed by powder X-ray diffraction (XRD) measurements, carried out using a Thermo ARL X’TRA powder diffractometer, operating in the Bragg-Brentano geometry and equipped with a Cu-anode X-ray source ($K_{\alpha 1}$, $\lambda = 1.54056$ Å; $K_{\alpha 2}$, $\lambda = 1.54433$ Å; $K_{\alpha 1}/K_{\alpha 2} = 2$), with a Peltier Si(Li) cooled solid state detector. The XRD patterns were collected with a scan rate of 1.2°/min and an integration time of 1.5 s in the 5–90° 2θ range. The phase identification was performed with the PDF-4 + 2008 database supplied by the International Centre for Diffraction Data (ICDD). Polycrystalline samples were ground in a mortar and then put in a low-background sample holder for the data collection. The crystal structures of the eulytite-type materials A$_2$M(PO$_4$)$_3$(A=Ca, Sr, Ba, M = La–Lu, Y) are well known to be cubic (space group number 220) and isomorphous with eulytine mineral (Bi$_4$Si$_3$O$_{12}$) [6]. The A$^{2+}$/M$^{3+}$ pairs of cations are disordered on a single crystallographic site whilst the oxygen atoms of the phosphate groups are distributed over three partially occupied sites [5]. The cell parameters do not appear to be significantly affected by the nature of the M$^{3+}$ ion. In fact, Sr$_3$Y(PO$_4$)$_3$ (PDF card 00-044-0320), Sr$_3$Tb(PO$_4$)$_3$ (PDF card 00-033-1353) and Sr$_3$Yb(PO$_4$)$_3$ (PDF card 00-048-0409) have almost the same cell volume (1033.29, 1033.06 and 1028.59 Å$^3$, respectively). The Pr$^{3+}$ dopant ions substitute in the single disordered cationic sites having C$_3$ point
group symmetry. The calculated densities of Sr$_3$La(PO$_4$)$_3$ and Ba$_3$Lu(PO$_4$)$_3$ are 4.32 and 5.06 g cm$^{-3}$ respectively.

The time-resolved VUV spectroscopy experiments were carried out at the SUPERLUMI station of HASYLAB (DESY, Germany) using the SR from the DORIS III storage ring as excitation source. For selective excitation and measurements of excitation spectra in the range of 3.7–20 eV a 2 m monochromator in McPherson mounting with a resolution of 3.2 Å was used. The detection of luminescence was performed with a 0.3 m ARC SpectraPro-308i monochromator equipped with a high-speed R3809U-50S (Hamamatsu) microchannel plate detector. Time-resolved spectra were recorded in two independent time windows (TWs) set for detection of luminescence signal within 2–14 ns (fast TW) and 72–172 ns (slow TW) relative to the beginning of the SR pulse. Time-integrated spectra were recorded within the full time range available between two sequential excitation pulses, viz. 192 ns. The measurements were performed in the ultra-high-vacuum chamber (up to $10^{-9}$ mbar) at T= 10 K and at 300 K. The excitation spectra were corrected for the wavelength-dependent variation of the SR intensity using the sodium salicylate signal.

3. Results and discussion

The RT emission spectra of Sr$_3$La(PO$_4$)$_3$:Pr$^{3+}$ and Ba$_3$Lu(PO$_4$)$_3$:Pr$^{3+}$ show significant dependence on excitation energy. Fig. 1 and 2 show time-resolved and time-integrated spectra of the samples recorded upon Pr$^{3+}$ 4f$^2 \rightarrow 4f^15d^1$ excitation (Fig. 1-a, 2-a) and excitation at the edge of intrinsic host absorption (Fig. 1-b, 2-b). The excitation ranges were chosen after analysis of the excitation spectra (see below).

