

Composition dependence of Pr^{3+} spectral characteristics in strontium lanthanum aluminate crystals

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Abstract

An analysis of the high resolution spectra of the Pr^{3+} in strontium lanthanum aluminates, charge compensated with magnesium $\text{Sr}_{1-x}\text{Pr}_y\text{La}_{x-y}\text{Mg}_x\text{Al}_{12-x}\text{O}_{19}$, (on a large composition range) is presented. The spectra are mainly dependent on the composition parameter x , and show more Pr^{3+} centers, two of them stable. Based on composition dependence and polarization data, structural models for the main two centers are proposed.

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1. Introduction

The Pr^{3+} doped materials are investigated as laser materials as well as luminescent phosphors for quantum cutting (cascade) conversion of the ultraviolet (VUV) 172 nm radiation of Xe dimmer into two visible quanta in materials in which the lowest 4f5d bands lies above the $^1\text{S}_0$ state of the 4f² configuration. The VUV radiation absorbed in the excited configuration 4f5d relaxes on the $^1\text{S}_0$ level from which a first emission takes place in the range 400–430 nm on the group of levels ($^3\text{P}_{0,1,2}$, $^1\text{I}_6$) or at higher energies when it ends on lower energy levels. The second emission step originates from metastable levels such as $^3\text{P}_0$ (blue, green, yellow, orange or red) or $^1\text{D}_2$ (red). The deep blue first emission is not suitable for phosphors and attempts to replace it by energy transfer to another ion such as Er^{3+} , Cr^{3+} , Mn^{2+} and so on, able to give emission in a more useful visible range, have been made. The Pr^{3+}

lasers emission is based on the visible emission of $^3\text{P}_0$ or $^1\text{D}_2$ levels or on infrared emission from lower levels.

The magnesium compensated strontium aluminate $\text{SrAl}_{12}\text{O}_{19}$ (SAM), investigated earlier as laser material [1,2] was the first oxide to show Pr^{3+} photon cascade starting from $^1\text{S}_0$ level [3–6]. The lanthanum diluted crystals $\text{Sr}_{1-x}\text{La}_x\text{Pr}_y\text{Mg}_x\text{Al}_{12-x}\text{O}_{19}$ have been also studied [7]. At low x values these systems have hexagonal magnetoplumbite structure and offer for substitution with Pr^{3+} a unique Sr^{2+} (2d) site of ideal D_{3h} symmetry, with 12O^{2-} coordination. The (2d) sites are placed in the mirror planes (perpendicular on the optical axis c), separated by two spinel type groups where Al^{3+} can occupy octahedral, tetrahedral and five-fold coordinated bipyramidal sites [8]. The Mg^{2+} ions occupy, most probably, tetrahedral sites [9]. The density of Sr^{2+} (2d) sites is rather low ($\sim 3.38 \times 10^{19}$ ions/cm³). The X-ray investigations have suggested [8] that for large x some of lanthanide ions could occupy also sites of lower symmetry (C_{2v}). The high coordination and the presence of small highly charged Al^{3+} ions around Pr^{3+} determine low nephelauxetic effect, which leads to high barycenters of the energy manifolds, and moderate crystal field effects.

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The previous low temperature spectroscopic investigation of 5–15 at.% Pr^{3+} in Mg^{2+} -compensated $\text{SrAl}_{11}\text{O}_{19}$ [1,2] considered the system as having Pr^{3+} in a single prevailing center of D_{3h} symmetry, though the lines shift with composition and present satellite structures in some transitions or polarizations. In $\text{Sr}_{1-x}\text{Pr}_y\text{La}_{x-y}\text{Mg}_x\text{Al}_{12-x}\text{O}_{19}$ ($x = 0.3$, $y = 0.1$), besides a prevailing center with the lowest 4f5d level above the 1S_0 level, a minority center with the lowest 4f5d level below 1S_0 has been reported [7], but no definite models have been proposed. Our high resolution spectral studies of Nd^{3+} in these crystals evidenced a systematic composition dependent two center structure, with distinct spectral characteristics [10,11], even at low x . It was then inferred that the presence of these centers is connected with the crystal field perturbations due to the charge disordering of the lattice by the multiple occupancy of specific sites by ions of different valence (Sr^{2+} , Nd^{3+} or La^{3+} in the (2d) sites, Mg^{2+} or Al^{3+} in the low-size sites).

The paper presents an analysis of the high resolution spectral data of Pr^{3+} in magnesium compensated $\text{SrAl}_{12}\text{O}_{19}$ and lanthanum diluted crystals $\text{Sr}_{1-x}\text{La}_{x-y}\text{Pr}_y\text{Mg}_x\text{Al}_{12-x}\text{O}_{19}$, with a large composition range.

2. Experimental

Single crystals of $\text{Sr}_{1-x}\text{Pr}_y\text{La}_{x-y}\text{Mg}_x\text{Al}_{12-x}\text{O}_{19}$ with $0.05 \leq x \leq 0.3$ and $0.05 \leq y \leq 0.2$ (melting point 1850 °C), have been grown by Czochralski method in iridium crucibles, in N_2 atmosphere by using (001) oriented crystalline seeds. The dilution with La^{3+} improves the crystal quality and avoids quenching at high RE^{3+} content. Growth of good quality crystals with small x (<0.2) proved to be difficult.

