Time-resolved spectroscopy of the luminescence in KBr:Sn^{2+} crystals

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The time behavior of the luminescence due to Sn^{2+} ions accompanied by a charge-compensating cation vacancy in KBr:Sn^{2+} has been investigated in the temperature region 15–300 K. In addition to a slow decay with a lifetime longer than 10 μs at 15 K, a fast decay with a lifetime shorter than 0.4 μs was found. The time-resolved study has revealed the presence of two emission bands with peaks at 520 and 545 nm that have lifetimes of 130 and 372 ns at 15 K, respectively. These emission bands have been assigned to the A_T emission bands that were not found in previous luminescence studies of KBr:Sn^{2+}. It is confirmed, from the observation of two A_T emission bands with different fast decay components, that the relaxed excited states responsible for these emissions are mainly determined by the presence of the vacancy effect, as expected.

I. INTRODUCTION

A considerable amount of study has been done on the optical properties of s^2-electron-configuration ion centers in alkali-halide crystals (see review articles, e.g., by Hizhnyakov and Kristoffel, by Ranfagni *et al.*[1] and by Jacobs[2]). Among the optical studies, a lifetime measurement has been made for the luminescence produced by the s^2 centers. Unlike the case of monovalent s^2 ion centers like Tl$^+$ and In$^+$, a charge-compensating cation vacancy is located close to divalent s^2 ions such as Sn^{2+} and Pb^{2+}, reducing the crystal symmetry around the s^2 ion.[1,3] The information of the electronic states including the symmetry can be obtained not only by the luminescence polarization but also by the lifetime study since the relaxed excited states (RES's) responsible for the luminescence reflect directly the level splitting caused by a reduction of the symmetry of the s^2 center.

The lifetime study of Sn^{2+} centers has mainly been made by Jacobs and collaborators[4–7] and by Zazubovich and collaborators.[8] They observed only a slow decay component with a lifetime of longer than 1 μs for the A_T emission, although they had expected an additional component, i.e., a fast component with a lifetime shorter than 1 μs.[5,6] The two decay components are considered to be caused by the vacancy. Therefore, to check the vacancy effect in the divalent s^2 ion centers, it is necessary to determine whether the theoretically expected fast component is present or not.

The present investigation was undertaken to find the fast component in Sn^{2+} centers in alkali-halide crystals. Here we investigate a sample of KBr:Sn^{2+}. A reason for choosing KBr:Sn^{2+} is the following: Unlike the case[7] of KI:Sn^{2+}, two resolved A_T emission bands have not been unambiguously observed in KBr:Sn^{2+}, although Scacco and Jacobs tried to resolve the observed A_T emission band with a single peak into two components by computer analysis.[9] The two emission bands are known to arise from the electrostatic perturbation on Sn^{2+} ions due to the presence of vacancies.[7,10] It is interesting to check

experimentally whether two A_T emission bands appear in KBr:Sn^{2+}. A time-resolved luminescence investigation was undertaken for the first time to find not only the fast component but also the two A_T emission bands.

II. EXPERIMENTAL PROCEDURE

Single crystals of KBr doped with 0.001–0.01 mol % SnBr$_2$ in the melt were grown by the Stockbarger method. The crystals were heated up to 620 °C for 2 h and quenched to room temperature on a copper plate to decay the Sn^{2+}-colloidal or aggregate centers. The crystal was cooled using a cold finger in an Iwatani Cryo-Mini closed helium-gas cryostat.

A Molectron UV14 N$_2$ laser was used as an excitation light source. The pulse width is 10 ns, the peak power is 425 kW, the average power is 180 mW, and the repetition rate is 30 Hz. An external triggering was operated using a Stanford DG535 pulse-delay generator. The crystal luminescence was collected at right angles to an entrance slit of a Jobin-Yvon HR 320 polychromator and detected by a Hamamatsu Photonics C3140 change-coupled device (CCD) camera attached with a Peltier-element cooled photodetector which allows detection of the luminescence in the spectral region of 400–1100 nm.

