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Site-selective spectroscopy of Pr^{3+} ions in sodium β -alumina crystals

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Abstract: We report on the results of a low-temperature optical spectroscopy study of Pr^{3+} -exchanged sodium β -alumina single crystals ($\text{Na}^+/\text{Pr}^{3+}$ β - Al_2O_3), containing different amounts of luminescent ions, in which excitation and fluorescence spectra have been carried out in σ and π polarization.

The $^3\text{P}_0 \rightarrow ^3\text{H}_4$ emission spectra, obtained under broad band excitation, show an intriguing structure consisting of several components even with crystals containing low Pr^{3+} concentrations. The excitation spectra indicate the presence of at least two sets of different sites, available to Pr^{3+} in the conduction plane of β -alumina. Independently of the crystal composition, a quite satisfactory site-selective emission from each sets of centres has been achieved under cw excitation of the 465.8 nm and 476.5 nm lines of an Ar^+ ion laser.

1. Introduction

The discovery that sodium β -alumina, already well known as one of the most promising solid electrolyte, is able to incorporate a large variety of luminescent ions via ion-exchange reactions at moderate temperature prompted much interest in the possible optoelectronic applications of this material. During the last years, the optical properties of trivalent lanthanide ions in the sodium β -alumina have been extensively investigated [1–3] and some compositions have been proved to lase [4]. Recently, we succeeded in exchanging lanthanide ions in sodium β -alumina [5], a structurally close related compound, thus obtaining a potential alternative laser material. Some highly exchanged $\text{Na}^+/\text{Pr}^{3+}$ β - Al_2O_3 crystals have been preliminarily investigated by optical spectroscopy methods [6] with the aim to identify the type of sites occupied within the conduction planes of the host matrix. Indications about the existence of unequivalent sets of centres, characterized by different local environments, were derived from low-temperature measurements of either excitation spectra or time-resolved fluorescence of the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition of the Pr^{3+} ions [6,7].

Hereafter we present a site-selective excitation spectroscopy study of the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} ions in ion-exchanged sodium β -alumina crystals to provide further evidences for a different site occupancy of trivalent luminescent cations in the crystal structure of this host material.

2. Experimental

Single crystals of sodium β -alumina were provided by Union Carbide Corp. and by Ceramtech Inc. Their composition was $(\text{Na}_2\text{O})_{1.23} \cdot 11\text{Al}_2\text{O}_3$ and $(\text{Na}_2\text{O})_{1.28} \cdot 11\text{Al}_2\text{O}_3$,

respectively. Small platelets of rectangular form (typical size: $2 \times 3 \times 0.5 \text{ mm}^3$) were obtained from larger boules, and were ion exchanged with Pr^{3+} by immersion in molten PrCl_3 under argon atmosphere [5, 8]. The amount of the exchange was determined by electron probe microanalysis, which revealed degrees of exchange up to 95% for the sodium ions [5]. For the optical measurements the crystals were mounted into an optical cryostat, cooled by liquid He, and the sample temperature was maintained below 10 K.

Broad band excitation and emission spectra were excited using a 250 W Xe arc-lamp source filtered by a Jobin Yvon monochromator (mod. H.20, focal length of 200 mm, equipped with a 1200 grooves/mm grating). A spectral resolution of $\sim 4 \text{ \AA}$ was adopted for the excitation. The incident beam was focused onto the sample through a lens of 25 cm focal length. The fluorescence was analyzed at 90° by a Jobin-Yvon double-monochromator (Ramanor, mod. HG2-S, focal length of 1000 mm, equipped with holographic gratings, 2000 grooves/mm, blazed at 514.5 nm) and detected by a photon counting system, with a Peltier cooled photomultiplier (RCA, mod. C31034A-02). In this case the spectral bandpass was $\sim 1 \text{ cm}^{-1}$ at 500 nm with 100 μm slits. The advancement of both spectrometers was provided by step motors. A microcomputer was used to store the photon counts.

Polarized excitation spectra were recorded with the incident radiation perpendicular to the *c* axis of the crystal ($\mathbf{k}_{\text{inc}} \perp \mathbf{c}$) and circularly polarized ($\sigma + \pi$ polarization). For the emission spectra a sheet polarizer allowed the collection of the radiation polarized perpendicularly to the plane of scattering, while the crystal orientation was changed so that the emission spectra were recorded with $\mathbf{E} \perp \mathbf{c}$ (σ) and $\mathbf{E} \parallel \mathbf{c}$ (π).

