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Title: Fast UV luminescence in Pr³⁺-doped eulytite double phosphates

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Abstract: The paper presents the synthetic procedure and the structural characterisation of Pr³⁺-doped eulytite double phosphates Sr₃La(PO₄)₃ and Ba₃Lu(PO₄)₃. The luminescence properties of these materials were studied employing time-resolved VUV spectroscopy upon excitation with synchrotron radiation. The 5d-4f emission of Pr³⁺ ions was detected and assigned. It was shown that energy transfer from host to Pr³⁺ 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.

Reviewer #1: *The paper reports new luminescence data on Pr³⁺-doped eulytite double phosphates which suits well the scope of OM and is thus worth to be published after some minor revision.*

Namely, the discussion dealing with the nature of the defect responsible for 3.4 eV emission is rather superficial and too general, could the authors be a bit more specific? Where is the band gap of the host, from Fig. 4 it might derived to be of about 7 eV and increase of excitation spectrum above 13-14 eV as due to the multiplication of electronic excitations? Is it rather defect emission or could be a trapped exciton one (excitation band at about 5.2 eV ??)? Is self-trapped exciton emission ruled out in these materials?

After the amendment of discussion the paper can be published.

We thank the referee for valuable comments and questions which were all taken carefully into account and persuaded us to revise the manuscript accordingly. Although focusing on the processes related to the host lattice excitations was not a main task of the paper, we found it really necessary to consider this issue in more detail.

All changes are made in the text and highlighted in green. Particularly, answers to the referee's questions can be found on page 5.

A number of minor changes were made throughout the text to improve grammar and style as well as to support the conclusions made in better way.

Thanks!

Research highlights

- The luminescence properties of Pr^{3+} -doped eulytites $\text{Sr}_3\text{La}(\text{PO}_4)_3$ and $\text{Ba}_3\text{Lu}(\text{PO}_4)_3$ were studied using time-resolved VUV spectroscopy upon excitation with synchrotron radiation
- 5d-4f emission of Pr^{3+} ions was detected and assigned.
- The energy transfer from the host to Pr^{3+} 5d states is inefficient, as defect-related emission is the main path for relaxation of host excitations.

Fast UV luminescence in Pr³⁺-doped eulytite double phosphates

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Abstract

The paper presents the synthetic procedure and the structural characterisation of Pr³⁺-doped eulytite double phosphates Sr₃La(PO₄)₃ and Ba₃Lu(PO₄)₃. The luminescence properties of these materials were studied employing time-resolved VUV spectroscopy upon excitation with synchrotron radiation. The 5d-4f emission of Pr³⁺ ions was detected and assigned. It was shown that energy transfer from host to Pr³⁺ 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 Pr³⁺ ion can give rise to 4f¹5d $\rightarrow$ 4f² luminescence located at shorter wavelengths than Ce³⁺, 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 Pr³⁺ ion [2] has led us to the synthesis and study of double phosphates, namely Sr₃La(PO₄)₃ and Ba₃Lu(PO₄)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 $\text{Sr}_3\text{La}(\text{PO}_4)_3$ and $\text{Ba}_3\text{Lu}(\text{PO}_4)_3$. 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 $\text{Sr}_3\text{La}(\text{PO}_4)_3$ and $\text{Ba}_3\text{Lu}(\text{PO}_4)_3$, 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 , $\text{NH}_4\text{H}_2\text{PO}_4$ (all reagent grade), Lu_2O_3 (99.99%) or La_2O_3 (99.99%) and Pr_6O_{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 ($K_{\alpha 1}$, $\lambda = 1.54056 \text{ \AA}$; $K_{\alpha 2}$, $\lambda = 1.54433 \text{ \AA}$; $K_{\alpha 1}/K_{\alpha 2} = 2$), with a Peltier Si(Li) cooled solid state detector. The XRD patterns were collected with a scan rate of $1.2^\circ/\text{min}$ and an integration time of 1.5 s in the $5\text{--}90^\circ$ 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 $\text{A}_3\text{M}(\text{PO}_4)_3$ ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$, $\text{M} = \text{La-Lu}, \text{Y}$) are well known to be cubic (space group number 220) and isomorphous with eulytine mineral ($\text{Bi}_4\text{Si}_3\text{O}_{12}$) [6]. The $\text{A}^{2+}/\text{M}^{3+}$ 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, $\text{Sr}_3\text{Y}(\text{PO}_4)_3$ (PDF card 00-044-0320), $\text{Sr}_3\text{Tb}(\text{PO}_4)_3$ (PDF card 00-033-1353) and $\text{Sr}_3\text{Yb}(\text{PO}_4)_3$ (PDF card 00-048-0409) have almost the same cell volume (1033.29, 1033.06 and $1028.59 \text{ \AA}^3$, respectively). The Pr^{3+} dopant ions substitute in the single disordered cationic sites having C_3 point

group symmetry. The calculated densities of $\text{Sr}_3\text{La}(\text{PO}_4)_3$ and $\text{Ba}_3\text{Lu}(\text{PO}_4)_3$ 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 $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Pr}^{3+}$ and $\text{Ba}_3\text{Lu}(\text{PO}_4)_3:\text{Pr}^{3+}$ show significant dependence on excitation energy. Fig. 1 and 2 show time-resolved and time-integrated spectra of the samples recorded upon $\text{Pr}^{3+} 4f^2 \rightarrow 4f^15d^1$ 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 $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Pr}^{3+}$ and $\text{Ba}_3\text{Lu}(\text{PO}_4)_3:\text{Pr}^{3+}$ 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 $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Pr}^{3+}$ and $\text{Ba}_3\text{Lu}(\text{PO}_4)_3:\text{Pr}^{3+}$ 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 ($^3\text{H}_J$). 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. $\text{MPO}_4:\text{Pr}^{3+}$ (M = Y, Lu) [7]. This behaviour is presumably explained by disorder of $\text{Sr}^{2+}/\text{Ba}^{2+}$ and $\text{La}^{3+}/\text{Lu}^{3+}$ 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 near 3.4 eV. The band clearly dominates in 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 $\text{Ba}_3\text{Lu}(\text{PO}_4)_3$ host than for $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Pr}^{3+}$.

