

Observation of persistent spectral hole burning of Eu^{3+} in β' -alumina at 110 K

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Persistent spectral hole burning (PSHB) has been observed at 110 K in Eu^{3+} exchanged Na^+ β' -alumina crystals. This is the highest burning temperature for PSHB in Eu^{3+} doped materials. It is found that the long lived holes at high temperature are caused by light-induced local motion of ions surrounding the Eu^{3+} ions. The results both of hole relaxation and temperature cycling measurements can be well interpreted by a hopping model with a Gaussian distributed barrier height.

I. INTRODUCTION

Persistent spectral hole-burning (PSHB) spectroscopy has been established as a powerful tool to investigate the structural and electronic properties of disordered materials.¹ Rare-earth ions have been used as optical centers for PSHB studies, because they show narrow optical absorption bands.² Especially, Eu^{3+} has been widely adopted as a guest ion, due to the simple excited energy levels. The mechanism of PSHB on Eu^{3+} doped materials may be caused by the two mechanisms: internal optical pumping between sublevels split by hyperfine interaction,^{2,3} and due to light-induced ion rearrangement around optical centers. The latter has not been reported. This is in contrast to the case of Pr^{3+} doped systems, in which PSHB is caused by configurational changes surrounding the Pr^{3+} ions.⁴ Since the spin-lattice relaxation between hyperfine splitting sublevels has a strong temperature dependence, the holes observed in Eu^{3+} doped materials are stable only at very low temperature.⁵ Recently, room temperature PSHB has been reported on Sm^{2+} doped materials.⁶ However, high temperature PSHB above liquid N_2 temperature is observed in only a few materials.

In this paper, we demonstrate persistent spectral hole burning in Eu^{3+} doped β' -alumina crystals at 110 K. This is the highest burning temperature among previously published data for Eu^{3+} doped systems.

β -alumina crystals (typically $\text{Na}_{1.67}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17}$ for Na^+ β' -alumina)⁷ belong to the family of β -alumina and are well known as a typical superionic conductor.⁸ Two-dimensional conduction planes are well separated by the spinel block which consists of close-packed layers containing aluminum, magnesium, and oxygen ions. There are two inequivalent well-defined crystallographic sites, the so-called Beevers-Ross (BR) site and the midoxygen (mO) site, for mobile ions in the conduction plane. Since as-grown crystals of β' -alumina have nonstoichiometric composition, mobile (Na^+) ions and vacancies always exist in the conduction plane at above 300 K. Thus structural disorder, which is induced by the randomness of the ion distribution, is introduced in the conduction plane. However, it should be noted that the framework (spinel block), which makes the periodic potential for mobile ions, does not have structural disorder,

but only the mobile ion distribution in the two-dimensional conduction plane becomes disordered in this material. In this sense, the structural properties of β' -alumina are considered to be intermediate between ordered and disordered materials, and are essentially different from those in glassy or amorphous materials.

One of the advantages of β' -alumina is that trivalent ions, for example Eu^{3+} and Na^{3+} , etc., which are very useful for optical measurements, can be introduced into the conduction plane by the ion-exchange technique at relatively low temperature.⁹ This is a property of β' -alumina that differs from that of β -alumina. Using this technique, the concentration of trivalent ions can be easily controlled by exchange time and temperature.

Eu^{3+} ions are introduced as optical centers in the two-dimensional conduction plane of β' -alumina crystals. Optical properties of Eu^{3+} doped β' -alumina have been extensively studied by Simkin's group using site-selective spectroscopy.^{10,11} They reported that Eu^{3+} ions occupy the mid-oxygen (mO) and BR sites. Using fluorescence line narrowing (FLN) spectroscopy, Yugami *et al.*¹² have measured the temperature dependence of the homogeneous linewidth (Γ_h) of the 5D_0 - 7F_0 transition of Eu^{3+} in β' -alumina on samples with different Na/Eu ratios.

