

## Luminescence Study of $O_2^-$ Centers in Alkali Halide Crystals

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### Part II – Luminescence from a Sample with a Thin Layer of High Concentration $O_2^-$ Centers in Alkali Halide Crystal

#### Abstract

Luminescence spectra of alkali halide crystals with a thin layer of high-concentration  $O_2^-$  centers have been studied at low temperature. A sample has been prepared by infiltration of  $KO_2$  or  $Na_2O_2$  melt into a crack which is artificially introduced in a host crystal. A thin layer of  $O_2^-$  centers is formed near the crack by simultaneous diffusion of  $O_2^-$  molecules into the host crystal through the crack interfaces. Concentration of the  $O_2^-$  centers in the as-grown layer amounts to  $\sim 5 \times 10^{19} \text{ cm}^{-3}$ , about 50 times higher than that in ordinary samples grown by the Kyropoulos method. As-prepared thin layers have been found to show luminescence spectra characteristic of the  $O_2^-$  center, though zero-phonon lines of the spectra show large inhomogeneous broadening and their phonon sidebands are deformed markedly. Upon annealing, the widths of inhomogeneous broadening of the lines are reduced and the spectra approach those of ordinary samples. The concentration of the  $O_2^-$  centers in annealed samples is reduced to  $\sim 3 \times 10^{18} \text{ cm}^{-3}$ . It has been found that annealed samples show superfluorescence.

Key words:  $O_2^-$  centers, thin layer, infiltration, inhomogeneous broadening, annealing, superfluorescence

#### §1. Introduction

In this work, the author has tried to prepare samples with thin layers of  $O_2^-$  centers in host crystals of KCl, KBr, NaCl and NaBr in order to extend the luminescence study to samples with a high concentration of  $O_2^-$  centers and to get high quality samples for superfluorescence study. Ordinary samples with the  $O_2^-$  centers, hereafter referred to as “bulk samples”, are usually grown by the Kyropoulos method from melt doped with  $KO_2$  or  $Na_2O_2$ . The  $O_2^-$  concentration in a bulk sample is at most about  $10^{18} \text{ cm}^{-3}$ . A sample with a thin layer of high concentration  $O_2^-$  centers has been prepared by infiltration of  $KO_2$  or  $Na_2O_2$  melt into a crack which is artificially introduced in a host crystal.<sup>1)</sup> In this new method,<sup>2)</sup>  $O_2^-$  molecules diffuse into a host crystal through the crack interfaces and a thin layer of high concentration  $O_2^-$  centers is formed near the crack. It has been confirmed that the  $O_2^-$  concentration in the as-grown thin layer amounts to  $\sim 5 \times 10^{19} \text{ cm}^{-3}$ , about 50 times higher than that in bulk samples. Hereafter the samples are referred as “thin layer samples”. The thin layer samples have been found to show luminescence spectra characteristic

of the  $O_2^-$  center in alkali halides,<sup>3)</sup> though zero-phonon lines of the spectra show large inhomogeneous broadening and their phonon sidebands are deformed significantly. Thin layer samples annealed at about 600 °C show the luminescence spectra similar to those of bulk samples. It has been found that superfluorescence appears under strong excitation with short UV pulses at 2K in the thin layer samples of  $KCl:O_2^-$ ,  $KBr:O_2^-$  and  $NaCl:O_2^-$ .

## §2. Experimental

### 2.1 Sample preparation

A sample with a thin layer of  $O_2^-$  centers has been prepared by the method shown in Fig.1. (1) A crack is introduced artificially in a host crystal of about  $5 \times 7 \times 10 \text{ mm}^3$  using a

razor blade. The crack gap is estimated to be about  $5 \sim 30 \mu\text{m}$  thick at the entrance of the crack. (2) A small amount of  $KO_2$  or  $Na_2O_2$  powder is placed near the entrance of the crack. All the treatment of  $KO_2$  or  $Na_2O_2$  is carried out in  $N_2$  atmosphere. (3) The crystal is heated to the melting point of  $KO_2$  ( $380^\circ\text{C}$ ) or  $Na_2O_2$  ( $460^\circ\text{C}$ ) in vacuum. Then melt of  $KO_2$  or  $Na_2O_2$  infiltrates into the crack which becomes filled with  $KO_2$  or  $Na_2O_2$ .

