

Luminescence of Cr^{3+} ions in mixed Na^+ - Cd^{2+} β -alumina crystals

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Luminescence spectra of Cr^{3+} ions, contained in traces in some mixed sodium-cadmium β -alumina crystals, were taken at temperatures of 82 and 300 K. Linewidths and lifetimes of luminescence spectra are measured as a function of crystal composition over a wide range of sodium-to-cadmium ratios. The results provide a new confirmation of the cation distribution model, recently postulated to account for ionic conductivity and Raman data.

INTRODUCTION

The superionic conductors of the β -alumina family have a layered structure formed by compact spinel blocks of aluminum oxide. In the region between two adjacent spinel blocks there is a two-dimensional array of interconnecting channels where it is possible to substitute a wide variety of cations.¹ The most common specimen of this family is sodium β -alumina, which grows in nonstoichiometric composition as $(\text{Na}_2\text{O})_{1+x} \cdot 11\text{Al}_2\text{O}_3$, where x represents the excess of soda. In the ideal stoichiometric compound, i.e., when $x=0$, the sites energetically more favorable to Na^+ ions are the so-called Beevers-Ross sites, while in the as-grown crystals Na^+ ions in excess should preferentially occupy the mid-oxygen positions.² Thus, in sodium β -alumina, a fraction x of mirror plane cells are doubly occupied by cations in pairs. Such pairs play a very important role in lowering the activation energy for the ionic conductivity, which is supported by sodium-ion diffusion, via an interstitial mechanism.³

Crystals in which the sodium content has been partially exchanged with divalent cations provide a rich family for new studies on the ionic distribution and on the diffusional dynamics. In fact, in these crystals it is possible to modify the number of interstitial Na^+ pairs, or even to produce cation vacancies, by varying the monovalent-to-divalent cation ratios. Therefore it becomes possible to study the behavior of pseudostoichiometric compositions, in which the number of cations is one per unit cell, or even of substoichiometric compositions, with fewer cations than the number of unit cells. As a matter of fact, the progressive substitution of Na^+ -ion pairs will not only reduce the sodium excess, but it will also leave a fraction of the mirror plane cells unoccupied. In addition, below the pseudostoichiometric composition, no interstitial pairs should exist and sodium-ion diffusion should occur by a vacancy mechanism with quite different activation energies, as calculated by Wang *et al.*⁴ Experimental evidence of the validity of these predictions was obtained some years ago by measuring the sodium-ion diffusion rate and the conductivity as a function of sodium content in mixed sodium-cadmium β -alumina crystals.^{5,6} Recent Raman data on this mixed system^{7,8} have been discussed and interpreted in connection with the model of cation distribu-

tion postulated to explain ionic conductivity behavior. It has been found that Raman bandwidths of some spinel-block modes are very sensitive to ion substitution, so that they can be considered as a reliable probe to test the degree of disorder in the ionic distribution over the conduction plane sites. As a matter of fact, the crystals with pseudostoichiometric composition show a higher degree of order; in contrast, those rich in cadmium, i.e., crystals containing a remarkable number of vacancies, indicate a strongly disordered structure, which allows for the observation of partial phonon density of states in the Raman spectrum.

In this work we use the luminescence spectroscopy of Cr^{3+} impurities, contained in traces in the same mixed system, as an alternative optical technique for extracting further, independent information on the structure and dynamics of the host crystal. Features like the linewidths and the lifetime of Cr^{3+} -ion emissions are very sensitive to crystal composition, and are discussed in connection with the previous Raman results.

EXPERIMENTAL DETAILS AND PROCEDURES

The crystals under study are those employed for the Raman measurements of Refs. 7 and 8. Mixed sodium-cadmium crystals were obtained from sodium β -alumina, originally supplied by Union Carbide Corporation as $(\text{Na}_2\text{O})_{1.22} \cdot 11\text{Al}_2\text{O}_3$. Partial substitution of Na^+ with Cd^{2+} ions was achieved in CdCl_2 melting at 650°C, as described by Sutter *et al.*⁶ Hereafter we shall refer to a specific mixed composition in terms of the fraction of replaced sodium.

In order to ensure a complete dehydration and a homogeneous distribution of Cd^{2+} ions, the crystals were annealed at about 650°C during a whole day in a controlled-atmosphere oven.

