PHYSICAL REVIEW B VOLUME 38, NUMBER 15 15 NOVEMBER 1988-II

Afterglow and photoconductivity in europium-doped alkali halides

I. Aguirre de Cárcer, F. Cussó, and F. Jaque
Departamento de Física Aplicada (C-IV), Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain

(Received 1 April 1988)

Luminescence persistence (afterglow) after uv irradiation of alkali halides doped with Eu^{2+} has been investigated. The wavelength dependence of the afterglow emission and excitation, photoconductivity, and thermoluminescence were measured in different host matrices (NaCl, KCl, KBr, KI:Eu^{2+}). Parallel behavior of the afterglow and photoconductivity data has been found, which leads us to consider Eu^{2+} ionization as the primary process of the afterglow. Thermoluminescence measurements in the liquid-nitrogen–room-temperature range show the existence of a distribution of electron traps, which could account for the temporal dependences observed in the luminescence emission.

I. INTRODUCTION

Luminescence persistence (afterglow) in alkali halides doped with different impurities (Ag^+,Tl^+,Eu^{2+}) has been observed after x or γ irradiation.[1-4] In all cases the phenomena have been related to a primary process of electron-hole pair formation with subsequent stabilization in the form of a variety of color centers V_K, F, F', etc. Later the excitation is transferred to the impurity, generating the corresponding emission. However, the transfer process is not well understood and different mechanisms have been proposed. Nevertheless, recently,[5,6] afterglow process have been observed under uv (250 nm) irradiation. In this low-energy range, it is difficult to consider a radiation damage process and hence mechanisms involving color centers seem to be hardly applicable.

In order to investigate alternate mechanisms, in the present work the afterglow process in different alkali halides doped with Eu^{2+} have been studied. In particular, emission, excitation, as well as photoconductivity wavelength dependence were investigated. There has been found a parallel behavior of the afterglow and photoconductivity data which leads us to consider Eu^{2+} ionization as the primary process responsible for the afterglow. Finally, thermoluminescence measurements evidenced the existence of several traps which could account for the luminescence temporal dependences observed.

II. EXPERIMENTAL PROCEDURES

NaCl,KCl,KBr,Ki:Eu^{2+} single crystals were grown in the Crystal Growth Laboratory, Departamento Física Aplicada, Universidad Autónoma, Madrid, using the Czochralski method under a controlled atmosphere (dry argon). Doping was achieved by adding to the melt different initial concentrations of EuX_2 (X=Cl,Br,I), previously reduced from $EuX_3\cdot 6H_2O$ using standard techniques.[7]

Impurity concentration was determined from their optical absorption spectra following procedures reported elsewhere.[8] Concentrations varied between 60 and 500 ppm.

Optical absorption measurements were made with a Cary-17 spectrophotometer. Luminescence and afterglow measurements were performed using a Jobin-Yvon JY-3CS spectrofluorometer.

Thermoluminescence measurements, in the liquid-nitrogen- (LNT) to room-temperature (RT) range, were obtained by placing the samples in the coldfinger of a cryostat adapted to the spectrofluorometer chamber. Thermoluminescence data were taken at 0.12 $K\,s^{-1}$ heating rates. Excitation was achieved by using an Applied Photophysic (Model U.V.90) photoirradiator.

Photoconductivity measurements were made under a dry N_2 atmosphere using silver electrodes on 3-mm-thick samples and a Cary-401 electrometer. With the setup used, dark current was less than 10^{-12} A at 800 V.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the time dependence of 430-nm emission intensity of NaCl:Eu^{2+} after excitation with 250-nm light at RT. A long decay lasting several minutes (afterglow) is observed which cannot be attributed to the Eu^{2+} intrinsic emission, whose lifetime is in the range of microseconds.[9-11] As can be seen in the figure, it is a nonexponential decay that fits nicely a $1/t$ law (inset). The afterglow is also observed in the LNT-RT range, following the $1/t$ dependence except in a narrow range of temperature, as will be discussed later.

The observed afterglow appears mainly in as-grown crystals and its intensity is drastically reduced when samples are quenched from 500 °C to RT. This clearly indicates that the afterglow is related to europium precipitates.

Similar results have also been observed in as-grown Eu^{2+}-doped KCl, KBr, and KI.

