

## Influence of radiation intensity and lead concentration in the room-temperature coloring of KBr

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The first stage of *F*-center coloring in quenched samples of lead-doped KBr has been investigated at room temperature as a function of impurity concentration and radiation intensity using optical absorption, photoluminescence, and ionic-thermocurrent techniques. For the range of lead concentration employed in this work (7 up to 250 ppm), the coloring increases monotonically with concentration when the samples are subjected to a radiation intensity of 10 R/min. Moreover, the amount of first-stage coloration was found to be proportional to the square root of impurity concentration, in agreement with the theoretical model recently proposed to account for *F*-center production in alkali halides doped with divalent cation impurities that change their valence state by irradiation. A quite different result was found to occur when the samples were irradiated at a higher radiation intensity (50 R/min). In this case, the coloring increases with lead concentration only at the very beginning of irradiation. As the irradiation time increases, however, the coloring curve for a heavily doped crystal crosses that for a slightly doped crystal in such a way that more coloring is produced during stage II of the *F*-center growth curve for the lower concentration. Moreover, as lead concentration increases, the coloring saturates more efficiently the higher the concentration. It was ascertained that the exposure of the crystals to the highest radiation intensity employed in this work also induces lead precipitation in the irradiated specimens as revealed by analyses of the emission and excitation spectra. This effect is produced by the ionizing radiation and not by the room-temperature annealing of the samples during the time in which the irradiations were performed. The influence of impurity precipitation occurring during stage I of the *F*-center growth curve on the kinetics of color-center formation is analyzed. It is proposed that the phenomenon of impurity precipitation induced by irradiation may be responsible for the experimental observation that more coloring is sometimes produced in slightly doped samples than in heavily doped samples.

## I. INTRODUCTION

The effects of ionizing radiation in alkali halides doped with doubly valent impurity ions ( $M^{2+}$ ) have been the subject of a considerable amount of work over the last three decades. Unfortunately, almost all this information has the disadvantage that it was obtained from samples in which the state of the impurity ions at the start of the irradiation process was unknown or only poorly characterized. This lack of information may produce a misleading interpretation of the results obtained, especially when the conclusions are mainly based on a comparison of the effects observed using different initial impurity concentrations. In fact, it has been recognized<sup>1-4</sup> that the characterization of the state of the impurity ions in the sample is an important determination if one wants to know precisely the kinetics of radiation-induced coloring in the alkali halides. This conclusion is based on the fact that the efficiency for coloring in this type of crystals is quite dependent on the nature of the impurity complexes which are present in the sample at the start of irradiation.

Recently, detailed work dealing with the effects of room-temperature x irradiation in alkali halides doped with  $\text{Eu}^{2+}$  ions has been carried out in our laboratory.<sup>3-6</sup> In all the systems investigated the ionizing radiation produced (a) a decrease in the number of  $\text{Eu}^{2+}$ -cation vacancy dipoles originally present in the crystal at the start of irradiation, (b) a change in the valence state of  $\text{Eu}^{2+}$ , (c)

the growth of the *F* and *M* bands, and (d) an enhancement of the rate of aggregation of dipoles. All the results obtained suggest that isolated  $\text{Eu}^{2+}$ -cation vacancy dipoles are the fundamental traps for the radiation-induced interstitial defects. On the other hand, the discovery of an enhanced dipole-aggregation rate by irradiation was important for obtaining a correct interpretation of the results obtained in these types of crystals. With regard to this phenomenon, Rubio *et al.*<sup>7</sup> have recently reported that in the system  $\text{NaCl}:\text{Mn}^{2+}$  the ionizing radiation also enhances the diffusion of the  $\text{Mn}^{2+}$ -cation vacancy dipoles originally present in the fast-quenched samples leading to the formation of a second-phase precipitate which was associated with the Suzuki phase of the manganese ions in the host NaCl according to the electron paramagnetic resonance and optical data. Moreover, these authors suggested that the impurity precipitation induced by ionizing radiation in this system may be responsible for the experimental finding that less coloring is achieved during stage II of the *F*-center growth curve as manganese concentration increases. According to these authors it is expected that if the process of manganese precipitation occurring during stage I of the coloring curve strongly competes with those leading to the formation of *F* centers, then the balance between them could result in lower coloring during stage II as the concentration increases, especially if the precipitates formed during irradiation are somewhat less efficient than the isolated dipoles for