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 the $^1\text{D}_2$ and $^3\text{P}_0$ levels to the ground state $^3\text{H}_4$. In contrast to the 5d-4f emission band, the 4f-4f features become more pronounced in the spectra with increasing the 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 2.06 eV (Pr^{3+} 4f-4f emission) for $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Pr}^{3+}$ are presented in Fig. 4. The data obtained for $\text{Ba}_3\text{Lu}(\text{PO}_4)_3:\text{Pr}^{3+}$ 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 (marked by symbol "A" on the figure). This band is assigned to transitions to Pr^{3+} 5d levels. The low-energy shoulder of the band A 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], taking into account the excitation data for Ce^{3+} in the same host [4]. The decrease of the excitation intensity of Pr^{3+} 5d-4f emission observed in spectral range from 6.67 to 7.35 eV corresponds to opposite behaviour of the excitation spectrum recorded for the defect related emission. The latter shows a strong complex excitation band with maximum near 7.12 eV (marked by symbol "B" on the figure). Around this maximum 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 $4f^15d^1$ 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+} ions, 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.

At the temperature of 10 K the defect emission excitation spectrum of $\text{Sr}_3\text{La}(\text{PO}_4)_3\text{:Pr}^{3+}$ reveals broadening of the band B in near VUV region and blue shift of its low-energy side for about 0.25 eV. We consider this band unlikely to originate from absorption of self-trapped excitons (STE) for the following reasons. First of all, the STE is ruled out as the relaxation energy would be very large and too large a relaxation energy would lead to thermal quenching. Next, it is clearly seen that the low energy side of the band A shows the same slope both at 10 K and RT (Fig. 4) that, in case of excitonic nature, would contradict the classical Urbach's rule for exciton-phonon interaction. Another important issue to be highlighted may come from consideration of interactions between the Pr^{3+} ion and electronic states of the host material. Although the eulytite double phosphates are lacking any published information about the absolute location of the lanthanide energy levels relative to the host states, we suppose that the Pr^{3+} ground state $4f(^3\text{H}_4)$ lies well above the top of valence band (probably around 2 eV) based on the known location of the lanthanide levels in other phosphates, namely in YPO_4 and LuPO_4 [10, 11] and in $\text{LiYP}_4\text{O}_{12}$ [12]. This would put the lowest Pr^{3+} 5d state approximately at 7.3 eV above the top of valence band. In this case, the presence of excitonic absorption around 6.8 – 7.5 eV and the close proximity of the bottom states of conduction band would mean significant temperature quenching of Pr^{3+} emission that is not the case. According to the Schwarz et al. [3], who studied the electronic structure of double phosphates by measuring VUV reflection spectra at 10 K, the interband transitions in $\text{Sr}_3\text{La}(\text{PO}_4)_3$ occur above 8.9 eV. This value correlates with the estimation of band gap in $\text{LiYP}_4\text{O}_{12}$ (~9.3 eV) [12] and YPO_4 and LuPO_4 (~8.55 eV) [10, 11, 13]. Obviously, excitation of the STE at energies well below the bandgap is not very likely due to the Franck-Condon principle. Bearing all this in mind we connect the nature of the band B to intrinsic defect absorption.

It is worth noting that the high energy side of this excitation band (7.8 – 8.9 eV) corresponds to a similar decrease in the reflection spectrum of $\text{Sr}_3\text{La}(\text{PO}_4)_3$ presented in [3]. 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. We do not expect to observe any effects of multiplication of electronic excitations, also for optical excitation, as it they in general are observed for energies exceeding 2.5 times the band gap [14], that it is out of our measurement range.

The time-integrated excitation spectrum recorded monitoring the Pr^{3+} 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 Pr^{3+} 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 Pr^{3+} ions and creates $4f^2$ excited states. We are convinced that the energy transfer chain includes defect states.

The time profiles of Pr^{3+} 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 Pr^{3+} 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 Pr^{3+} intra-center excitation (see inserts on Fig. 4-a,b). This is quite advantageous for fast scintillator application, however, the lack of efficient energy transfer from intrinsic electronic excitations, hampers the materials considered to be developed as scintillators.

4. Conclusions

We have presented the time-resolved luminescence VUV spectroscopy of Pr^{3+} -doped eulytite double phosphates. These materials show efficient 5d-4f emission of the Pr^{3+} 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 near 3.4 eV and characterised by long decay time. All these observations do not encourage the development of Pr^{3+} eulytite double phosphates as scintillators.

Acknowledgements

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Captions for figures

Fig. 1 Time-integrated and time-resolved emission spectra of $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Pr}^{3+}$ 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 $\text{Ba}_3\text{Lu}(\text{PO}_4)_3:\text{Pr}^{3+}$ 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 $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Pr}^{3+}$ (a) and $\text{Ba}_3\text{Lu}(\text{PO}_4)_3:\text{Pr}^{3+}$ (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 $\text{Sr}_3\text{La}(\text{PO}_4)_3:\text{Pr}^{3+}$ 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.

Figure 1

Figure 2

Figure4