Simultaneously  $O_2^-$  molecules diffuse into the region near the crack of the host crystal. (4) The sample is cooled down to room temperature within about half an hour. It should be noted that the present method for the preparation of the thin layer samples has the following advantages as compared with that for the bulk samples. 1) It is easy to prepare the thin layer samples and easy to control the concentration of the  $O_2^-$  centers in the layer by proper annealing treatment. 2) In the case of the Kyropoulos method, the chemically active dopant  $KO_2$  or  $Na_2O_2$  is heated up to high temperature near the melting point of the host material. Then the dopant dissolves or reacts with the crucible, resulting in the introduction of impurity or contamination into the samples. In the present method, the active dopant is heated to its melting point in vacuum and infiltrates into the crack of the host crystal directly without touching the vacuum vessel. Thus contamination of the samples seems to be suppressed.

Thickness of the layer of  $O_2^-$  centers was estimated by microscope observation of the layers under UV irradiation at room temperature. Photographs of luminescent layers and

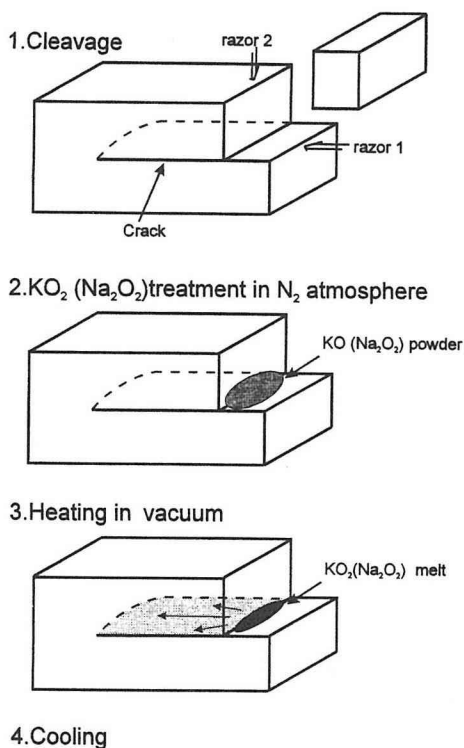


Fig. 1: Method for preparation of a sample with a thin layer of high-concentration  $O_2^-$  centers in alkali halide crystal.

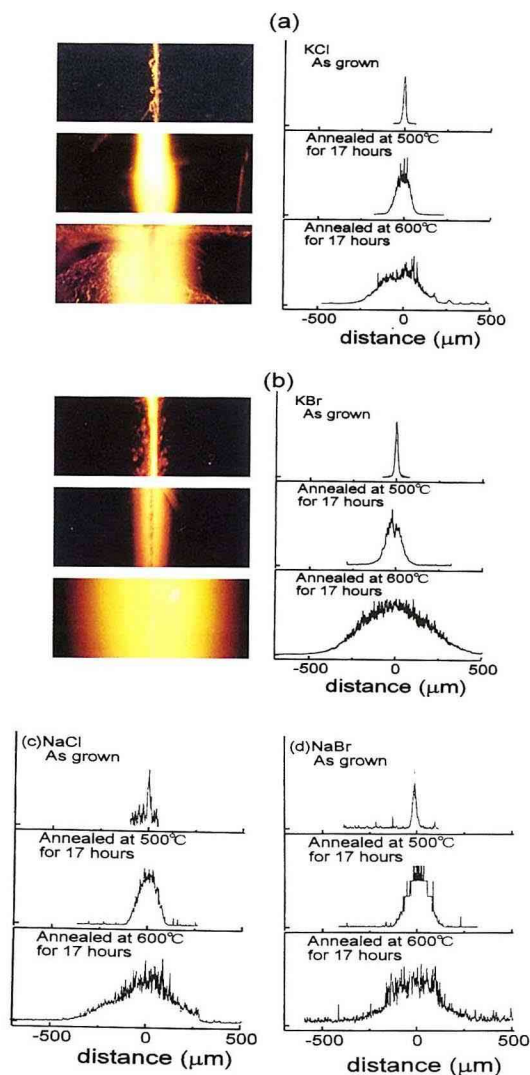


Fig. 2 : Photographs of as-grown and annealed thin layers of  $O_2^-$  centers under irradiation with UV light observed at room temperature and microphotometer traces of the images of the thin layers observed by a microscope: (a) KCl and (b) KBr, Microphotometer traces of thin layers: (c) NaCl and (d) NaBr.

