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THERMOLUMINESCENCE AND F-CENTERS IN DIVALENT-IMPURITY DOPED NaCl CRYSTALS

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ABSTRACT: The formation and growth of F-centers in Ca- and Cd-doped NaCl crystals have been determined by optical absorption methods. It is found that, as reported by other authors, Ca enhances the F-center formation and Cd inhibits it. Moreover, by partial thermal bleaching of the thermoluminescence glow curves, glow peaks are found which, after bleaching, destroy the optical absorption associated with the F-band. By using the model proposed by Halperin and Braner the activation energies of these peaks are calculated. The results show that the activation energy for Ca is 0.58 ev and for Cd is 1.67 ev. Finally, comments on the possible implications that the results may bear on the Crawford and Nelson model are made.

INTRODUCTION

The role of divalent impurities in the formation and growth of F-centers in alkali halide crystals continues to be a matter of debate up to the present. Whereas some workers[1] report similar enhancements of x-ray coloration upon addition of these impurities, others find that this enhancement depends strongly on the kind of impurities that are introduced. In particular it is found that Ca enhances the F-center formation more than any other impurity so far studied[2-5], while Cd even inhibits it[5,6].

Crawford and Nelson[7] have proposed a mechanism to explain the enhancement observed in Ca-doped crystals. According to their model, the positive ion vacancies created by the divalent impurities to maintain the overall electrical neutrality of the crystal do not remain associated with the impurity. Such a free vacancy would then be converted to an F-center during x-irradiation, when an adjacent anion captures a positive ion vacancy. This process would then imply an increase in the number of F-centers due to the extra positively charged vacancies created, all else remaining the same.

Due to these circumstances we decided to undertake a systematic study of the influence of divalent impurities on the kinetics of the formation and growth of F-centers in NaCl crystals by correlating thermoluminescence and optical absorption studies. In this work we are reporting some of the results obtained for Ca and Cd.

EXPERIMENTAL

Pure and doped NaCl crystals were grown from reagent grade materials by the Kyropoulos method in the open air, using techniques and equipment described elsewhere[8]. Two "highly-pure" crystals obtained from different sources[9] were also used in our experiments. Equivalent samples were obtained from a slice cut perpendicularly to the growth axis of the crystal to insure a uniform average concentration of impurities. Since it is known[10] that even for these slices there are radial fluctuations in the concentration, areas large compared with these fluctuations were used throughout the experiments. For the crystals doped with $CaCl_2$ and $CdCl_2$ the impurity concentration in our samples was: 0.28% in weight for Ca and 0.46% in weight for Cd, obtained by atomic absorption spectroscopic methods.

The same samples were used both for the optical and thermoluminescent measurements for a given series of runs to allow direct comparison of the results. The final size of the sample was approximately $6.0 \times 6.0 \times 0.8$ mm^3 and they were pretreated thermally at a temperature of 650°C during 0.5 hours and then quenched to room temperature before being exposed to an x-ray dose rate of 14000 R/min. The equipment used was a Harshaw Thermoluminescence Analyzer Model 2000 and a Coleman Spectrophotometer Model EPS-3T.

DISCUSSION

In Figs. 1 and 2 we present the results obtained for the three pure crystals and for the Ca- and Cd-doped ones. As shown in Fig. 1, our results confirm the previously reported dependence of the F-center growth curves on the impurities[2-6]. Figure 2 shows the different glow curves obtained when the same dose is applied to the five crystals. Ca enhances the first peak of the glow curves and Cd inhibits it, with respect to the pure crystals. Moreover, there seems to be a dependence of the area under the second peak on the total impurity content, which if true, would allow characterization of crystals by thermoluminescence methods.

By partial thermal bleaching we have identified some thermoluminescence peaks whose destruction is associated with the bleaching of the F-band. For the crystals used in this work we find that the highest temperature peaks are the ones correlated to the F-band (see Fig. 2 and Table I). It would be tempting to assume that they are associated with the emptying of the F-center traps and that consequently, their being destroyed causes in turn the annihilation of the F-centers. However, we believe that the activation energies found by using the model of Halperin and Braner[11, 12] (see Table I), are much too low to represent such a process, even if the Frank-Condon Principle is invoked (at least for Ca). Nevertheless, we are presently carrying out experiments to elucidate the nature of the carriers freed when the bleaching traps are emptied.

Two mechanisms determine the number of F-centers that may be formed in a given crystal. The first refers to the number of positively charged vacancies that the crystal has, and it is this feature that most models refer to when trying to explain the Ca enhancement. The other one is the number of "available" electrons created during the irradiation process. Clearly, the behaviour observed will be limited by the mechanism that saturates first.

Assuming that both Ca and Cd remain in the NaCl crystals as divalent impurities, the negatively charged vacancies created to insure

TABLE I

Temperatures and activation energies of the thermoluminescence peaks that bleach F-centers

Crystal	Activation Energy (ev)	Temperature (kelvins)
E[a]	1.22 ± 0.16[b]	419
R[a]	1.22 ± 0.10	447
B[c]	1.22 ± 0.15	461
Ca	0.58 ± 0.08	390
Cd	1.67 ± 0.12	368

[a] See Ref. 9.