The afterglow excitation spectra for NaCl, KCl, KBr, and KI europium-doped samples are given in Fig. 2 (dashed line). The spectra were corrected for the experimental setup response. In the same figure, the optical absorption spectra are included (solid line) to facilitate comparisons. It can be seen that the excitation occurs in the high-energy region of the spectra, roughly coincident with the Eu^{2+} high-energy absorption band for NaCl,

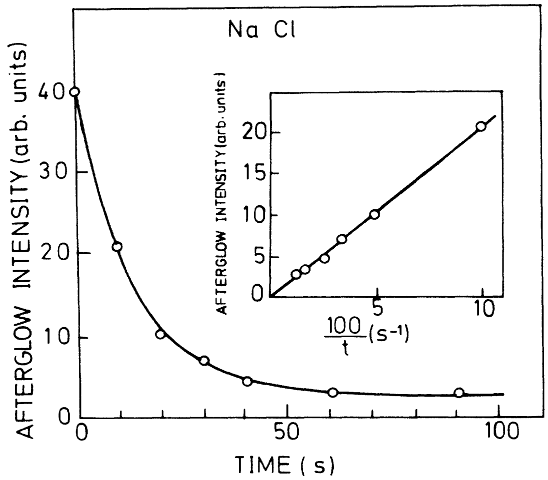

FIG. 1. Time dependence of the 430-nm emission intensity of NaCl:Eu^{2+} after excitation at 250 nm. The inset shows the hyperbolic dependence.

KCl, KBr, and KI. In the first three cases the excitation spectrum appears at slightly higher energies than the corresponding absorption bands. In the KI samples this high-energy band is partially hidden by the fundamental absorption of the host crystal. In all cases the afterglow is not excited in the low-energy absorption band.

Figure 3 shows the afterglow emission spectra (open circles) for NaCl, KCl, KBr, and KI host crystals. In all cases the excitation was performed in the peak of the respective excitation band. Figure 3 shows also the Eu^{2+} luminescence emission spectra from continuous excitation in the low (dashed line) and high (solid line) excitation bands. As can be appreciated clearly in the figure, both afterglow and Eu^{2+} intrinsic luminescence have the same emission spectrum which corresponds to the well-known Eu^{2+} $[t_{2g}(4f^6 5d)\rightarrow {}^8S_{7/2}(4f^7)]$ transition. However, this transition presents an exponential decay with a lifetime of the order of microseconds[9–11] and therefore an explanation of the long persistence of the afterglow in Eu^{2+}-doped alkali halides must be looked for.

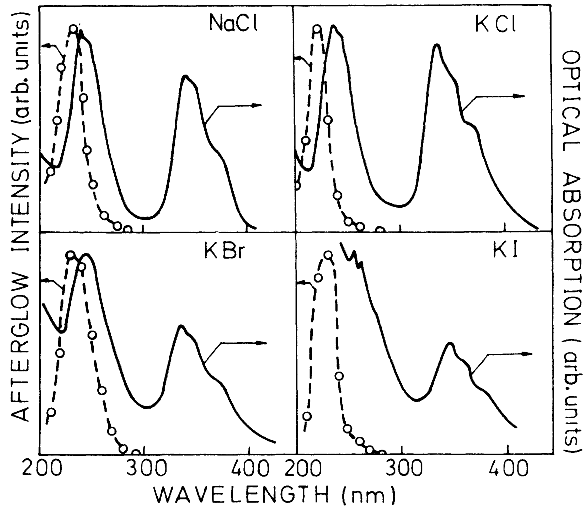

FIG. 2. Afterglow excitation spectra (dashed line) compared with the absorption spectra (solid line) of Eu^{2+}-doped alkali halides.

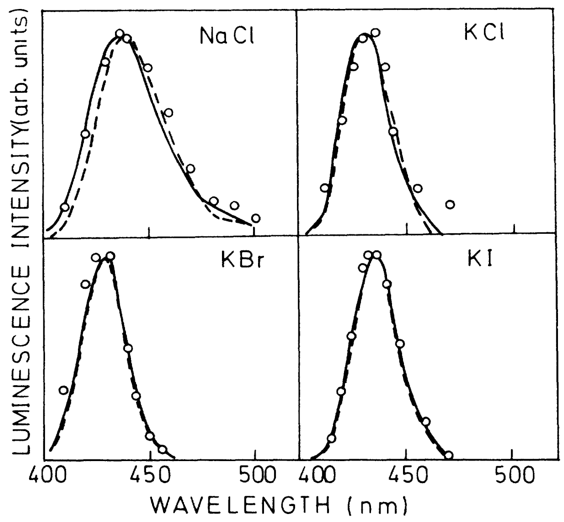

FIG. 3. Afterglow emission spectra (open circles) compared with the Eu^{2+} luminescence spectra by excitation in the low-energy (dashed line) and high-energy (solid line) absorption bands.

Lifetime enhancement could be caused by the participation of some excited state of the $4f^7$ configuration (${}^6P_{7/2}$), but the lifetime reported for the Eu^{2+} level in different host matrices is of the order of microseconds,[11,12] which can hardly account for the afterglow persistence. Furthermore, the narrow emission peak corresponding to the $4f^7\rightarrow 4f^7$ transition reported elsewhere[12–14] has been thoroughly searched after uv excitation with negative results.