microphotometer traces of their images on the photographic films are shown in Fig.2. Photographs for NaCl and NaBr are similar to those for KCl and KBr and only the microphotometer traces are shown for NaCl and NaBr in Fig.2. Spatial distributions of the luminescence intensity were determined from the photometer traces of the images of which blackness was calibrated by exposure time. The distribution of the luminescence intensity corresponds to that of the  $O_2^-$  centers in a host crystal. Thicknesses of the as-prepared layers were estimated to be about  $20 \mu\text{m}$  in KCl, KBr, NaCl and NaBr from the observed intensity distributions. Concentration of the  $O_2^-$  centers was estimated by the measurement of UV absorption due to the  $O_2^-$  centers. It varied from spot to spot of the thin layer. The maximum  $O_2^-$  concentration of the as-prepared layers in all samples studied here

was  $\sim 5 \times 10^{19} \text{ cm}^{-3}$ , which is more than 50 times higher than that in the bulk samples. The concentration of the annealed layers was  $2 \sim 5 \times 10^{18} \text{ cm}^{-3}$  in all the samples annealed at  $600^\circ\text{C}$  for 17 hours.

## 2.2 Luminescence measurement

Spectra of the luminescence from the thin layer samples are measured under continuous irradiation with UV light of 280-350nm from a 500W high-pressure mercury lamp. The luminescence was collected at a right angle to the excitation light, led to a double monochromator through a cut-off filter and detected with a cooled photomultiplier.

For the measurements of time response of superfluorescence from the samples, they were excited with  $4\omega$  pulses of a Q-switched Nd:YAG laser with a time duration of about 4ns. The luminescence was detected with a rapid response biplanar phototube Hamamatsu R1328U-03UV. The output signal from the photomultiplier was recorded by a high speed digitizing oscilloscope LeCroy 9362 of which bandwidth is 1.5 GHz and sampling rate is 10 GS/s.

## §3. Luminescence spectra of thin layer samples

### 3.1 Comparison of luminescence spectra of bulk samples and thin layer samples

Figures 3a~d show the luminescence spectra of the as-prepared thin layer samples of

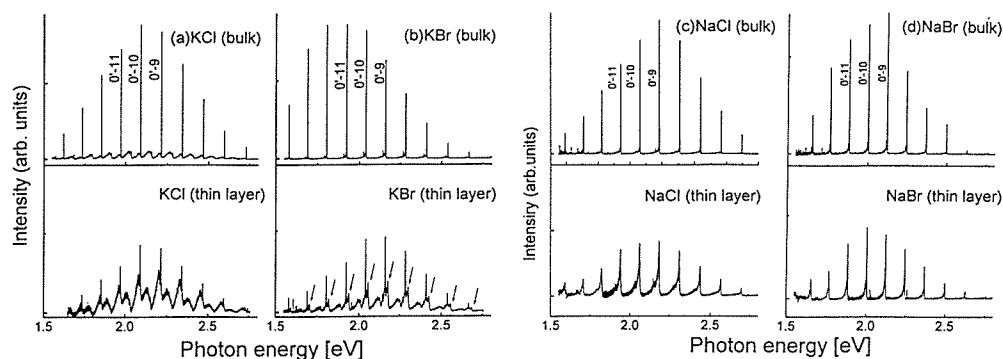


Fig. 3 : Spectra of thin layer samples (below) and those of the bulk samples (above) measured at 2K. a)  $\text{KCl}:\text{O}_2^-$ , b)  $\text{KBr}:\text{O}_2^-$ , arrows indicate zero-phonon lines of extra series, c)  $\text{NaCl}:\text{O}_2^-$  and d)  $\text{NaBr}:\text{O}_2^-$ .