[b] Error quoted is one standard deviation

[c] Pure crystal grown in our laboratory.

electrical neutrality would seem to be of the same order of magnitude for comparable concentrations of both elements. This, together with the assumed vacancy-to-F-center transformation of the Crawford and Nelson model, would imply a similar behaviour of the F-center growth curve for the impurity-doped crystals. Our results show this not to be true. However, even though the number of positively charged vacancies may be the same for a given concentration of any divalent impurity (a fact supported by results of ionic conductivity measurements of divalent impurity-doped alkali halide crystals[13]), the number of available electrons and/or the mobility of the positive-ion vacancies may vary as a function of the impurity introduced.

Our results seem to point out that it is the availability of electrons which makes the difference between Ca- and Cd-doped crystals. If the impurities introduce carrier traps in the energy gap and if, as discussed above, the bleaching traps are not the F-centers themselves, the impurity levels must be hole traps. In this manner the liberation of holes by heating the irradiated sample would increase the recombination hole-F-center electron thereby decreasing the optical absorption of the F-band. Therefore, the closer to the valence band the bleaching trap is, the easier it is to trap holes and consequently, more electrons will be available during the x-irradiation process, producing more F-centers. However, more experimental work is needed to make such a speculation become a sensible model, and we shall not discuss it further at this time.

In view of these possibilities we believe that the Crawford and Nelson model is not contradicted by the different growth curves reported in the literature as claimed, since there does not seem to be a determination of how the availability of electrons changes when impurities are introduced. It appears that this factor should not be decisive since in principle, by irradiation you can get all the electrons you need. However, recombination processes and electron affinity of the impurities introduced should be a determining factor in experiments like this, and should be accounted for when interpreting the data.

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This sample is referred to as R. The other was kindly given to us by Mrs. Estrella de Laredo and it was grown in her laboratory at the I.V.I.C., Caracas, Venezuela from spectroscopically pure salt. This is referred to as E.

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RESUMEN

Por métodos ópticos se determina la formación y crecimiento de centros F, en monocristales de NaCl conteniendo impurezas de Ca y Cd. Se encuentra que el Ca favorece su formación mientras que el Cd la inhibe. Mediante borrados parciales del espectro de termoluminiscencia se encuentran picos que al ser borrados anulan la absorción óptica de la banda F. Utilizando el modelo de Halperin y Braner se calculan las energías de activación de los picos que borran centros F obteniendo E = 0.58 ev para Ca y E = 1.67 ev para Cd. Finalmente, se discute las posibles implicaciones que nuestros resultados tienen para el modelo de Crawford y Nelson.