The absorption spectra at 15 K and 300 K were measured with a set-up consisting of a tungsten halogen lamp, a 1 m double monochromator ($\sim 0.3 \text{ cm}^{-1}$ resolution), using photon counting with a multichannel analyzer Turbo-MCS system and a closed cycle He cryostat.

3. Results and discussion

Various transitions in the visible range (16000–23000 cm^{-1}) of absorption spectra of Pr^{3+} in $\text{Sr}_{1-x}\text{Pr}_y\text{La}_{x-y}\text{Mg}_x\text{Al}_{12-x}\text{O}_{19}$ in unpolarized light with propagation along optical axis c show composition dependence (Fig. 1).

Similar to Nd^{3+} [10,11] the spectra depend mainly on the composition parameter x , but much less on y . A strong dependence on x is remarked in the region of the $^3\text{H}_4 \rightarrow ^3\text{P}_1, ^1\text{I}_6$ transitions of Pr^{3+} (Fig. 2(a)), but it is difficult to resolve it spectrally, probably due to the interference of the lines belonging to the two manifolds. The absorption is dominated by a line peaking at 21447 cm^{-1} in the crystal with $x = 0.1$, $y = 0.1$ this transforms to a band peaking at 21505 cm^{-1} for $x = 0.3$, $y = 0.1$; both these bands are asymmetric showing unresolved structure. However, a clear two-line structure (C_1 and C_2) with the components separated by $\sim 25 \text{ cm}^{-1}$ is observed in the first line of the

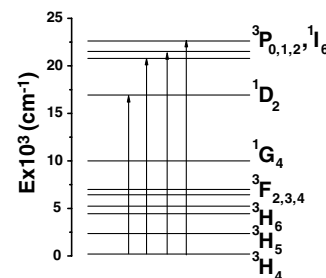


Fig. 1. Partial energy level scheme of $\text{Sr}_{1-x}\text{Pr}_x\text{La}_{x-y}\text{Mg}_x\text{Al}_{12-x}\text{O}_{19}$.

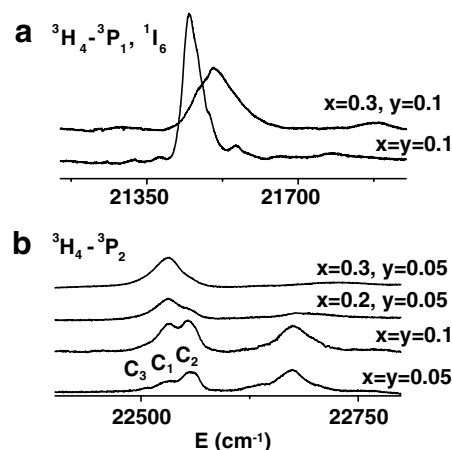


Fig. 2. The composition dependence of $\text{Sr}_{1-x}\text{Pr}_x\text{La}_{x-y}\text{Mg}_x\text{Al}_{12-x}\text{O}_{19}$ absorption spectra at 15 K in (a) $^3\text{H}_4 \rightarrow ^3\text{P}_1, ^1\text{I}_6$ and (b) $^3\text{H}_4 \rightarrow ^3\text{P}_2$ transitions.

$^3\text{H}_4 \rightarrow ^3\text{P}_2$ transition (Fig. 2(b)). The relative intensities of these lines depend strongly on x , C_2 is prevailing at $x = 0.05$ and is negligible at $x = 0.3$, where C_1 is dominant; a third line C_3 of smaller intensity at lower energies is resolved at small x (0.05). The widths of these lines are quite different ($\sim 30 \text{ cm}^{-1}$ for C_1 , and $\sim 15 \text{ cm}^{-1}$ for C_2 center in the $x = 0.1$, $y = 0.1$ sample). This structure has not been remarked before, though variations in the heights, widths, and other small features, have been observed in Refs. [1,2].

The spectra corresponding to the $^3\text{H}_4 \rightarrow ^3\text{P}_0$ transition show a single main line with no structure, whose shape and width depend on x ; this unique line was a determining factor for the single center model, considered previously. The line shifts with composition ($\sim 10 \text{ cm}^{-1}$ for the $x = 0.1$ – 0.3 range), suggesting the presence of two composition dependent unresolved components (Fig. 3). As remarked also before [1], the line is accompanied, at high energies, by two satellites at ~ 85 and $\sim 190 \text{ cm}^{-1}$.

In order to obtain information on the symmetry of the Pr^{3+} centers, the polarization spectra were measured with light propagation along the a -crystal axis. Generally, the lines in σ polarization ($\vec{E} \perp c$) are more intense than the $\pi(\vec{E} \parallel c)$ lines, $\vec{E}$ being the electric field direction. In the D_{3h} local symmetry group the Pr^{3+} J manifolds are split

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