$\text{KCl}:\text{O}_2^-$ ,  $\text{KBr}:\text{O}_2^-$ ,  $\text{NaCl}:\text{O}_2^-$  and  $\text{NaBr}:\text{O}_2^-$  at 2K as well as those of bulk samples under steady excitation with the mercury lamp. All samples show the luminescence spectra with a series of sharp lines accompanied by sidebands. Positions of the sharp lines are exactly the same as those of the zero-phonon lines of the bulk samples<sup>3)</sup> as seen in Fig.3<sup>†</sup>.

<sup>†</sup> :Series of the zero-phonon lines are denoted by the notation "0'-v" which expresses the transition from the lowest vibrational level of the excited state to the v-th vibrational level of the ground state of the  $\text{O}_2^-$  molecule.

Therefore the luminescence is ascribed to the  $O_2^-$  centers in the respective crystals. However, the zero-phonon lines of the thin layer samples are relatively weak and show large inhomogeneous broadening and their phonon sidebands are deformed significantly as compared with those of bulk samples.

Luminescence spectrum of the thin layer sample of  $KCl:O_2^-$  shows relatively enhanced double-structure sidebands, as compared with those of the bulk  $KCl:O_2^-$ .<sup>3)</sup> The thin layer sample of  $NaCl:O_2^-$  and  $NaBr:O_2^-$  also show relatively enhanced sidebands. The thin layer sample of  $KBr:O_2^-$  shows the extra zero-phonon lines<sup>4)</sup> indicated by arrows on the high-energy sides of the ordinary zero-phonon lines. Their phonon sidebands are deformed markedly, and the sample shows the double structure sidebands. The ordinary zero-phonon lines and the single-structure sidebands of the bulk  $KBr:O_2^-$  are due to the  $O_2^-$  centers of  $\langle 111 \rangle$  orientations in the excited state.<sup>4)</sup> As discussed in Part I, extra zero-phonon lines and the double-structure sidebands of  $KBr:O_2^-$  are due to the  $O_2^-$  centers of  $\langle 110 \rangle$  orientations<sup>5,6)</sup>, which are probably caused by the local strain due to a high concentration of  $O_2^-$  centers in the layer. Thus, it is noted that there exist  $O_2^-$  centers of both orientations in the thin layer sample of  $KBr:O_2^-$ .

### 3.2 Annealing effect

Effects of annealing on the luminescence spectra and on spatial distribution of the  $O_2^-$  centers in the host crystals were investigated by heating the thin layer samples at different temperatures. Since the  $O_2^-$  molecules in the thin layer near the entrance of the crack escaped from the crystal during annealing, the image and luminescence of the thin layer near the innermost part of the crack were observed. Thicknesses of the layers were

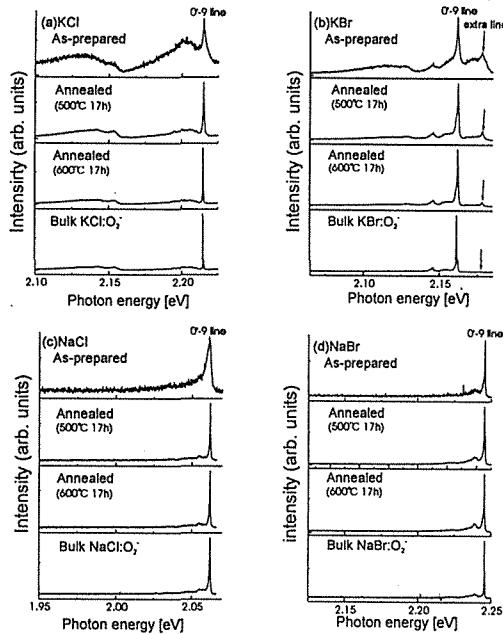


Fig. 4 : Spectral change of the  $O_2^-$  luminescence in thin layer samples of a)  $KCl:O_2^-$ , b)  $KBr:O_2^-$ , c)  $NaCl:O_2^-$ , and d)  $NaBr:O_2^-$  by annealing. Spectra of bulk samples are shown for comparison.