Traces of chromium are present as natural impurities in the as-grown sodium β -alumina, where they enter substitutionally for Al^{3+} ions in the octahedral sites of the spinel blocks.

For the luminescence spectra we used both the 514.5-nm line of a cw Ar^+ -ion laser and the 647.1-nm line of a cw Kr^+ -ion laser. For time-resolved luminescence spectra and for decay-time measurements, the laser beam was

mechanically chopped. A more detailed description of the experimental conditions and procedures is reported in Ref. 9.

RESULTS AND DISCUSSION

The luminescence spectra of the mixed $\text{Na}_{1-y}\text{-Cd}_{y/2}$ crystals fall in the region between 15000 and 13000 cm^{-1} , showing rather common features and similar shapes. The fluorescence is originated from the ${}^2E\text{-}{}^4A_2$ transition of the Cr^{3+} ion in octahedral sites.⁹ In Fig. 1 we report the luminescence spectra from the crystal with $\sim 33\%$ sodium replacement, obtained at 82 K under excitation of the 514.5-nm line. Two nonequivalent octahedral Al sites are available for Cr^{3+} ions:¹⁰ site Al(4), with D_{3d} site symmetry, which lies in the center of the spinel block, and site Al(1), nearer to the mirror plane, with lower symmetry (C_s site symmetry). Under cw excitation we observe [Fig. 1, spectrum (b)] the luminescence from Cr^{3+} ions in both sites. However, by means of time-resolved spectroscopy techniques it is possible to separate the emissions from the nonequivalent sites. In fact, because of the inversion symmetry, which inhibits the electric-dipole (ED) transitions between even electronic states, the luminescence from the Al(4) site has a very long decay time ($T \sim 50$ msec), as compared with the luminescence from the Al(1) site ($T \sim 1\text{--}3$ msec).⁹ At long delay after the laser pulse the luminescence from the Al(4) site is easily isolated [Fig. 1, spectrum (a)]. The spectrum presents two relatively sharp zero-phonon lines

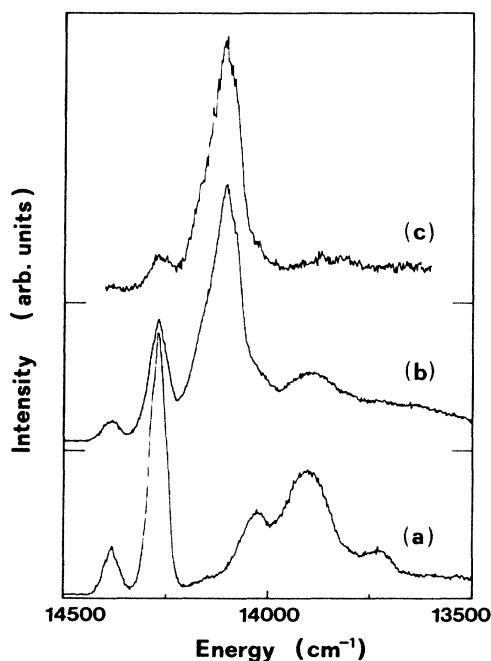


FIG. 1. Luminescence spectra of $\text{Na}_{1-y}\text{-Cd}_{y/2}$ β -alumina doped with Cr^{3+} , with $y = 0.33$ at 82 K, obtained by exciting with the 514.5-nm line. (a) excitation with a pulse of 50 msec, detection from 16 to 55 msec after laser switchoff; (b) continuous excitation; (c) excitation with a pulse of 3 msec and simultaneous detection.

(ZPL's), due to the splitting of the 2E excited state under trigonal distortion, with a one-phonon sideband (SB). In the following the ZPL's will be indicated as R1 and R2 lines, respectively. Their full widths at half maximum (FWHM) are about 40 cm^{-1} .

On the contrary, with a shorter laser pulse (~ 3 msec) and simultaneous detection, the emission from the Al(1) sites turns out to be predominant [Fig. 1, spectrum (c)]. In this case, the spectrum is dominated by a single, broader line (FWHM about 100 cm^{-1}), peaked at lower energy with respect to those arising from Al(4) sites. Here the splitting of the 2E state is not resolved.