The deep UV Pr$^{3+}$ intra-centre excited emission spectra of Sr$_3$La(PO$_4$)$_3$:Pr$^{3+}$ and Ba$_3$Lu(PO$_4$)$_3$:Pr$^{3+}$ recorded in the time-integrated mode are dominated by a complex emission band at about 4-5.5 eV. This band represents a fast decaying emission and is mostly pronounced in the fast TW spectra. Decay profiles of the 4-5.5 eV emission in Sr$_3$La(PO$_4$)$_3$:Pr$^{3+}$ and Ba$_3$Lu(PO$_4$)$_3$:Pr$^{3+}$ recorded upon Pr$^{3+}$ intra-center excitation are presented in Fig. 3-a, b (curves 1). For both compounds the time profiles demonstrate a single exponential behaviour with approximate life time 16 - 17 ns. We unambiguously assign this emission to interconfigurational radiative transitions from the lowest component of the 4f$^15d^1$ configuration to the lowest states of 4f$^2$ configuration ($^3$H$_J$). It should be noticed that the shape of the 4-5.5 eV emission band hardly reveals any resolved subbands connected with 5d-4f transitions to particular 4f$^2$ states, as typically observed in other phosphate hosts, e.g. MPO$_4$:Pr$^{3+}$ (M = Y, Lu) [7]. This behaviour is presumably explained by disorder of Sr$^{2+}$/Ba$^{2+}$ and La$^{3+}$/Lu$^{3+}$ cations potentially substituted by Pr$^{3+}$ and by a substantially
higher Stokes shift. The general similarity of shape and spectral position of Pr$^{3+}$ 5d-4f emission observed is in agreement with results obtained for Ce$^{3+}$ doped in eulytite hosts [4, 8].

Increasing the excitation energy to 7.18 eV, corresponding to the beginning of the intrinsic absorption of the host lattice, leads to significant transformation of the emission spectra (Fig. 1-b, 2-b) due to the appearance of a broad emission band peaked around 3.4 eV. The band clearly dominates the slow TW spectra and demonstrates a smooth Gaussian shape with half width of about 1 eV. We tentatively assign this spectral feature to defect emission. The decay time of this emission lies in the microsecond range (see Fig. 3-a,b, curves 3) and cannot be determined from the synchrotron experimental measurements. The nature of the defect emission is presently unknown, but it is worth pointing out that its intensity is higher for the Ba$_3$Lu(PO$_4$)$_3$ host than for Sr$_3$La(PO$_4$)$_3$:Pr$^{3+}$.

In the visible spectral range the slow TW emission spectra present narrow features at 2.06 and 2.56 eV corresponding to 4f$^2$ - 4f$^2$ transitions of Pr$^{3+}$ ions from $^1D_2$ and $^3P_0$ levels to lower lying states. In contrast to the 5d-4f emission band, the 4f-4f features become more pronounced in the spectra with increasing excitation energy.

The time-integrated excitation spectra of the emission bands at 4.6 eV (Pr$^{3+}$ 5d-4f emission), 3.4 eV (defect emission) and 605 nm (Pr$^{3+}$ 4f-4f emission) for Sr$_3$La(PO$_4$)$_3$:Pr$^{3+}$ are presented in Fig. 4. The data obtained for Ba$_3$Lu(PO$_4$)$_3$:Pr$^{3+}$ are very similar and not shown in the paper. The 5d-4f emission shows a strong structured excitation band with maximum around 6.04 eV. This band is assigned to transitions to Pr$^{3+}$ 5d levels. The low-energy shoulder of this band situated around 5.5 eV evidently corresponds to population of the lowest 5d level, that is in good agreement with the position (5.47 eV) predicted using the model proposed by Dorenbos [9], using the excitation data for Ce$^{3+}$ in the same host [4]. The decrease of the excitation intensity of Pr$^{3+}$ 5d-4f observed in spectral range from 6.67 to 7.35 eV corresponds to opposite behaviour of the excitation spectrum for defect related emission. When the latter reaches its maximum near 7.12 eV (at RT) the excitation efficiency of Pr$^{3+}$ 5d-4f emission drops to about 5% of the value observed upon direct 4f-5d excitation. Increasing of excitation energy above 7.15 eV leads to further gradual decrease of 5d-4f emission intensity to its minimum value. Above 8 eV no remarkable excitation features are observed. This peculiarity clearly shows that energy transfer from the host to the 4f$^4$5d$^1$ configuration in this class of materials is quite inefficient. A potential reason is that host lattice excitation results in defect related emission, with too low an energy to feed the 5d-4f emission of Pr$^{3+}$, as there is no spectral overlap between the defect emission and the 4f-5d absorption. This interpretation is in accordance with the fact that host lattice excitation feeds Pr$^{3+}$ 4f-4f emission, see below.
The maximum of RT defect emission excitation spectrum represented by the band peaking at 7.12 eV shifts of about 0.4 eV towards higher energy when temperature is 10 K. The nature of this band is probably connected with intrinsic defect absorption and/or formation of defect localised excitons. It is important to note that the high energy side of this excitation band (7.8 – 8.9 eV) corresponds to a similar decrease in the reflection spectrum of Sr₃La(PO₄)₃ presented in [3]. According to the authors [3], the interband transitions in Sr₃La(PO₄)₃ occur above 8.9 eV. Correlation of this value with spectroscopic features observed in this work is worth further investigation which might provide additional knowledge about defect formation in eulytite double phosphates. The excitation spectrum of the defect emission maintains significant intensity in the higher energy range obviously corresponding to the formation of separated electron-hole pairs.

