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P. Nelson, D. Vickers, O. Stafsudd. Approximate polarization selection rules for the $3P_0 \rightarrow 3H_4$ transition in Pr: β'' alumina single crystals. Journal de Physique IV Proceedings, 1994, 04 (C4), pp.C4-419-C4-422. 10.1051/jp4:19944100 . jpa-00252549

HAL Id: jpa-00252549

<https://hal.science/jpa-00252549>

Submitted on 1 Jan 1994

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Approximate polarization selection rules for the ${}^3P_0 \rightarrow {}^3H_4$ transition in $\text{Pr}:\beta''$ alumina single crystals

P.R. NELSON, D.J. VICKERS and O.M. STAFSUDD

Department of Electrical Engineering, University of California, Los Angeles, 56-125B Engineering IV, Los Angeles, CA 90024-1594, U.S.A.

Abstract: Emission spectra of the ${}^3P_0 \rightarrow {}^3H_4$ transition in $\text{Pr}:\beta''$ alumina single crystals excited by both a broad-band blue source and by dye laser excitation at various wavelengths within the inhomogeneously-broadened ${}^3H_4 \rightarrow {}^3P_0$ absorption line are considered. These spectra are strongly polarized, and are therefore due to Pr^{3+} ions in the Beevers-Ross (BR) sites. An approximately-axial model for the crystal field at a BR site predicts crystal field splitting of the 3H_4 level and polarization selection rules which approximately match those we have observed.

The discovery by Dunn and Farrington¹ of an ionic exchange process for inserting trivalent cations into single crystals of $\text{Na}:\beta''$ alumina and subsequent demonstration of laser action in $\text{Nd}:\beta''$ alumina² suggested the possibility of a laser material in which the crystal growth and doping could be separated so that each process could be conducted under optimum chemical conditions. Some typical rare earth laser ions have been studied in this host, but applications seem unlikely due to the difficulty of growing large single crystals. However, this material is still of scientific interest because dopant rare earth ions may occupy sites which are significantly different from rare earth sites in conventional materials. This host may thus provide tests of our understanding of the interaction between lanthanide ions and their surroundings in solids.

The structure of $\text{Na}:\beta''$ alumina consists of layers of densely-packed Al and O called spinel blocks, which are connected by Al-O-Al bonds. In addition to these connecting "column" oxygens, the regions between the spinel blocks contain mobile Na ions.³ In the ionic exchange process, three sodium ions are replaced by a trivalent rare earth ion. The x-ray structure determinations of several completely-exchanged rare earth isomorphs of the parent Na compound indicate that most of the rare earth ions occupy the mid-oxygen (mO) site, which has eight neighboring oxygens and approximately C_{2h} symmetry, while the rest are in the Beevers-Ross (BR) site, which has only four nearest neighbors and point symmetry C_{3v} .⁴ Structural studies of partially-exchanged rare earth compositions by x-ray diffraction are complicated by the defect nature of the material.

Polarized optical spectroscopy should be useful in establishing the structure of the partially-exchanged materials, since the various sites should exhibit distinctive spectra. The mO site has inversion symmetry so that its electric dipole transitions are forbidden, while for the BR site electric dipole transitions are allowed and polarized. Distorted mO sites have such low symmetry that their spectra will not be polarized. Unfortunately, polarized spectra are difficult to obtain because the available crystals are only a few tenths of a mm thick, so that they act as dielectric waveguides whose modes mix the polarizations somewhat. In particular, a π -polarized emission must propagate as a linear combination of the TM modes, and will thus also have a σ component. Since the platelets cleave easily in planes normal to the c axis, cutting and polishing are difficult. The samples used in this study were cut from crystals grown by flux evaporation. They are platelets a few mm on each side, with the crystallographic c axis normal to the large faces.

The optical spectra of several rare earth ions in this host have been investigated.⁵⁻⁸ The spectra are complex, and it is frequently not possible to assign good quantum numbers to the observed lines. Thus, we have chosen to use the Pr^{3+} ion as a probe of the crystal field because of the relative simplicity of its spectrum. Low-temperature polarized emission spectra of the $\text{Pr}^{3+} {}^3P_0 \rightarrow {}^3H_4$ transition have been obtained from three crystals with different dopant concentrations. The crystals are 9%, 55% and 88% exchanged. (The exchange percentage represents the fraction of Na⁺ ions replaced by Pr^{3+} .) All of the spectra in this study were obtained with the

crystal mounted in a closed-cycle helium refrigerator at a sample temperature of approximately 10K. The spectra were analyzed with a 1m Czerny-Turner monochromator with a 600 line/mm grating used in first order, detected by a photomultiplier with an S-20 photocathode, and collected by a computer-controlled data acquisition system. The pump light was directed normal to the observed emission, and both the pump and emission edges of the sample were polished.

The spectra shown in Fig. 1 were obtained by illuminating the samples with a 50 W Tungsten lamp and a dielectric filter having a transmission passband between 4500 and 4750 Å, which is in the region of the 3H_4 to 3P_1 absorptions, and thus should excite ions in all sites. The portions of the curves for wavelengths smaller than 4750 Å represent a combination of pump illumination and crystal absorption, while wavelengths larger than 4750 Å represent emission spectra. (The pump portion of the curve was omitted from the spectrum of the lightly-doped sample because it is very strong in comparison to the emission.)