II. EXPERIMENT

Single crystals of sodium β' -alumina were grown by the flux method from an eutectic melt of Na_2O (30 mol %), MgO (8.5 mol %), and Al_2O_3 (61.5 mol %).¹³ This composition is richer in Na_2O than β' -alumina and melts at about 1983 K in a Pt crucible. This temperature were kept for 150 h. Typical dimensions of grown crystals are 0.7 cm^2 (*c* plane) $\times 0.5 \text{ cm}$. Eu^{3+} β' -alumina crystals were prepared by the previously mentioned ion exchange technique⁹ by sealing sodium β' -alumina crystals in a quartz tube together with EuCl_3 , and heating to 923 K for 10 to 60 h. Clear colorless crystals were obtained. Since Eu^{3+} ions in β' -alumina easily change into Eu^{2+} during the ion exchange, the oxidation state of the Eu ion was checked by x-ray absorption near-edge-structure (XANES) spectroscopy. It was found from XANES spectra

that only Eu^{3+} ions existed in the so prepared samples. In this study, we used 90% exchanged samples, i.e., the concentration ratio of Na^+ to Eu^{3+} ions was 0.1. This value was determined by x-ray fluorescence analysis. The error of the estimated ratio of $\text{Na}^+/\text{Eu}^{3+}$ is about $\pm 5\%$.

Luminescence spectra under ultraviolet (UV) light excitation were obtained by using the 308 nm line of a XeCl excimer laser. The laser beam was focused onto the sample in a closed-cycle He refrigerator which can cool the sample down to 15 K. The luminescence was analyzed with a double monochromator (resolution limit of 2 cm^{-1}) equipped with a photomultiplier and a boxcar integrator. The gate of the boxcar integrator was opened from 0.1 to 2 msec after excitation.

A single-mode scanning ring dye laser (COHERENT 899-21) with a nominal linewidth of 1 MHz was used as a light source for hole burning. The dye laser was operated with rhodamine 6 G for excitation of the Eu^{3+} ions. The laser power was stabilized by a power controller (Cambridge Research Inc. LPC-vis) and was changed by neutral density filters. The laser power was typically 400 mW/cm^2 for burning and at least two orders of magnitude less for reading.

The holes were detected by measuring the luminescence excitation spectrum. The luminescence from the sample was dispersed by a monochromator ($f=30\text{ cm}$) equipped with a cooled photomultiplier (Hamamatsu R943-02). Signals were detected by a lock-in amplifier and were accumulated 10–30 times by a digital storage oscilloscope. The frequency of ring laser was scanned by a wave generator. The scan time is set to 0.5–2 s/scan.

The samples were placed in a cryostat (Oxford Instruments CF-1204) and could be cooled down to 5 K. The temperature was controlled by a temperature controller (Oxford Instruments CF-1240) between 5 and 300 K, and was monitored by a calibrated germanium resistor (accuracy of 0.1 K).

III. RESULTS AND DISCUSSION

Figure 1 shows the ${}^5D_0\text{-}{}^7F_0$ transition region of the luminescence spectrum of Eu^{3+} exchanged β' -alumina (90% exchanged) excited at 308 nm. According to the assignment of Simkin *et al.*,¹¹ the bands at 572 and 577 nm correspond to the emission of Eu^{3+} at BR and mO sites, respectively. Since the relative intensity of these bands changes with a change in the Na/Eu concentration ratio, the site occupancy of Eu strongly depends on its concentration.¹²

In this study, we tuned the laser wavelength within the inhomogeneously broadened ${}^5D_0\text{-}{}^7F_0$ transition to the 577 nm band (mO band). When holes are burned at 577.5 nm, which is the high energy side of the mO band, narrow and short-lived holes accompanied by antiholes are predominantly observed. The hole area rapidly decreases after the burning laser is removed. The life time of the holes is about 2 min at 5 K. These are the characteristic features of hole-burning spectra observed in various Eu^{3+} doped glasses. From these results, we concluded that this short-lived hole is created by optical pumping of ground-state nuclear hyperfine levels, which has been usually observed in Eu^{3+} -doped materials.