The broadening of the zero-phonon lines is of inhomogeneous character. At low temperature, in fact, fluorescence line-narrowing measurements performed on a crystal of Ag β -alumina doped with Cr^{3+} show very narrow lines. The homogeneous contribution to the linewidth turns out to be negligible for the line of spectrum (a) (Ref. 11) as well as for that of spectrum (c).¹² The disorder which affects the energy of the involved levels and originates the broadening also affects the radiative transition rates. In particular, a continuous distribution of decay times (between 1 and 3 msec) is observed in case (c). The distribution of decay times of Cr^{3+} ions in Al(4) sites is less dispersed. Beyond the first ~ 20 msec, the decay-time curve is quite well fitted by a single exponential. Furthermore, spectrum (a) of Fig. 1 is not sensitive to the employed time delay, provided it is long enough, i.e., more than 20 msec. However, the decay-time profiles show also luminescence from Cr^{3+} in distorted Al(4) sites with shorter decay times. Their contribution to the R1 luminescence is evident in Fig. 1, spectrum (c), where it appears as a shoulder of the dominant feature on the high-energy side. We observe that the R lines in spectrum (a) appear sharper than in spectrum (b) because in long-decay-time spectra, the emissions from less distorted centers are favored.

The width of the lines measures the degree of disorder in the crystals with different composition. In Fig. 2 we show the emission spectra, obtained at 82 K, for the centers with shorter decay time, from some $\text{Na}_{1-y}\text{-Cd}_{y/2}$ crystals characterized by different values of the y parameter, which range from 0, spectrum (a) to 0.88, spectrum (g). It is evident that for high cadmium concentrations there is an increasing of the broadening, and some structures grow in the shape of the line. A similar trend is observed in the room-temperature spectra (Fig. 3). Here, the selection of the Al(1) site is obtained by selective excitation at 647.1 nm. In fact, this frequency falls just in the low-energy side of the ${}^4A_2\text{-}{}^4T_2$ broadband absorption transition for the Cr^{3+} ion in Al(1) sites. The corresponding transition for the Al(4) sites occurs at higher energies, as observed in time-resolved excitation spectra.¹² The linewidth behavior is shown in Fig. 4(a) where the FWHM of the lines in the spectra of Figs. 2 and 3 are plotted versus the percent of sodium replacement. For comparison, in Fig. 4(b) the bandwidth of two typical Raman bands of the host crystal are reported. All of these linewidths present a common trend versus the crystal composition. They pass through more or less pronounced minima in the compositional range that corresponds to

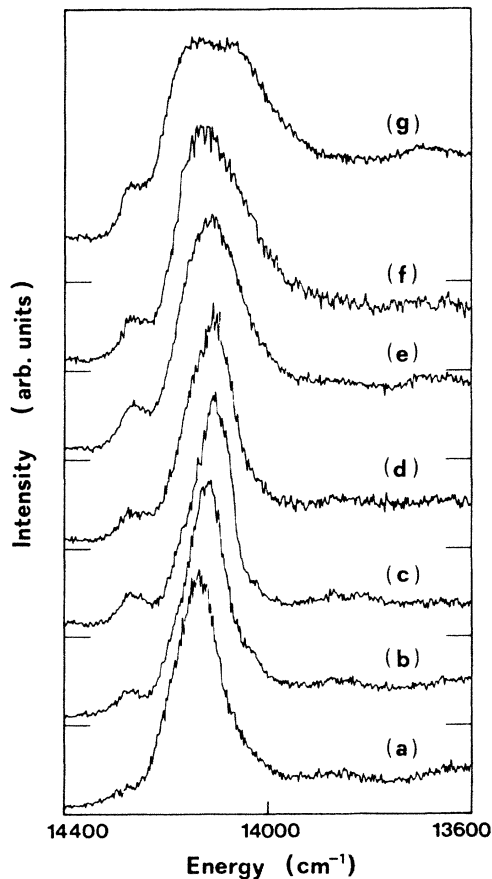


FIG. 2. Time-resolved luminescence spectra of Cr^{3+} in mixed $\text{Na}_{1-y}\text{-Cd}_{y/2}$ β -alumina crystals at 82 K. Excitation with a 3-msec pulse of the 514.5-nm line and simultaneous detection: (a) $y=0$, (b) $y=0.14$, (c) $y=0.33$, (d) $y=0.49$, (e) $y=0.55$, (f) $y=0.71$, and (g) $y=0.88$.

