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Using Eu^{3+} as an atomic probe to investigate the local environment in $LaPO_4$–$GdPO_4$ monazite end-members

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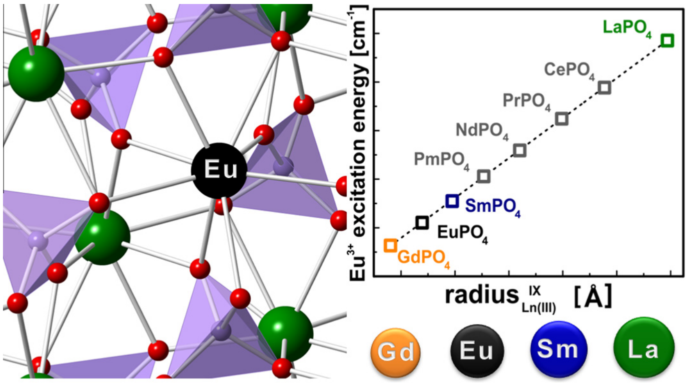
GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, we have investigated the luminescent properties of Eu^{3+} as a dopant in a series of synthetic lanthanide phosphates from the monazite group. Systematic trends in the spectroscopic properties of Eu^{3+} depending on the size of the host cation and the dopant to ligand distance have been observed. Our results show that the increasing match between host and dopant radii when going from Eu^{3+}-doped $LaPO_4$ toward the smaller $GdPO_4$ monazite decreases both the full width at half maximum of the Eu^{3+} excitation peak, as well as the $^7F_2/^7F_1$ emission band intensity ratio. The decreasing Ln···O bond distance within the $LnPO_4$ series causes a systematic bathochromic shift of the Eu^{3+} excitation peak, showing a linear dependence of both the host cation size and the Ln···O distance. The linear relationship can be used to predict the energy band gap for Eu^{3+}-doped monazites for which no Eu^{3+} luminescent data is available. Finally, mechanisms for metal-metal energy transfer between host and dopant lanthanides have been explored based on recorded luminescence lifetime data. Luminescence lifetime data for Eu^{3+} incorporated in the various monazite hosts clearly indicated that the energy band gap between the guest ion emission transition and the host ion absorption transition can be correlated to the degree of quenching observed in these materials with otherwise identical geometries and chemistries.

1. Introduction

Crystalline lanthanide orthophosphates ($LnPO_4$) doped with other elements of the lanthanide group have recently gathered substantial attention due to the favorable electronic properties of

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Abbreviations: TRLFS, time-resolved laser fluorescence spectroscopy.

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the 4*f* elements that can be employed for applications ranging from light display systems [1] and nanoelectronic devices [2], medical and biological labels for in vitro imaging [3] to applications in targeted drug release [4]. Orthophosphates offer an easily synthesized and robust solid matrix for the dopants, and $LnPO_4$ nanoparticles can be tailored for a variety of purposes. The chemical durability and structural flexibility of $LnPO_4$ make lanthanide phosphates crystallizing in the monazite structure attractive as host phases for the conditioning of long-lived radionuclides produced during the nuclear fuel cycle or in the dismantling of nuclear weapons [5–10]. The monazites are known to incorporate large quantities of actinides (>20%) [6,11], and several studies report on the structural incorporation of actinides such as U, Th, Pu, Am, and Cm, within the monazite structure either through direct substitution by a trivalent actinide on the host cation site [12,13], or through coupled substitution of an actinide of higher oxidation state with a mono- or divalent cation to preserve charge neutrality [14,15]. Eu^{3+} is often chosen as dopant in the investigated phosphates mainly due to its luminescent properties. Eu^{3+} is a preferred choice as an activator ion in the development of red-emitting phosphors due to its strong, long-lived luminescence emission [16,17]. Furthermore, crystal-field perturbation results in a fine structure in the luminescence spectra that depends on the site symmetry of the Eu^{3+} ion which, thus, can be used as a local structure probe for the determination of site symmetries in a host lattice [18]. In general, luminescent properties of lanthanide ions depend on the host composition and structure as well as the concentration (i.e. interatomic distance) of luminescent centers present in the materials [19–22]. Therefore, local changes in the host material and the concentration range of dopants used will alter the spectroscopic properties of the luminescent probe and, depending on the application, may affect the suitability of the material.

In the present work we have studied Eu^{3+} incorporation and the impact of systematic trends within the host crystal structure on the dopant luminescence in a series of $LnPO_4$ end-members ($LaPO_4$–$GdPO_4$) crystallizing in the monazite structure. The ionic radius of the host cation in these monazite end-members decreases systematically from La^{3+} (r_{ion}^{IX} = 1.216 Å) [23] toward Gd^{3+} (r_{ion}^{IX} = 1.107 Å) [21] by ~10%. A preferential incorporation of Eu^{3+} in monazites with a host cation radius similar to Eu's (r_{ion}^{IX} = 1.120 Å) [23], e.g. $SmPO_4$ or $GdPO_4$, could be expected. In addition, the systematic decrease of the $Ln\cdots O$ bond distance in the series of monazite hosts with otherwise identical symmetry and chemistry provides an opportunity to study the impact of bond distance on the ligand field effect and the luminescent properties of the Eu^{3+} ion. Finally, by comparing the Eu^{3+} doped monazites with isolated fluorescent centers (c_{Eu} = 500 ppm) with pure $EuPO_4$, the influence of the lanthanide concentration in terms of metal-metal concentration quenching effects can be evaluated.