Luminescence persistencies have also been found, in various hosts, associated with impurity ionization which allows electron migration and trapping while the hole is localized in the impurity.[15–17] The subsequent detrapping and recombination produces light emission with a time dependence imposed by the recombination rate. In order to explore this hypothesis it is necessary to look for the appropriate photoconductivity data.

In all the materials investigated a strong photoconduction at RT has been detected. Figure 4 shows the photoconductivity spectra per incident photon (at RT) in the absorption range of Eu^{2+} for the different host crystals considered. It must be noted that photoconduction takes place only in the high-energy region of Eu^{2+} absorption, and comparing Figs. 2 and 4 it can be seen that the photoconductivity spectrum is coincident with the afterglow one. These results confirm that Eu^{2+} ionization is taking place and therefore it is possible to think that during illumination the ionized electron can get trapped, the hole remaining at the impurity site as Eu^{3+}.

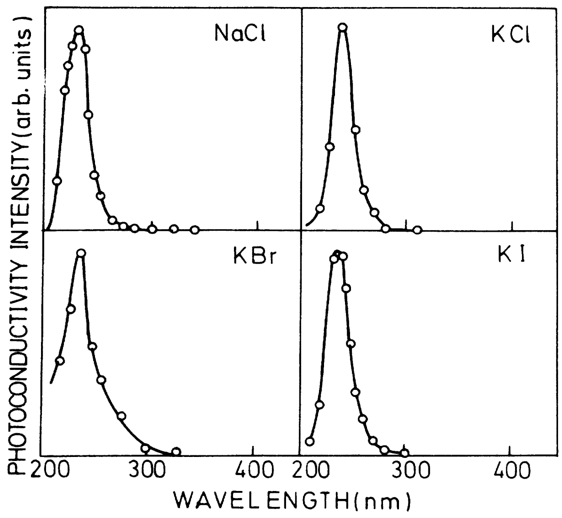

FIG. 4. Photoconductivity spectra, per incident photon, of Eu^{2+}-doped alkali halides.

Nevertheless, at variance with the afterglow, photoconductivity is also detected in freshly quenched and in very dilute samples, indicating that photoionization is taking place independently of the precipitation state of the impurity. Then, the differences in the afterglow intensity between as-grown and quenched samples can only be due to differences in the electron trapping process.

The existence of such electron traps can be confirmed by studying the thermoluminescence signal (TL) after uv irradiation at LNT. Figure 5 shows the thermoluminescence spectra for as-grown samples of the four materials considered after a 10-s excitation in the afterglow or photoconductivity peak. As can be seen in all cases, we can differentiate several TL peaks in that temperature range, indicating the presence of a variety of electron traps. Furthermore, TL emission spectra match exactly the Eu^{2+} luminescence spectra in every sample, providing strong arguments for considering a $Eu^{3+}+e\rightarrow(Eu^{2+})^*\rightarrow Eu^{2+}+h\nu$ process.

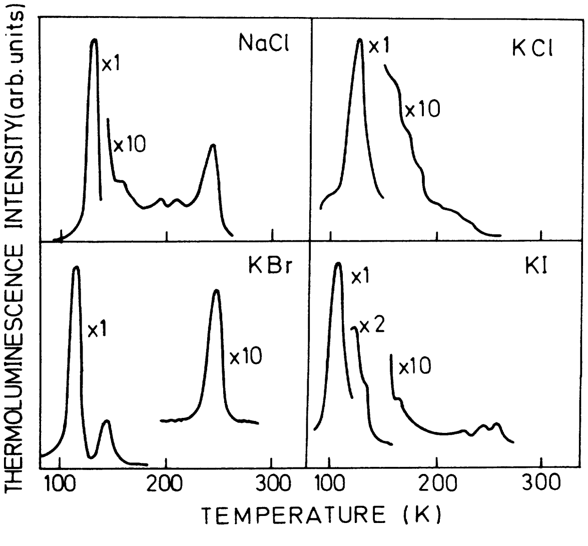

FIG. 5. Thermoluminescence spectra of Eu^{2+}-doped alkali halides after uv irradiation.

The TL signal is strongly reduced when the samples are quenched from high temperature, which indicates that the electron trapping and consequently the formation of Eu^{3+} is connected with the existence of europium precipitates. The small residual TL signal can be explained by considering that, except for very dilute samples, even the fastest quenching treatment cannot avoid the formation of some precipitates.[18,19]

Differences in Eu^{3+} production between the quenched and the precipitated samples have also been detected after x-ray irradiation. It has been reported[20] that this production takes place when Eu^{2+} precipitates are present before irradiation. It should be remarked that Eu^{3+} ions have been detected, by absorption measurements, only after high-dose x-ray irradiation.[20] Unfortunately, under uv irradiation the induced damage is much lower, and Eu^{3+} was not detected by means of its absorption or emission spectra, neither at RT nor LNT.