The luminescence decay and time-resolved spectrum were obtained using a Hamamatsu Photonics C2830 Streak Camera system (the allowed sweep time varies between 10 ns and 1 ms), and the data were transferred to a Hamamatsu Photonics Temporal Analysis computer for averaging, storage, and analysis. The laser pulse was synchronized with the streak sweep within a jitter of less than 2 ns.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Slow decay component

A broad emission band with a peak at about 528 nm was observed at room temperature in a crystal before

quenching. This was measured using a streak sweep time of 5 μs after excitation. As shown in Fig. 1(a), the emission band is changed into a narrow band with a peak at 510 nm when measured immediately after quenching the crystal. This behavior is the same as that observed previously using a cw excitation light.[9] The luminescence decay curve of the 510-nm band is shown in Fig. 1(b). The decay occurs along a long exponential line with a lifetime of 1.68 μs. This value is near the one obtained by Sivasankar et al.[6] Similarly, a long, exponential decay line was obtained for the emission in the crystal before quenching. No difference was observed in the lifetime between the low- and high-energy sides of the 510-nm bands, indicating that the 510-nm band does not consist of two or three bands with different lifetimes but it is a single band.

In Fig. 2, we plot, against temperature, the lifetime of the emission appearing in a crystal before quenching and in the same crystal after quenching. Figure 2 also shows a temperature-dependence curve derived by Sivasankar et al.[6] for the emission observed after quenching. They obtained its curve from a parameter fitting for the RES constructed taking into account the vacancy and Jahn-Teller effects on Sn^{2+} ion in KBr. The lifetime of the emission observed after quenching is close to the semi-theoretical curve. The emission observed before quenching, i.e., the 528-nm emission at room temperature, is believed to be caused by the Sn^{2+}-aggregate center, while the emission observed after quenching is due to Sn^{2+} with a cation vacancy at the neighboring position.[9] It is noted that the lifetime of the emission due to the Sn^{2+} aggregate is found not to be largely different from one due to the Sn^{2+}-vacancy center, indicating that almost the same electronic state of Sn^{2+} ions are responsible for both emissions.

In the following, our description is confined to the Sn^{2+}-vacancy luminescence observed after quenching.
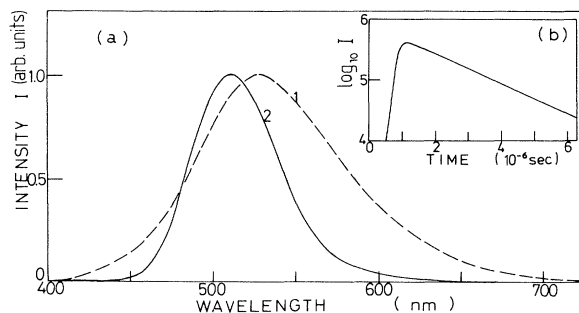

FIG. 2. Temperature variation of the lifetime of the luminescence in $KBr:Sn^{2+}$ before (solid circle) and after (open circle) quenching. A solid line was obtained by Sivasankar et al. (Ref. 6).

B. Fast decay component

When temperature was decreased from 300 K, a single lifetime of more than 1.6 μs was obtained in a temperature region of 300–40 K, but in addition to the slow component a fast decay component with a lifetime of shorter than 0.4 μs was found below about 40 K as seen in Fig. 3. It was difficult to find such a fast decay component at high temperatures clearly. In Fig. 4 are presented the time-resolved luminescence spectra of the fast component observed at 15 K. The spectra were obtained, using the same gate time of 34 ns, every 48 ns after 21 ns from the excitation pulse. As time is evolving, the emission band is observed to shift its peak from 520 nm to the longer-wavelength side and to 545 nm in about 200 ns after the pulse excitation, and simultaneously the emission band comes to have a doublet structure consisting of the 520- and 545-nm band components. Such a doublet structure, however, was not observed above 40 K. No change was

FIG. 1. (a) Time-resolved luminescence spectra (normalized), at 300 K, of a $KBr:Sn^{2+}$ crystal before (curve 1) and after (curve 2) quenching, which were recorded with a gate time of 5 μs after pulse excitation. (b) Luminescence decay curve, at 300 K, observed after quenching.