TABLE I. Peak positions of the absorption and emission bands associated with free dipoles, aggregates, and precipitates of lead in monocrystalline KBr at 77 K. The data are taken from the work of Zaldo and Agulló-López (Ref. 11). The numbers in parentheses represent the peak positions of the bands in those cases in which small differences have been found in this work.

Complex	Absorption (nm)	Emission (nm)
Dipoles	298	366 467
	295	366
Small aggregates		467
	302 (305)	390
		467
Precipitated phases	308	
	323	555 (550)
	338	

enhancing coloring.

On the other hand, very little information is available to date on the influence of radiation intensity on color-center formation in alkali halides in which the state of the doubly valent impurity ions has been fully characterized at the start of irradiation. Given that the impurity precipitation induced by irradiation may be strongly enhanced as the radiation intensity used to obtain the data is increased, it is expected (following the suggestion of Rubio *et al.*) that the kinetics of color-center formation does not always follow the predictions of the theoretical models recently proposed to explain *F*-center production in doped alkali halides.<sup>8-10</sup> In view of this situation, it appears that if the role of cation impurities on the kinetics of radiation-induced coloring in alkali halides is to be firmly established, then systematic investigations in which the combined influence of radiation intensity and impurity concentration on color-center formation is accounted for must be carried out. Special emphasis must be put on the determination of the influence of impurity precipitation induced by irradiation on the *F*-center production.

In the present paper measurements of optical absorption, photoluminescence, and ionic thermocurrents (ITC) have been carried out in order to perform a detailed investigation of the first stage of the room-temperature *F* coloring of lead-doped KBr as a function of radiation intensity and lead concentration. This system was selected to perform this study since quite a good optical picture of the different states in which  $Pb^{2+}$  can be found in KBr is available.<sup>11</sup> This information is given in Table I. Therefore, from the analyses of the emission and excitation spectra, a reasonable characterization of the different lead complexes which may be present in the crystal before each measurement can be gathered.

## II. EXPERIMENTAL

Single crystals of potassium bromide doped with lead were grown in our laboratory by the Czochralski method

under a 300-Torr argon atmosphere. Lead concentration in the samples was determined either by atomic-absorption spectrophotometry or from the optical-absorption spectrum of the quenched samples. In the latter case, the lead concentration was obtained from the intensity of the *A*-band peak at 298 nm, using Smakula's equation with a value for the oscillator strength of 0.1.<sup>12</sup> The results obtained using both methods were quite similar and did not differ by more than 15%. Thermal quenching was performed by heating the "as-grown" samples for 1 h at 873 K and then quenching them onto a copper block at room temperature or in acetone.

Optical-absorption, photoluminescence, and ITC measurements were carried out with the experimental setup described elsewhere.<sup>5</sup> Irradiation of the samples was performed with a Phillips stabilized dc generator. The x rays were always filtered through a 1-mm aluminum filter. Special care was taken to avoid the heating of the samples during irradiation, since this effect might confuse the origin of the results obtained.

## III. RESULTS

### A. Preirradiation

#### 1. Ionic-thermocurrent measurements

Before x irradiation the ITC measurements performed in the quenched samples showed a single current peak with a maximum at  $210 \pm 1$  K, yielding an activation energy of  $0.56 \pm 0.05$  eV. From the area under the observed ITC peak the dipole density ( $N_D$ ) was calculated in the doped samples assuming nearest-neighbor reorientation. Once  $N_D$  was determined in a series of crystals doped with different initial concentrations in the melt, a plot was performed of  $N_D$  against the total concentration of lead ( $C$ ) as determined from the absorption spectrum. The results are summarized in Fig. 1. The inset in this figure shows the observed ITC peak and the fitting of this curve