In contrast to 577.5 nm excitation, wide and long-lived

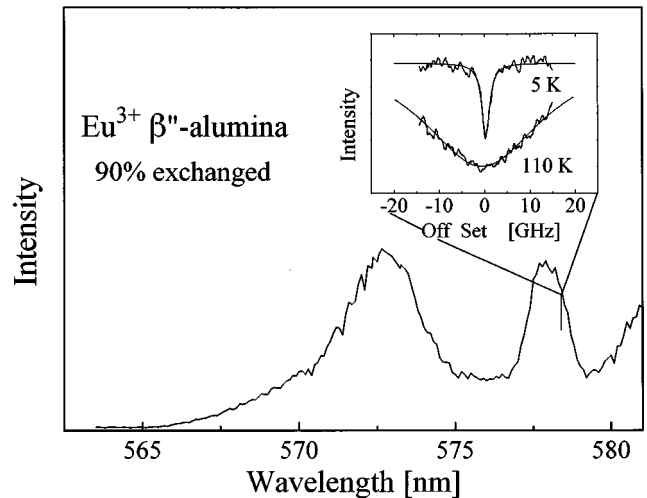


FIG. 1. Luminescence spectra of Eu^{3+} -exchanged Na^+ β' -alumina under UV light excitation at 15 K. The inset shows hole spectra at 5 and 110 K. These spectra are well reproduced by a Lorentzian curve (smooth lines). The burning time and fluence are 300 sec and 400 mW/cm^2 , respectively. The probe light is attenuated with a neutral density filter(1/400).

holes, which are shown in the inset of Fig. 1, are observed at 578.5 nm. Such long-lived holes are dominant only in the region around $578.5\pm 0.5\text{ nm}$. The reason why the PSHB occurs in only a narrow part of the absorption band is not clear at present. The typical hole depth is about 15–20%. Since antiholes are not observed in the long-lived hole spectra and the hole width is larger than that of the short-lived holes, we assigned that the long-lived hole in Eu^{3+} in β' -alumina is caused by a photoinduced rearrangement of the local structure surrounding the optical centers.

The remarkable feature of this system is that holes can be burned up to 110 K. As mentioned above, hole burning in Eu^{3+} doped systems has been caused by the optical pumping mechanism in previous studies, and is stable only at very low temperature. The burning temperature of 110 K is the highest temperature reported literature for Eu^{3+} doped materials.

The refilling dynamics of holes, burned and probed at 110 K, is shown in Fig. 2. This figure is plotted as a function of time after the burning laser is removed. The hole area after burning reveals a highly nonexponential time behavior which has been commonly observed in disordered materials. Such nonexponential behavior has been interpreted by tunneling models with a distribution of tunneling parameters.^{14,15} In our study, holes are burned and probed at relatively high temperature (110 K). Thus we have analyzed with a thermally activated model, which has been applied to high temperature PSHB in Sm^{2+} doped materials.¹⁶

The relaxation rate of holes R is given by

$$R = R_0 \exp(-V/kT); \quad (1)$$

here R_0 is the attempt frequency of particles and V is the

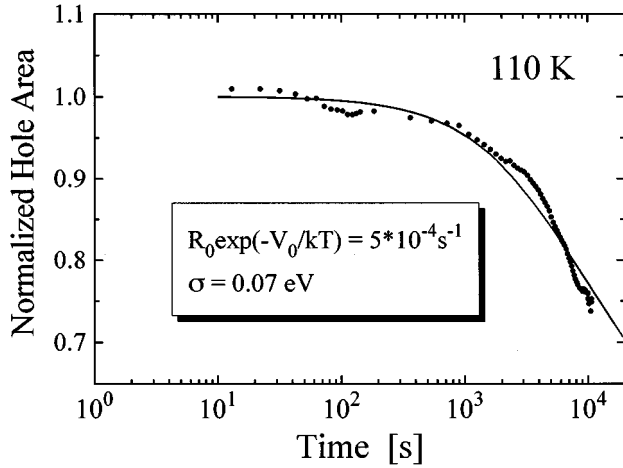


FIG. 2. Hole relaxation at 110 K for 90% exchanged Eu^{3+} β' -alumina. The hole area is normalized to unity at $t=0$. The burn and probe conditions are the same as in the inset of Fig. 1. The solid curve is a fit to a Gaussian distribution of barrier heights with the values of parameters shown in this figure.