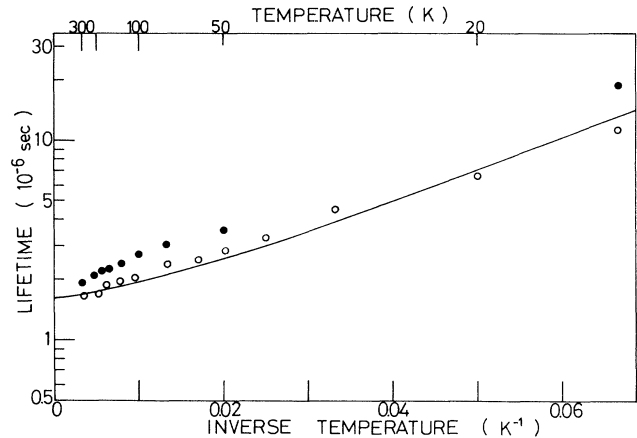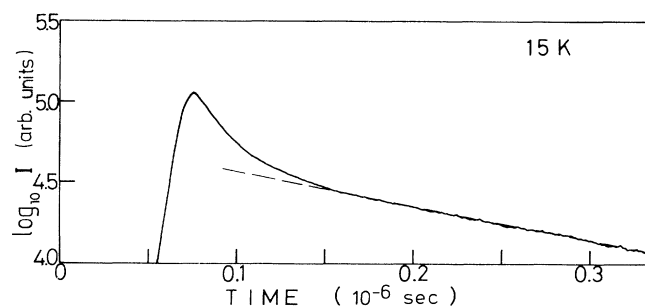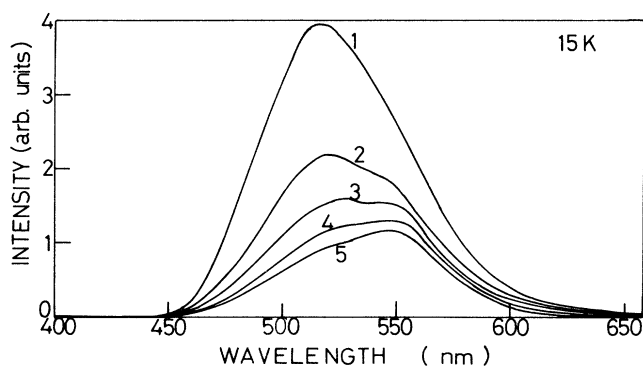FIG. 3. Decay curve of the 545-nm luminescence band at 15 K.

FIG. 4. Time-resolved luminescence of $KBr:Sn^{2+}$, at 15 K, recorded after 21 ns (curve 1), 69 ns (curve 2), 117 ns (curve 3), 165 ns (curve 4), and 213 ns (curve 5) from the excitation in the same time interval of 34 ns.

also observed regarding its peak position and the band shape of the single emission band, from the time-resolved measurement using various delay times between 0.1–4.0 μs.

From the decay curve of the 520- and 545-nm emission bands at 15 K, it was found that the 520-nm band has a short lifetime of 130 ns in addition to the long lifetime, while the 545-nm band has a lifetime of 372 ns. In the estimation of these values, care was taken to avoid the overlap between the two bands. A lifetime of 235 ns was obtained for the whole luminescence containing the two bands, whose value is close to the average of the above-mentioned two values. Therefore it is concluded that each of the two emission bands has a different short lifetime. Sivasankar *et al.* suggested, from their observation of no trace of such a fast decay component, that the relaxation following absorption results in populating only

the lowest singlet level in the RES.[6] The observation of the fast component, however, indicates that the relaxation is not only into the lowest level but also into the upper level in the RES (see Fig. 7 of Ref. 7), leading to the appearance of two A_T emission bands.

So far, two A_T emission bands have been observed by the excitation in the A absorption band in $KI:Sn^{2+}$ as mentioned in Sec. I. In $KBr:Sn^{2+}$, an unresolved, single A_T emission band has been observed although two emission bands are expected as the case of $KI:Sn^{2+}$. The 520- and 545-nm emission bands, which were found by the present time-resolved luminescence measurement, are attributable to the two A_T emission bands in $KBr:Sn^{2+}$. The two A_T emissions showed almost the same lifetime of about 10 μs at 15 K (see Fig. 2) as the slow decay component, although their fast components are considerably different from each other. Regarding the two A_T emissions in $KI:Sn^{2+}$, their lifetimes are about 3 ms at 4.2 K and these values are close to each other.[11] Our result for the slow component is consistent with the case of $KI:Sn^{2+}$. Therefore it is believed that the same luminescence mechanism is possible for both KI and KBr.