2. Experimental section

2.1. Lanthanide phosphate synthesis and characterization

The lanthanide phosphates $LaPO_4$ to $GdPO_4$ crystallizing in the monazite structure were synthesized by precipitation (excluding the redox sensitive $CePO_4$ and radioactive $PmPO_4$) similar to the procedure described in Roncal-Herrero et al. [24].

Lanthanide nitrate salts were dissolved in deionized water (MilliQ) in concentrations of 0.3–0.5 M. A 14.8 M aqueous solution of H_3PO_4 was slowly added to the solution, causing precipitation of $LnPO_4{:}Eu^{3+}$ according to Reaction (1). Details on the reagents used in the synthesis can be found in the supporting information (S.I.).

$$Ln(NO_3)_3 + H_3PO_4 \xrightarrow{500\ \text{ppm}\ Eu^{3+}} LnPO_4 : Eu^{3+} + 3HNO_3 \qquad \text{(Reaction1)}$$

The suspension was heated in an oven at 90 °C for 1 week to complete the precipitation. The solid was recovered by centrifugation (10,000 rpm, 10 min) and washed with MilliQ water. The washing step was repeated several times until the supernatant was free of nitrate ions (NO_3^- test strips). Subsequently the powders were dried in an oven at 90 °C for 12 h. The dry powders were milled in an agate mortar and calcined for 2 h at 600 °C in order to remove any nitrate residues. As a final step, sintering of $LnPO_4$ was carried out at 1450 °C for 5 h to obtain the crystalline monazite solids. Characterization of the synthetic monazites was done with X-ray powder diffraction (XRD), using a D4 Endeavor diffractometer with a θ–2θ geometry (Bruker AXS GmbH) operating at 50 kV and 30 mA with a Cu Kα radiation (λ = 1.5418 Å) in the range 2θ = 10–100°. The XRD patterns of all synthesized monazites are in perfect agreement with the corresponding data from the ICDD database, confirming the sole presence of highly crystalline, monoclinic monazite. XRD patterns for pure $EuPO_4$ and Eu^{3+}-doped $GdPO_4$ are shown in Fig. 1. For the XRD patterns of all synthetic monazites the reader is referred to the S.I., Fig. S1.

2.2. Time-resolved laser fluorescence spectroscopy TRLFS

The Eu^{3+} ion exhibits many favorable luminescence properties, such as a non-degenerate ground state ($^7F_0$) as well as emitting state ($^5D_0$) and an even number of *f*-electrons ($4f^6$) for which the number of crystal field levels is dependent on the site symmetry of the ion [25]. Therefore, Eu^{3+} is ideally suited for systematic studies of the structural incorporation of Eu^{3+} in crystalline solid phases, such as this series of synthetic monazites.

Detailed information on the Eu^{3+} environment in crystalline solids can be obtained by combining the luminescence data obtained from recorded excitation spectra, emission spectra, and luminescence lifetimes, as discussed below. Selective excitation of the Eu^{3+} ion from the $^7F_0$ ground state to the $^5D_0$ excited state, which both are non-degenerate due to their J = 0 nature, allows for the determination of the number of non-equivalent species present in the solid matrix. In an excitation spectrum (integrated luminescence intensity as a function of excitation energy) of the $^7F_0 \rightarrow {}^5D_0$ transition, one singlet signal is obtained for every Eu^{3+} species present in the system. The signal position, gives a first indication of the local environment of the respective Eu^{3+} species, where a stronger ligand field generally results in a lower energy transition and consequently in a stronger bathochromic shift of the signal [26,27]. For Eu^{3+} incorporation in the synthetic monazites only one singlet species corresponding to the structural incorporation of the dopant on the host lanthanide site is expected.

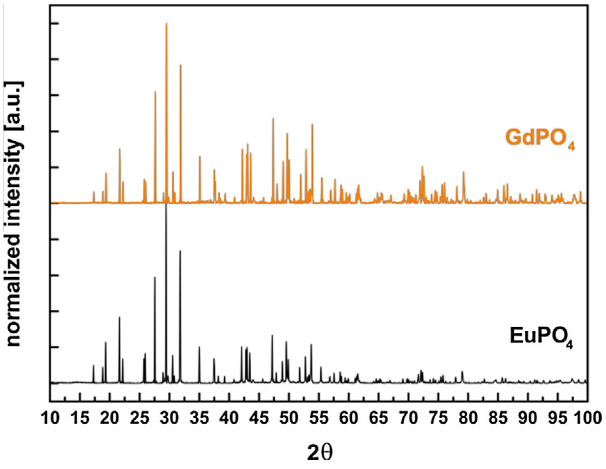

Fig. 1. XRD patterns of synthetic $EuPO_4$ monazite and Eu^{3+}-doped $GdPO_4$ monazite.