pseudostoichiometry. The line narrowing reflects, of course, the development of a more ordered ionic distribution in the conduction planes as the number of ions approaches the pseudostoichiometric value. In this situation a minimum in the crystal-field distribution is "felt" by the impurity ions as well as by the ionic groups whose vibrational motions contribute to the Raman spectrum. Such a distribution can be produced if the Cd^{2+} ions preferentially replace Na^+ ones in doubly occupied cells for y values up to about 0.4, as has been suggested by Sutter *et al.*⁶ On the other hand, above this range of y the Cd^{2+} ions replace Na^+ ions in singly occupied cells, and produce an increasing number of vacancies in the conduction plane. The introduction of divalent ions and cation vacancies results in a progressive disordering in the cation sublattice. Apart from the lattice distortion due to the relaxation around Cd^{2+} ions and vacancies, the main effect on the Cr^{3+} crystal field would be the excess of positive and negative charges. A broadening and possibly a growth of structures on the lines is therefore expected and actually observed in Cr^{3+} luminescence spectra (see Figs. 2 and 3) as well as in the Raman ones.⁷

The effect of Cd^{2+} replacement is less evident on the

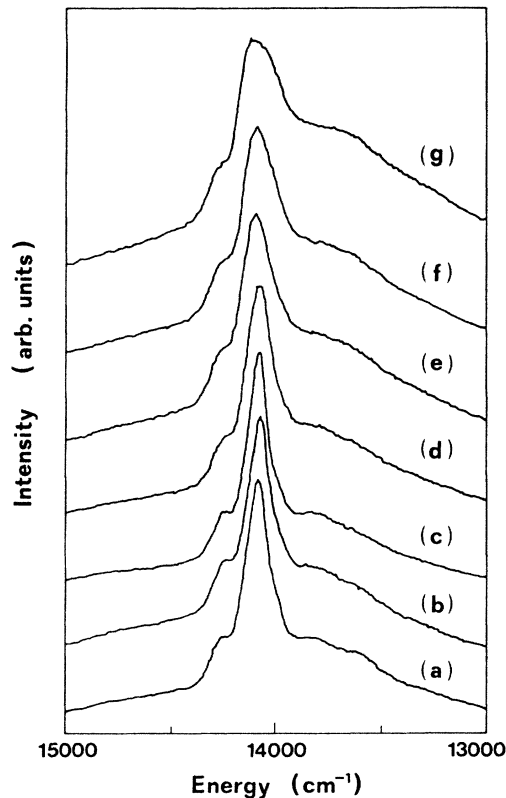


FIG. 3. Luminescence spectra of Cr^{3+} in mixed $\text{Na}_{1-y}\text{-Cd}_{y/2}$ β -alumina crystals at 295 K, with cw excitation of the 647.1-nm line: (a) $y=0$, (b) $y=0.14$, (c) $y=0.33$, (d) $y=0.49$, (e) $y=0.55$, (f) $y=0.71$, and (g) $y=0.88$.

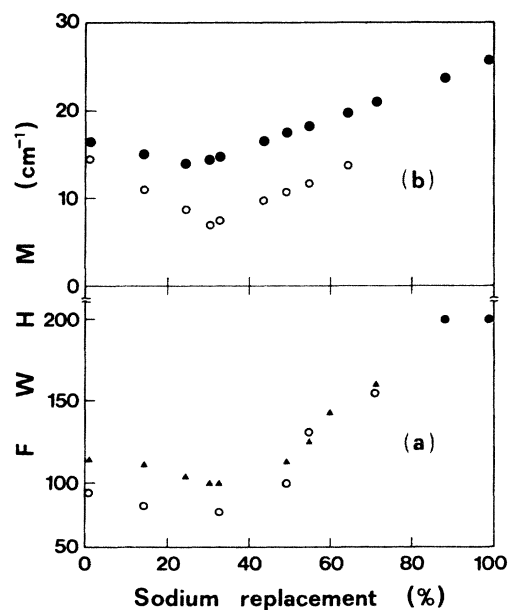


FIG. 4. Dependence on the sodium exchanged for cadmium of the linewidths of (a) 2E_4A_2 luminescence line of Cr^{3+} ions in Al(1) sites at 82 K (open circles) and at 295 K (triangles); (b) Raman bands peaked at 256 cm^{-1} (solid circles) and at 422 cm^{-1} (open circles) in the room-temperature spectra (Refs. 6 and 7).