Spectra from all three crystals are strongly polarized, indicating that the dominant emission is from ions which occupy relatively high-symmetry sites, which we assume to be approximately BR sites. An axial crystal field with a large, positive A_{20} has been proposed for rare earth ions in BR sites in this host⁹ on the basis of the unusually-large Judd-Ofelt parameter T_2 for Nd¹⁰, the EPR data for Ce¹¹, and preliminary polarized absorption and emission spectra for Pr⁹. In particular, the intensities of transitions between triplet and singlet levels are anomalously weak for Pr³⁺ in this host, indicating that the triplet and singlet wavefunctions may not have been mixed very much by the crystal field.⁹ This model is not intended to represent exactly the crystal field at any particular Pr³⁺ ion site, but it can be a useful predictor of the general features of the presumably inhomogeneous sites which contribute to the experimentally-observed spectra.

Table 1 lists estimated peak positions and polarizations for the observed emission spectra shown in Fig. 1. The upper state for the observed emission spectra (3P_0) has $J=0$, so these lines are due to splitting of the 3H_4 level by the crystal field. The experimentally-observed polarizations are those expected if the ground state (for which M_J is either zero or ± 4 in the axial model) is ± 4 .⁹ The three different sets of axial crystal field parameters (in Stevens' operator equivalent normalization) which approximately fit the data in Table 1 are shown in Table 2. The fits use published values of the Slater integrals and spin-orbit parameter.¹² Of these, the set with a large positive A_{20} is most consistent with both the Judd-Ofelt intensity parameters for Nd³⁺ and with the EPR data for Ce³⁺, and it is this one which we examine further. The relative energies of the 3H_4 states as calculated from the axial model with dominant A_{20} are also shown in Table 1. In order to obtain the peak position of the lowest-energy σ peak, it is necessary to account for depolarization of the nearby strong π peak by waveguide propagation. Thus, this peak position has significant uncertainty. In addition, the spectrum of the 9%-exchanged sample has poor signal-to-noise ratio, and therefore the largest error in peak positions.

One simple comparison of the three samples is possible based on the spectra in Fig. 1. Both absorptions and emissions exhibit monotonic shifts with concentration. The x-ray structure determinations mentioned above show that the fully-exchanged rare-earth isomorphs of the parent Na composition have unit cells which are significantly smaller in the c -axis direction. Since the spinel blocks are densely packed, the change in c must be due to a decrease in the distance between the blocks, which translates to a decrease in the distances from the Pr ion to the neighboring oxygens in the adjacent spinel blocks. The monotonic line shifts observed in our data are

Figure 1. Polarized spectra of the $^3P_0 \rightarrow ^3H_4$ emission, together with the broadband pump. a, b: 88% exch.; c, d: 55% exch.; e, f: 9% exch.

qualitatively consistent with this assumption. To the accuracy of the model and the fits, the differences in A_{40} and A_{60} are not significant and $A_{20} = 764 - 2.80 \times (\% \text{ exch.})$.

We have also used a dye laser to selectively pump within and near the observed 3P_0 absorption. These spectra are qualitatively the same as those shown in Fig. 1. The lines are still quite broad, although there are some shifts in line position with pump wavelength. These results do not significantly affect the analysis above. The search for evidence of a second site is unfortunately complicated by the presence of a pattern of weak emission lines which track the pump emission. A similar phenomenon has been reported in Pr: β alumina.¹³ These lines are exactly reproduced around the pump, whether or not there is a Pr^{3+} absorption at the pump wavelength, and therefore cannot be due to the electric transitions between states of the Pr^{3+} ion which are the subject of the current research. Since the peak intensity of the focused pulsed dye laser pump used in these experiments was approximately 100 MW cm^{-2} , and the lines are also observed with the sample at room temperature, these lines are probably stimulated Raman scattering which has been scattered from crystal imperfections and trapped in the slab waveguide.

In summary, we have obtained polarized emission spectra of the $^3P_0 \rightarrow ^3H_4$ transition of Pr^{3+} in single crystals of β alumina. These spectra are consistent with the assumption that in partially-exchanged samples the dominant emission is from rare-earth ions which occupy BR sites. The observed spectra can be modeled approximately using an axial crystal field with a large, positive A_{20} and a linear dependence of A_{20} on the exchange percentage. We interpret this relationship to the variation of the distance between adjacent spinel blocks with dopant concentration. This model is highly unusual in that for typical rare earth sites it is A_{66} which dominates the crystal field.

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Table 1. $^3P_0 \rightarrow ^3H_4$ emission line positions and derived crystal field splitting of the 3H_4 level as a function of Pr^{3+} concentration

% exch.	ν (cm $^{-1}$)	polarization	$\Delta\nu$ from ground state (cm $^{-1}$)	
			meas.	calc.
9	20,870	σ	-	-
	20,460	π	410	384
	20,370	σ	500	511
	20,120*	σ	750	691
	20,070	π	800	776
55	20,780	σ	-	-
	20,505	π	275	260
	20,415	σ	365	356
	20,220	σ	560	520
	20,165	π	615	601
88	20,812	σ	-	-
	20,495	π	317	314
	20,435	σ	377	375
	20,280	σ	532	504
	20,202	π	610	573

Table 2. Crystal field parameters of the axial model as a function of Pr^{3+} concentration. (Parameters are in Stevens's normalization.)

% exch.	A_{20}	A_{40}	A_{60}
9	755	0	-35
	450	380	-10
	-255	-315	-150
55	570	-20	-30
	315	300	-10
	-195	-250	-110
88	540	15	-35
	330	280	-20
	-160	-220	-120