increased significantly by annealing in all samples as seen in Fig.2. They were about  $100\ \mu\text{m}$  after annealing at  $500^\circ\text{C}$  for 17 hours. In this case, the  $\text{O}_2^-$  concentration was about  $3\sim 5\times 10^{18}\ \text{cm}^{-3}$ . The thicknesses were about  $300\sim 500\ \mu\text{m}$  after annealing at  $600^\circ\text{C}$  for 17 hours as seen in Fig.2. In this case, the  $\text{O}_2^-$  concentration was about  $2\sim 4\times 10^{18}\ \text{cm}^{-3}$ .

The annealing effect on the luminescence spectra is revealed in Fig.4, which show the change of the spectral profiles of the  $0'-9$  zero-phonon lines and their phonon sidebands of thin layer samples of  $\text{KCl}:\text{O}_2^-$ ,  $\text{KBr}:\text{O}_2^-$ ,  $\text{NaCl}:\text{O}_2^-$  and  $\text{NaBr}:\text{O}_2^-$  at 2 K before and after annealing. The spectra of bulk samples are also shown for comparison. After annealing at  $600^\circ\text{C}$  for 17 hours, the zero-phonon lines became as narrow as those of the bulk samples and the phonon sideband became relatively weak and their profiles approached those of the bulk samples. However, the concentration of the  $\text{O}_2^-$  centers was reduced by one order of magnitude after annealing at  $600^\circ\text{C}$ . In  $\text{KBr}:\text{O}_2^-$ , the extra lines became much weaker by annealing.

#### §4 Superfluorescence from a thin layer samples of $\text{KCl}:\text{O}_2^-$ , $\text{KBr}:\text{O}_2^-$ and $\text{NaCl}:\text{O}_2^-$

In order to investigate superfluorescence from the thin layer samples under strong excitation, they were excited with  $4\omega$  of the Q-switched YAG laser at 2K under the experi-

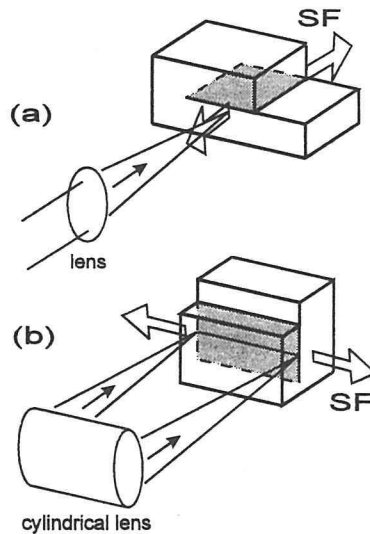


Fig. 5 : Configuration for observation of superfluorescence from a thin layer sample.

mental configurations shown in Fig.5. Under the strong excitation, highly directional strong light pulses were emitted from the samples of  $\text{KCl}:\text{O}_2^-$ ,  $\text{KBr}:\text{O}_2^-$  and  $\text{NaCl}:\text{O}_2^-$  annealed at  $600^\circ\text{C}$ . In the spectra of strong emission, the  $0'-11$  zero-phonon line of  $\text{KCl}:\text{O}_2^-$ , the  $0'-12$  zero-phonon line of  $\text{KBr}:\text{O}_2^-$  and the  $0'-10$  and  $0'-11$  zero-phonon lines