In relation to the nature of the electron traps, they could be connected with minor traces of additional impurities incorporated into the precipitates or into the precipitate-host crystal interface. In particular, it is obvious to seek for the existence of Eu^{+} ions. However, absorption measurements, during the afterglow process after uv irradiation did not detect Eu^{+} ions. Eu^{+} has been observed under high-dose x-ray irradiation,[21] but in very low concentrations, which could explain the uv irradiation negative results.

In relation with the afterglow time dependence, $1/t$ kinetics could be theoretically explained assuming a uniform distribution of trap depths.[2,22] The TL spectra shown in Fig. 5 present a wealth of peaks, which implies different depths of electron traps. This situation could be regarded as an approximation to the "uniform distribution" of traps and account for the $1/t$ kinetics.

Finally, in the TL spectra we can also observe a narrow range of temperatures (around 120 K) where a clear peak is distinguished showing up the liberation of a particular trap and, in accordance with the previous arguments, the $1/t$ kinetics should be lost. In fact, a $1/t^2$ law is approached in this region, as has been previously reported for NaCl:Eu^{2+}.[23] This law is theoretically predicted when a single trap is activated assuming the possibility of retrapping.[22]

In conclusion, the afterglow observed in Eu^{2+}-doped NaCl, KCl, KBr, and KI can be attributed to the recombination of Eu^{3+} and electrons released from several traps previously activated by the photoionization of the Eu^{2+} ions after illumination in the uv absorption band.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Dr. García-Solé for his fruitful discussions and remarks. This work has been partially supported by the Comisión Interministerial de Ciencia y Tecnología.

[1] C. J. Delbecq, Y. Toyozawa, and P. H. Yuster, Phys. Rev. B **9**, 4497 (1974).

[2] C. J. Delbecq, D. L. Dexter, and P. H. Yuster, Phys. Rev. B **17**, 4765 (1978).

[3] I. A. Parfianovich, E. I. Shuraleva, and P. S. Ivakhnenko, J. Lumin. **1/2**, 669 (1970).

[4] Y. Vassilev, M. Karamikhailova, M. Mladenova, and M. Georgiev, Phys. Status Solidi B **100**, 463 (1980).

[5] I. Aguirre de Cárcer, F. Cussó, J. García-Solé, F. Jaque, and P. Aceituno, Cryst. Lattice Defects Amorphous Mater. **17**, 39 (1987).

[6] I. Aguirre de Cárcer, F. Cussó, and F. Jaque, J. Lumin. **40/41**, 169 (1988).

[7] R. A. Cooley and D. M. Yost, Inorg. Synth. **2**, 71 (1964).

[8] J. Hernández A., W. K. Cory, and J. Rubio O., Jpn. J. Appl. Phys. **18**, 533 (1979).

[9] J. E. Muñoz-Santiuste, F. Jaque, J. García-Solé, and P. Aceituno, Cryst. Lattice Defects Amorphous Mater. **16**, 249 (1987).

[10] E. Mugenski and R. Cywinski, Phys. Status Solidi B **128**, K75 (1985).

[11] L. O. Merkle, R. C. Powell, and T. W. Wilson, J. Phys. C **11**, 3103 (1978).

[12] R. A. Henes and M. V. Hoffman, J. Lumin. **3**, 261 (1971).

[13] M. V. Hoffman, J. Electrochem. Soc. **119**, 905 (1972).

[14] U. Fritzler and G. Schaack, J. Phys. C **9**, L23 (1976).

[15] C. Pedrini, D. S. McClure, and C. H. Anderson, J. Chem. Phys. **70**, 4959 (1979).

[16] D. S. McClure and C. Pedrini, Phys. Rev. B **32**, 8465 (1985).

[17] C. Pedrini, R. Rogemond, and D. S. McClure, J. Appl. Phys. **59**, 1196 (1986).

[18] G. Taylor, J. E. Strutt, and E. Lilley, Phys. Status Solidi A **67**, 263 (1981).

[19] P. Aceituno, C. Zaldo, F. Cussó, and F. Jaque, J. Phys. Chem. Solids **45**, 637 (1984).

[20] M. Aguilar G. J. García-Solé, H. Murrieta S., and J. Rubio O., Phys. Rev. B **26**, 4507 (1982).

[21] J. O. Rubio, M. C. Flores, H. Murrieta, J. Hernández, F. Jaque, and F. J. López, Phys. Rev. B **26**, 2199 (1982).

[22] H. W. Leverenz, *An Introduction to Luminescence of Solids* (Dover, New York, 1968).

[23] P. Aceituno, J. I. del Barrio, F. Cussó, J. García-Solé, F. Jaque, F. J. López, J. R. Rebato, and F. M. G. Tablas, J. Mol. Struct. **143**, 219 (1986).