Finally, laser excitation of the Pr^{3+} ion in β -alumina crystals was obtained using the different lines of a Ar^+ ion laser (Spectra Physics, mod. 161), while the remainder of the experimental apparatus was the same as for the broad band excitation described above.

3. Results and discussion

Typical σ and π polarized fluorescence spectra of a 60% Pr^{3+} -exchanged sodium β -alumina crystal, recorded at 10 K under broad band excitation within the $^3\text{P}_2 - ^3\text{P}_1(^1\text{I}_6)$ region, are shown in Fig. 1 with an assignment of the different transitions observed. The emission lines from the $^3\text{P}_0$ level which terminate on the $^3\text{H}_4$, $^3\text{H}_5$, $^3\text{H}_6$ and $^3\text{F}_2$ occur in the region between 21000 cm^{-1} and 15000 cm^{-1} and are characterized by strong inhomogeneous broadenings.

Fig. 1: Luminescence spectra obtained at 10 K from a Pr^{3+} -exchanged (60%) β -alumina crystal under broad band excitation at 457 nm, in σ -polarization (continuous line) and in π -polarization (dashed line).

Some $\sigma + \pi$ polarized excitation spectra, obtained under excitation of a Xe lamp from the same composition, are plotted in Fig 2. The spectra correspond to three different emission lines of the $^3P_0 \rightarrow ^3H_4$ transition. The top (Fig. 2 a) and bottom (Fig. 2 c) spectra clearly originate from two different sets of centres: they have to be related to distinct occupied sites of Pr^{3+} ions in the conduction plane of β -alumina. Besides the peak positions, the most striking differences are related to the width of spectral lines, which are inhomogeneous in character and indicate a different spread in the site-distribution of each set of centres. The mid spectrum (Fig. 2 b) is mostly the superposition of the two spectra a and c, but some extra features are present. Apart from the peak at ~ 454 nm, it closely resembles the σ -polarized absorption spectrum of an 94%-exchanged crystal, which has been reported elsewhere [6], where this peak appeared with a negligible intensity.

Fig. 2: Broad band excitation spectra of the $^3P_0 \rightarrow ^3H_4$ emission lines at: (a) 20586 cm^{-1} ; (b) 20503 cm^{-1} ; and (c) 20000 cm^{-1} . The spectra were recorded at 10 K with $\mathbf{k}_{\text{inc}} \perp \mathbf{c}$ in $\sigma + \pi$ polarization.

Very similar spectra, either in excitation or in emission, were obtained from crystals with lower Pr^{3+} ion contents.

The emission spectra of the $^3P_0 \rightarrow ^3H_4$ transition, excited at various wavelengths within the $^3P_2 - ^3P_1(^1I_6) - ^3P_0$ region by a cw Ar^+ ion laser, show very complex structures with many, strongly polarized components in the region between 21000 cm^{-1} and 19800 cm^{-1} . However, a quite satisfactory site-selective emission is achieved using proper excitation lines, as shown in Fig 3. In particular, the fluorescence spectra excited at 465.8 nm (Fig. 3 a) and 476.5 nm (Fig. 3 c), are mostly related to the two different sets of centres identified in Fig. 2 a and c, respectively. These spectra, even if very structured due to the presence of several, partially overlapping components, indicate remarkable differences in the ground state splittings of their respective centres, which are roughly twice for the set preferentially excited at 476.5 nm. Moreover, their peculiar polarization characters further confirm the different site occupancy by Pr^{3+} in the conduction plane of β -alumina. Finally, the spectra of Fig. 3 b contain the contributions from both sets of centers, thus correlating with Fig. 2 b.

4. Conclusions

Our excitation and emission study provide new indications of a different site occupancy of lanthanide ions in β -alumina crystals. It also shows that a satisfactory site-selective fluorescence from single sets of centres may be achieved under cw laser-excitation.

Fig. 3: ${}^3P_0 \rightarrow {}^3H_4$ emission spectra in σ -polarization (continuous line) and in π -polarization (dashed line) of a 60% ion-exchanged $\text{Na}^+/\text{Pr}^{3+}$ β -alumina crystal at 10 K excited at 465.8 nm (a), at 472.7 nm (b) and at 476.5 nm (c) as indicated by the arrows.

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