thermal barrier height. We have assumed that V has a Gaussian distribution given by

$$g(V) = (2\pi\sigma^2)^{-1/2} \exp[-(V-V_0)^2/2\sigma^2]. \quad (2)$$

The time dependence of the hole area $A(t)$ for a sequence of filling is fitted by the following equation:

$$A(t) = \int_{-\infty}^{+\infty} g(V) \exp(-Rt) dV. \quad (3)$$

A fit of the data using Eq. (3) is shown in the solid curve in Fig. 2, where the fit parameters are the dominant relaxation rate $R_0 \exp(-V_0/kT) = 5 \times 10^{-4} \text{ s}^{-1}$ and $\sigma = 0.07 \text{ eV}$. If we assume that the frequency R_0 is equal to the attempt frequency of a Na ion in the conduction plane (33 cm^{-1}), which has been obtained by Raman scattering,¹⁷ the barrier height V_0 is estimated to be 0.33 eV. The hole relaxation by the thermal process has been reported in Sm^{2+} doped SrFCl .¹⁶ The distribution of barrier heights estimated in our study is far smaller than that obtained in the Sm^{2+} system. The relatively small distribution of barrier heights in β' -alumina may be due to its intermediate nature between an ordered and disordered material. Especially, in the case of β' -alumina, the ordered and disordered regions are separated each other, i.e., only the two-dimensional conduction plane contributes to the structural disorder. This feature is quite different from the other crystalline disordered system, for example SrFCl (Ref. 16) and yttria-stabilized zirconia,¹⁸ etc., in which the two-level tunneling system model has been successfully applied.

The distribution of barrier heights for this system can be also investigated by measuring the thermal recovery of holes. In this experiment, a hole is burned at a certain temperature (T_b), and the hole area is measured. After cycling through a certain temperature T_{max} , its area is measured again at T_b .

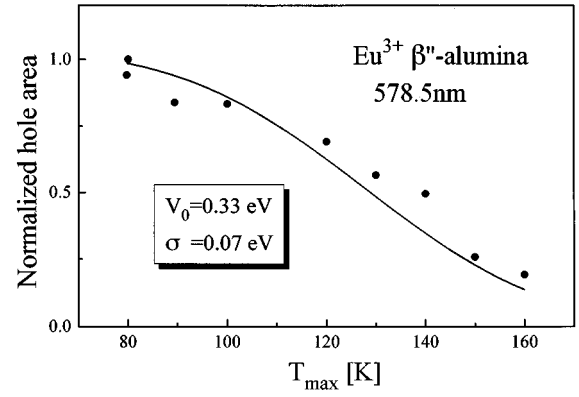


FIG. 3. Hole area plotted as a function of the cycling temperature T_{max} . The burn and probe conditions are the same as in the inset of Fig. 1. The solid curve is a fit to a Gaussian distribution of barrier heights with the values of the parameters shown in this figure.

During this process, the hole is partially refilled by the thermal process across the barriers in the ground state.

The dependence of the hole area A on the cycling temperature is shown in Fig. 3. The hole is burned at 80 K. For a system with a distribution of barriers, $g(V)$, the fraction f of the hole that remains after thermal cycling to T_{max} is given by¹⁹

$$f = 1 - \int_0^{kT_{\text{max}} \ln(R_0 t)} g(V) dV; \quad (4)$$

here t is the holding time at T_{max} . In this case t is 30 s. The data shown in Fig. 3 are well described by this model with a Gaussian barrier height distribution represented in Eq. (2) using $V_0 (=0.33 \text{ eV})$ and $\sigma = 0.07 \text{ eV}$. These are exactly the same values used for the fitting of Fig. 2. Since the result of two independent experiments can be reproduced with the same values of the parameters, it is confirmed that the hole dynamics is well described with our model.

The high temperature part of homogeneous linewidth (Γ_h) in this system have been studied by FLN spectroscopy.¹² The hole width observed above 80 K is consistent with the Γ_h determined by FLN. The preliminary study of low temperature PSHB reveals that the temperature dependence of Γ_h as well as the Γ_h at a given temperature strongly depends on $\text{Na}^+/\text{Eu}^{3+}$ ratios in crystals. The results of temperature dependence of Γ_h for different compositions will be published elsewhere.

The potential barrier heights between neighboring Na^+ sites is estimated to be 0.37 eV using the path-probability method.²⁰ This value is very close to the barrier height estimated in this study. This suggests that PSHB is caused by optically activated motion of a residual Na^+ ion near the optical centers. However, the structure of the conduction plane has not been fully resolved in Eu^{3+} exchanged Na^+ β' -alumina. More detailed structural studies of the conduction plane will be needed to clarify the origin of this PSHB, and, furthermore, will lead to the development of high temperature PSHB in Eu^{3+} -doped materials.

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