The time-integrated excitation spectrum recorded monitoring the Pr³⁺ 4f-4f emission (Fig. 4) shows a completely different behaviour from the excitation spectrum of the 5d-4f emission. In the UV and near VUV ranges the spectrum contains structured features corresponding to population of Pr³⁺ 5d levels and defect absorption. At higher energies up to 19 eV the spectrum is characterised by a progressive rise of intensity with increasing energy of the incident photons. This indicates that host electronic excitations transfer energy to Pr³⁺ ions and creates 4f² excited states. We are convinced that the energy transfer chain includes defect states.

The time profiles of Pr³⁺ 5d-4f emission recorded upon excitation above 7.5 eV demonstrate a significant contribution of the slow component, caused by overlapping of defect emission and present as a constant level pedestal (see curves 2 on Fig. 4 for example). The intensity of the slow component gradually increases with increasing excitation energy (not shown). It is important to note that we did not observe any significant rise time in Pr³⁺ 5d-4f emission time profiles. The rise time of 5d-4f emission excited above 7.5 eV was estimated not to exceed 0.5 ns and does not differ from the one observed for direct Pr³⁺ intra-center excitation (see inserts on Fig. 4-a,b). This is advantageous for fast scintillator application, however, for the materials considered the lack of efficient energy transfer from intrinsic electronic excitations, prevents application as a scintillator material.

4. Conclusions

We have presented the time-resolved luminescence VUV spectroscopy of Pr³⁺-doped eulytite double phosphates. These materials show efficient 5d-4f emission of the Pr³⁺ ions upon direct intra-centre excitation. However, this emission is not excited efficiently upon VUV photon host excitation. Presumably the disordered nature of the host induces the presence of defects which actively trap the host electronic excitations. As a consequence no efficient host-to-impurity energy transfer is observed, due to the fact that the defect emission occurs at lower energies than the 4f-5d
excitation. Radiative relaxation of the defect excited states results in the appearance of broad emission band with maximum at 3.4 eV and characterised by long decay time. All these observations prevent the development of Pr\textsuperscript{3+} eulytite double phosphates as scintillators.

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**References**


Fig. 1 Time-integrated and time-resolved emission spectra of Sr$_3$La(PO$_4$)$_3$:Pr$^{3+}$ recorded at RT upon excitation at 6.52 eV (a) and 7.18 eV (b).

Fig. 2 Time-integrated and time-resolved emission spectra of Ba$_3$Lu(PO$_4$)$_3$:Pr$^{3+}$ recorded at RT upon excitation at 6.52 eV (a) and 7.18 eV (b).
Fig. 3 Time profiles of the Pr$^{3+}$ 5d-4f emission monitored at 4.6 eV and defect emission at 3.4 eV in Sr$_3$La(PO$_4$)$_3$:Pr$^{3+}$ (a) and Ba$_3$Lu(PO$_4$)$_3$:Pr$^{3+}$ (b) recorded at RT. Inserts show initial stage of Pr$^{3+}$ 5d-4f emission time profiles recorded with higher time resolution.

Fig. 4 Time-integrated excitation spectra of Sr$_3$La(PO$_4$)$_3$:Pr$^{3+}$ recorded monitoring Pr$^{3+}$ 5d-4f emission at 4.6 eV and 4f-4f emission at 2.05 eV at RT and the intrinsic defect emission at 3.4 eV at RT and $T = 10$ K.