Figure 5(a) shows the luminescence spectra, at various temperatures, measured after 212 ns from the excitation pulse. In all the spectra of Fig. 5(a) the emission intensities accumulated in the same gate time of 34 ns were recorded. The delay time of 212 ns corresponds to the time region where the fast decay component of the luminescence remains predominantly but the slow component begins to appear. It is observed, as temperature is increased, that the peak luminescence band shifts from 545 to 510 nm and the luminescence intensity increases considerably [see Fig. 5(b)]. The latter behavior is different from the temperature dependence of the emission intensity observed by Scacco and Jacobs,[9] who
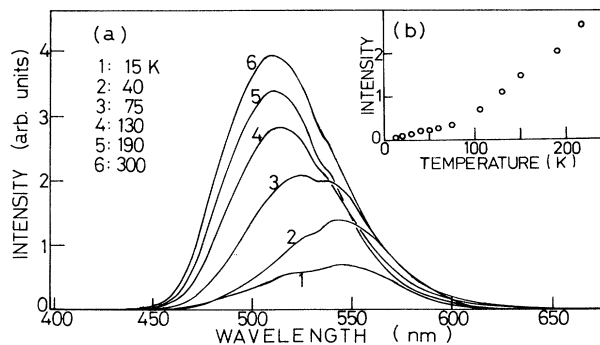

FIG. 5. (a) Time-resolved luminescence at various temperatures, recorded the intensity produced for 34 ns after 212 ns from the excitation. Curves 1, 2, 3, 4, and 5 were enlarged by 20, 7, 6, 2, and $\frac{10}{7}$ times, respectively. (b) Temperature dependence of the peak intensity of luminescence in the fast-decay component.
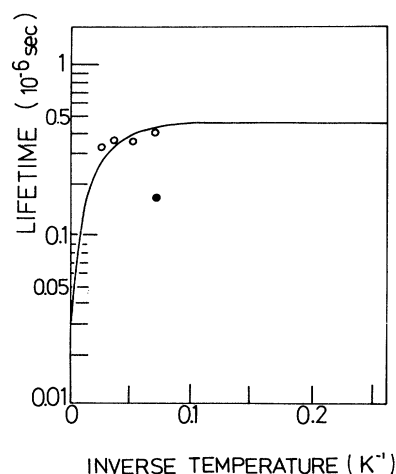

FIG. 6. Temperature variation of the lifetime of a fast-decay component in the 545-nm (open circle) and 520-nm (solid circle) emission bands (see text).

found, without using the time-resolved spectroscopic technique, that the intensity is almost constant in the temperature region 15–150 K.

The 510-nm emission observed at high temperatures [Fig. 5(a)] was determined to have a lifetime of longer than 1 μs as shown in Fig. 2. It was difficult to obtain a fast component with a lifetime of shorter than 100 ns for the 510-nm band. Such a short lifetime was expected from the theoretical curve of Sivasankar et al.[6] In Fig. 6, we plot the lifetime of the fast component against temperature, together with the theoretical curve. It is found that the obtained short-lifetime value is close to the curve although we need the curves for two emission bands to compare with the experimental result rigorously.

IV. SUMMARY

A slow-decay component with a lifetime of longer than 1 μs was observed for the luminescence by a Sn^{2+}-vacancy center in the temperature region 15–300 K, in agreement with the previous results. In addition to the slow component, a fast component with a lifetime of 100–400 ns was found at low temperatures below 40 K in $KBr:Sn^{2+}$, the value is close to the semitheoretically derived one. The time-resolved spectroscopy has revealed that there are two fast components at 15 K: the shorter one is produced by the 520-nm emission band, the other is produced by the 545-nm emission band. Our observation of these two emissions and their fast decay indicates that the energy level splitting of the RES by the charge-compensating cation vacancy[5,7,12] is certainly present in $KBr:Sn^{2+}$.

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