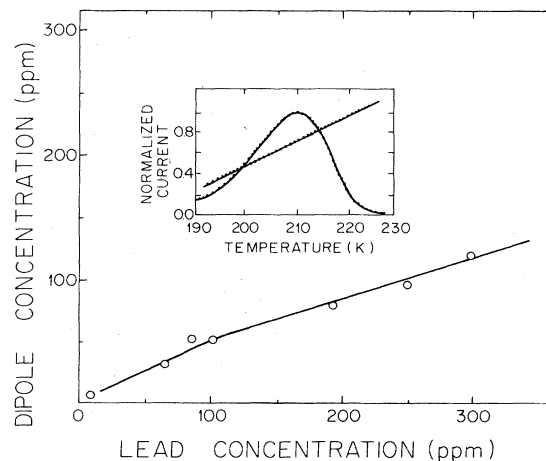


FIG. 1. Dipole density measured by ITC as a function of the absorption coefficient of the 298-nm band in the absorption spectrum of quenched samples of  $KBr:Pb^{2+}$ . The inset shows the observed ITC peak (points) as well as the fitting which was performed on this curve using the area method (solid curve).

which was performed using the area method. Reference to this figure shows that  $N_D$  was found to be equal to  $C$  only for the slightly doped sample (7 ppm). As concentration increases,  $N_D$  was equal or less than one-half of  $C$ . The values for the ratio  $N_D/C$  which were determined in crystals quenched onto acetone were only slightly larger than those determined in the same samples after quenching into a massive copper block. The above results indicate that lead is a very insoluble impurity in KBr, and that some other lead complexes, different from the isolated dipoles, were present in our samples after the quenching treatment.

## 2. Optical-absorption and photoluminescence measurements

In order to get better insight into the nature of the lead complexes present in our quenched crystals before the irradiations were performed, optical-absorption and luminescence measurements were carried out in parallel. Absorption measurements in the range 250–2600 nm revealed that the spectrum consisted of the spin-forbidden  $A$ -band peak at 298 nm. This band has been ascribed to the transition  $^1S_0 \rightarrow ^3P_1$  of the  $Pb^{2+}$  ions by several workers.

The 77-K emission spectrum of these crystals portrayed in Fig. 2(a) consists of two broadbands peaking at 369 and 467 nm, when the excitation is performed with light lying in the absorption  $A$  band. On the other hand, the excitation spectra of these two bands are very similar. They consist of two overlapping bands peaking at 298 and 305 nm, the peak position of the latter band being slightly different to that reported by Zaldo and Agulló-López<sup>11</sup> (i.e., 302 nm). The relative intensities of the 298- and 305-nm bands are strongly dependent on the wavelength selected within the 369-nm band to obtain the excitation spectrum,

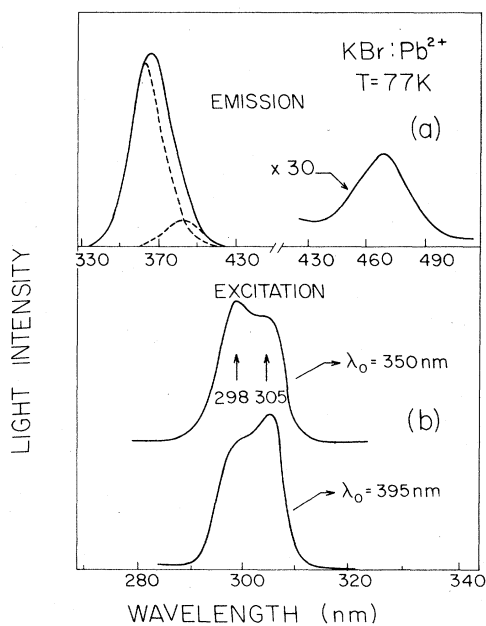


FIG. 2. (a) Emission and (b) excitation spectra of quenched samples.