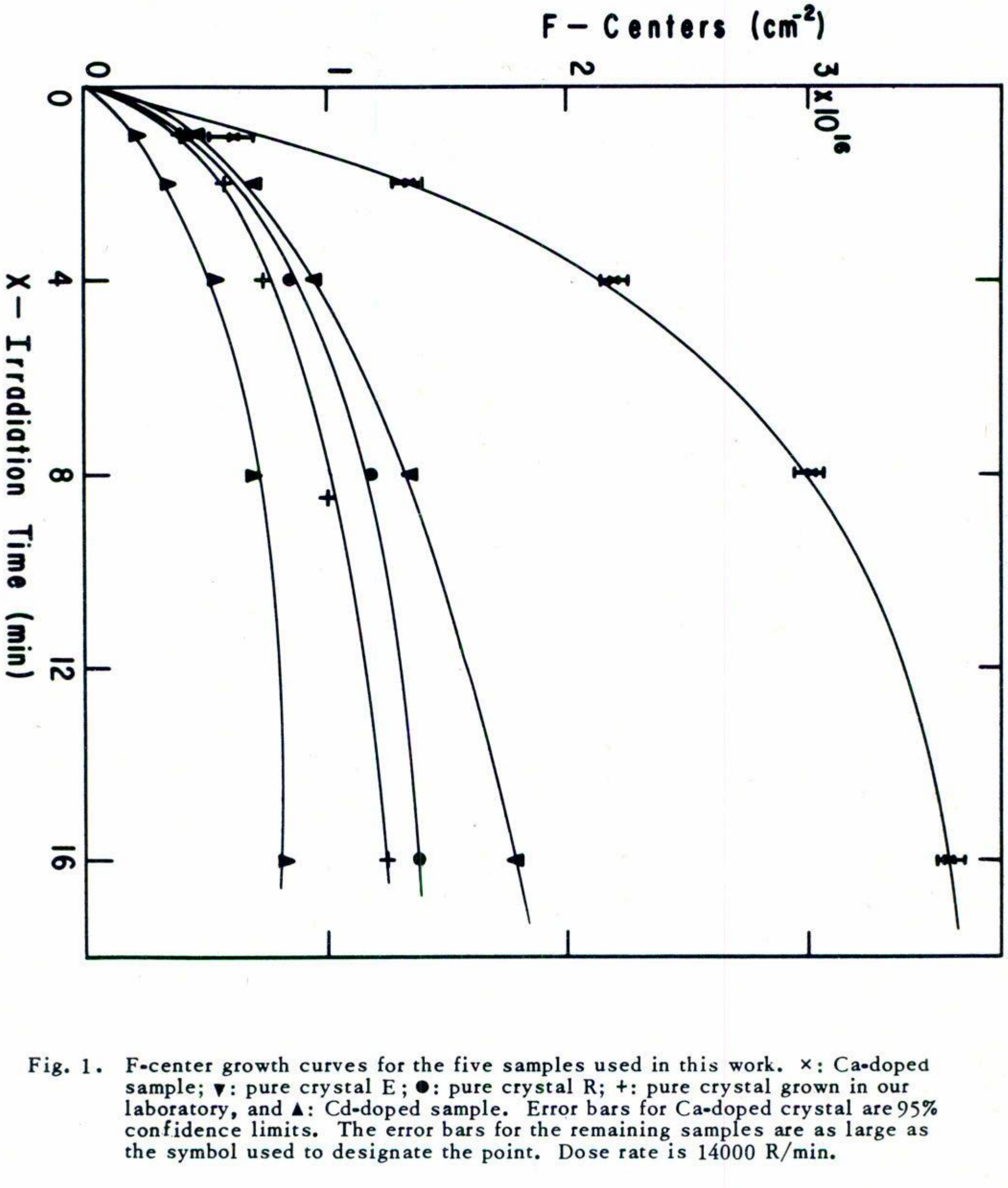

Fig. 1. F-center growth curves for the five samples used in this work. ×: Ca-doped sample; ▼: pure crystal E; ●: pure crystal R; +: pure crystal grown in our laboratory, and ▲: Cd-doped sample. Error bars for Ca-doped crystal are 95% confidence limits. The error bars for the remaining samples are as large as the symbol used to designate the point. Dose rate is 14000 R/min.

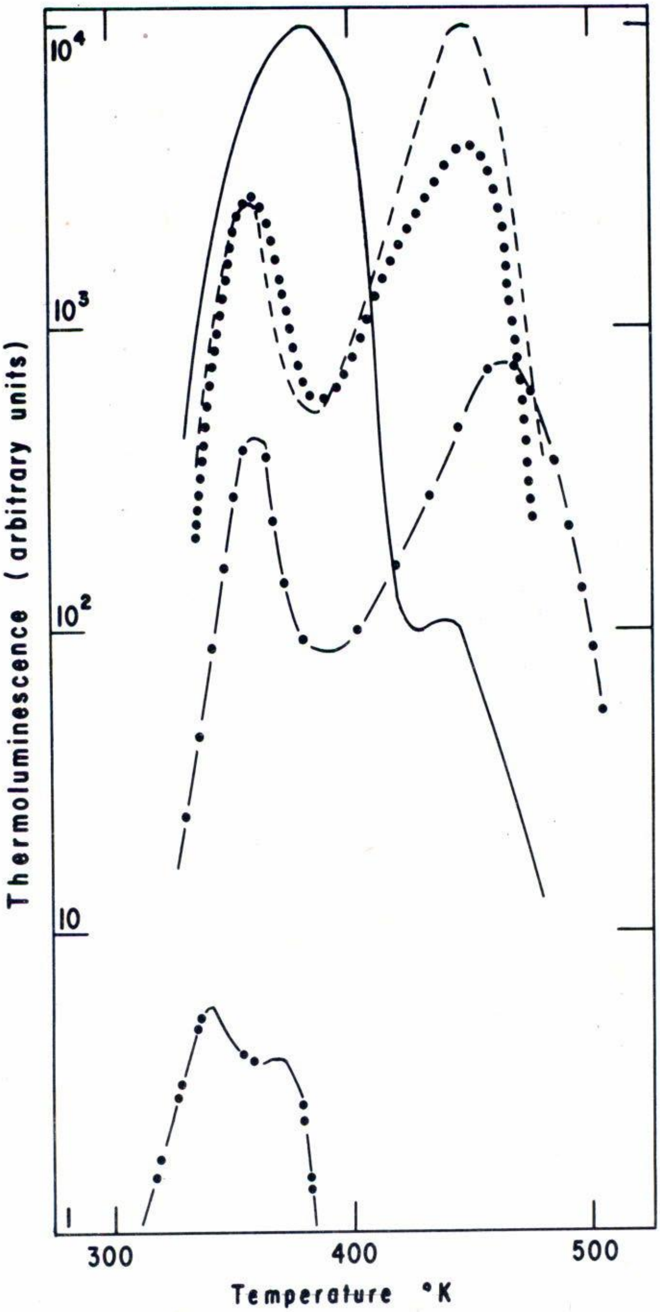

Fig. 2. Glow curves for the same samples shown in Fig. 1. Irradiation time is 4 min., dose is 56000 R. ————: Ca-doped crystal; — — — —: pure crystal R; ......: pure crystal E; . — . — .: pure crystal grown in our laboratory; .. — .. —: Cd-doped crystal. The highest temperature peaks are the ones that bleach the F-band.