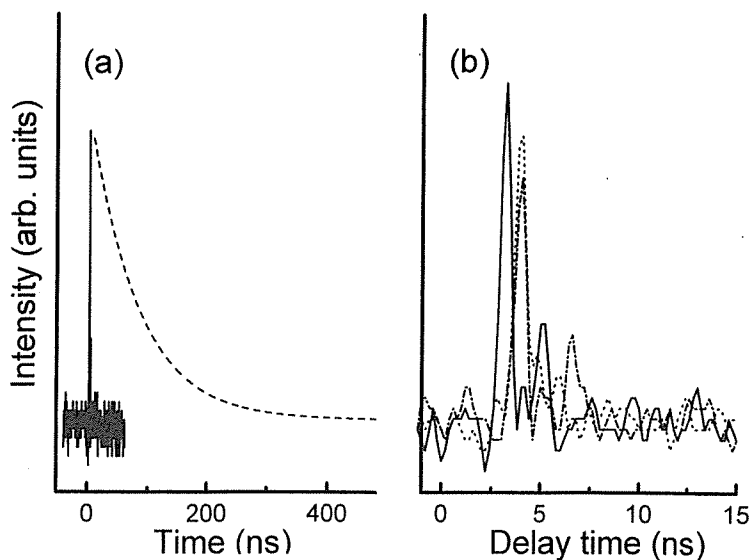


Fig. 6 : Time response of the superfluorescence from a thin layer sample of  $KCl:O_2^-$  at 2K. (a) A typical superfluorescence pulse (solid curve) and the decay curve of ordinary luminescence (broken curve). (b) Fluctuation of the superfluorescence pulses under the same excitation condition. The abscissa shows time delay of the superfluorescence pulse from the excitation pulse.

of  $NaCl:O_2^-$  were strongly enhanced. Figure 6(a) shows a typical example of time response of the strong emission from  $KCl:O_2^-$  and the decay curve of the corresponding ordinary luminescence. Though peak heights of both curves in the figure are normalized, the actual peak height of the strong emission is much greater than that of the ordinary luminescence. The peak height of the strong emission and its time delay from the excitation pulse fluctuated from shot to shot as shown in Fig.6(b). The characteristics of the strong emission mentioned above are similar to those of the superfluorescence from  $KCl:O_2^-$  reported in ref.8 and the present emission pulses are believed to be the superfluorescence. The thin layer samples of  $KBr:O_2^-$  and  $NaCl:O_2^-$  showed similar behavior under strong pulse excitation. The threshold excitation powers for the superfluorescence in the thin layer samples were lower than those in the bulk samples. Threshold excitation powers under the configuration shown in Fig.5(a) were about  $30 \mu J$  for  $KCl:O_2^-$ ,  $9 \mu J$  for  $KBr:O_2^-$  and  $90 \mu J$  for  $NaCl:O_2^-$ . Since the superfluorescence was not observed in the as-prepared thin layer samples in which the zero-phonon lines were broadened inhomogeneously as seen in Fig.4, it is assumed that large inhomogeneous broadening of the zero-phonon line suppresses the superfluorescence.

It should be noted that the bulk samples deteriorate rather quickly under strong pulse irradiation and superfluorescence ceases after a few tens of shots. In the case of the thin layer samples, superfluorescence prolongs more than several tens of shots. Deterioration

of the samples under strong UV irradiation is likely due to dissociation of  $O_2^-$  molecules and/or reaction of  $O_2^-$  molecules with other impurities.<sup>3)</sup> Thin layer samples are more suitable for the superfluorescence study than bulk samples, since the contamination of the former are suppressed as compared with the latter as mentioned in §2.

## §5. Summary

The thin layers of  $O_2^-$  centers in alkali halide crystals were prepared by the diffusion of  $O_2^-$  molecules through the crack interface. The concentration of  $O_2^-$  centers in the as-grown thin layers was about  $\sim 5 \times 10^{19} \text{ cm}^{-3}$ , about 50 times higher than those in bulk samples. The samples show luminescence spectra characteristic of the  $O_2^-$  centers. The zero-phonon lines of the spectra show large inhomogeneous broadening. The inhomogeneous broadening was remarkably reduced by annealing. The concentrations of the annealed thin layer samples were reduced by factor  $\sim 10$ , but still higher than those of bulk samples. It has been found that the annealed samples of  $KCl:O_2^-$ ,  $KBr:O_2^-$  and  $NaCl:O_2^-$  show superfluorescence under strong pulse excitation. It has been also found that threshold powers for the superfluorescence from the thin layer samples are lower than those from the bulk samples and quality of the thin layer samples is much better than that of the bulk samples. It should be noted that the thin layer samples are much useful for the study of superfluorescence from  $O_2^-$  centers in alkali halide crystals.

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