width of the R lines of Cr^{3+} in $\text{Al}(4)$ sites. The widths of $R1$ and $R2$ lines increase by only about 15% in the Cd^{2+} fully replaced samples. This result is not surprising because Cr^{3+} in $\text{Al}(4)$ sites, at the center of the spinel block, should be relatively less sensitive to the cation arrangement in the mirror plane. For this type of center, however, more sensitive probes of the change in the ionic distribution over the mirror plane sites are provided by the luminescence decay times and by the intensity ratios between zero-phonon lines and the sideband, as shown in Fig. 5. Here, we plot the decay times obtained by a fit of the long-decay-time region, where a single exponential decay is present.

In D_{3d} symmetry the ${}^2E-{}^4A_2$ ZPL transitions are magnetic dipole (MD) allowed. As for the sideband it is well known that the electron-phonon interaction for the ${}^2E-{}^4A_2$ transition is very small, because both states derive from t^3 strong crystal-field state. However, the occurrence of a strong one-phonon sideband is expected, due to the vibrations of odd-parity phonons which make the ED transitions allowed by mixing the involved even electronic states with highly excited, odd-parity electronic states. A static, odd distortion makes zero-phonon transitions electric-dipole allowed; therefore, when such an odd distortion becomes stronger a decrease of the lifetimes and of the intensity ratios between sideband and zero-phonon lines is expected. The following relation should be satisfied:

$$1/\tau = P_{\text{ZPL}} + P_{\text{SB}} + P_{\text{NR}}, \quad (1)$$

where $P_{\text{ZPL}} = (P^{(\text{MD})} + P^{(\text{ED})})_{\text{ZPL}}$ accounts for the contributions of magnetic $P^{(\text{MD})}$ and electric $P^{(\text{ED})}$ dipole transition rates to the ZPL's, P_{SB} is the transition rate with emission of one phonon, and P_{NR} indicates the probability for nonradiative transitions. Data of Fig. 5 can be interpreted as the progressive increase of the $P_{\text{ZPL}}^{(\text{ED})}$ with the cadmium content. In fact, the behaviors of the lifetimes and of the intensity ratios can be reasonably well reproduced by Eq. (1) if $P_{\text{NR}} = 0$ and $P_{\text{SB}} = \text{const}$. Therefore, our results indicate a progressive mean increase of an odd crystal-field component acting on the $\text{Al}(4)$ site, derived from the presence of locally noncompensated electrical charges in the mirror plane cells. These charges are due to the presence of Cd^{2+} ions in some cells, where they act as a positive charge in excess, and to the presence of as many vacant cells, each providing one negative charge. The data show that the disorder in the electric charge dis-

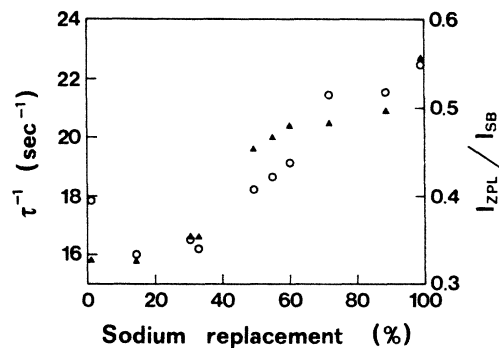


FIG. 5. Dependence on sodium replacement of the inverse of luminescence decay times from Cr^{3+} ions in $\text{Al}(4)$ sites (triangles and scale on the left side), and of the intensity ratios between zero-phonon lines and sideband (open circles and scale on the right side). Data are relative to spectra at 82 K.

tribution due to the odd distortion has more effect on the lifetimes (transition probabilities) than on the energy-level positions and their distribution.

This could be interpreted as evidence of some correlation degree in the site occupation of Cd^{2+} ions in the mirror plane cells; in fact, an ordered, alternating array of cadmium ions and vacancies should originate an odd distortion on the $\text{Al}(4)$ site, while not producing any appreciable broadening in the linewidth.

In conclusion, our present results strengthen the structural model developed in order to account for the electrical conductivity data on mixed sodium-cadmium β -alumina,^{5,6} already supported by recent Raman findings.^{7,8} In addition, they demonstrate the sensitivity of the spectroscopic techniques on impurities to give a measure of the disorder degree and of the distortion in compounds where the composition can be varied in a controlled way.

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