as shown in Fig. 2(b). The observation of these bands gives evidence, according to the data given in Table I, that not only isolated  $Pb^{2+}$ -cation vacancy dipoles but also small lead complexes are present in the crystal after quenching, in agreement with the ITC data in Fig. 1. It also suggested that lead emission should be observed at both 366 and 390 nm. To corroborate this expectation a decomposition of the 369-nm band was performed. The result of this decomposition revealed that this band was, in fact, composed of two overlapping bands peaking at 366 and 390 nm. In order to make this decomposition, the emission spectrum of a slightly doped sample (7 ppm) was first obtained. In this case, lead emission occurring at 366 and 467 nm was due only to the isolated dipoles as established from the ITC data given in Fig. 1. With the width of the 366-nm band the emission band peaking at 369 nm observed in the more heavily doped crystals was decomposed and the result is also shown in Fig. 2.

At this point, it is important to remark that excitation with light at either 308, 323, or 338 nm did not produce in any of the crystals employed lead emission in the range 500–600 nm. This result indicated that second-phase precipitates were not present in our samples after the quenching treatment.

## B. Irradiation

Figure 3 shows the absorption spectrum of a KBr crystal doped with 100 ppm of  $Pb^{2+}$  after quenching from 873 K (dashed curve) and after 2 h of room-temperature x irradiation (solid curve). Besides the  $F$  and  $A$  bands, the spectrum of the irradiated specimen consists of a well-defined Gaussian-type band peaking at 275 nm. Its intensity was found to be almost independent of sample temperature, indicating that it arises from a dipole-allowed transition. Moreover, the intensity of this band grows during optical bleaching of the  $F$  band. From all of these observations it is believed that the 275-nm band is similar to that observed by Tsuboi<sup>13</sup> in the absorption spectrum of irradiated lead-doped KCl peaking at 253 nm and ascribed to  $Pb^+$ , the latter being formed when one electron is trapped by  $Pb^{2+}$ .

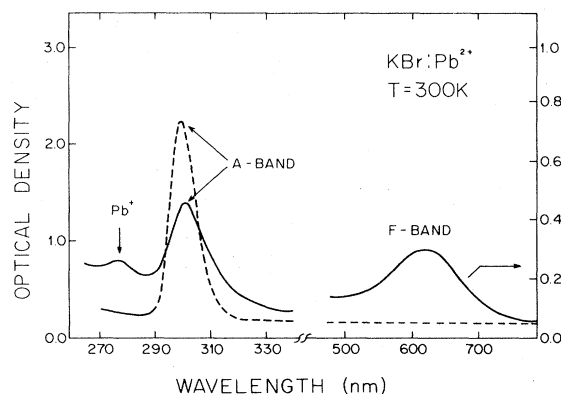


FIG. 3. Optical-absorption spectrum of a KBr crystal doped with 100 ppm of  $Pb^{2+}$  after quenching from 873 K (dashed curve) and after 2 h of room-temperature irradiation (solid curve).

Room-temperature coloration curves for quenched samples irradiated with x rays at a radiation intensity of 50 R/min are portrayed in Fig. 4(a) for three selected impurity concentrations. It is important to point out that the  $F$  coloring increases with lead concentration at the very beginning of irradiation. However, the coloring rates after the initial rise are smaller the higher the concentration. In fact, the coloring curve for a 155-ppm-doped sample crosses that for a 66-ppm-doped sample after  $\approx 20$  min irradiation, so that more coloring is observed for the lower concentration during state II of the  $F$ -coloring curve. As lead concentration increases, the coloring was found to saturate more efficiently the higher the concentration. Similar observations have been reported for the systems KCl:Sr,<sup>14</sup> KCl:Pb,<sup>1</sup> and NaCl:Mn.<sup>2</sup> However, the origin of this effect has not been yet established.

Figure 4(b) shows coloring curves for the same lead concentrations as in Fig. 4(a), but obtained with a lower radiation intensity (10 R/min). It is observed that in this case, in contrast to the above results, the coloring increases as lead concentration increases. Moreover, the curves do not cross for lead concentrations up to  $\sim 250$  ppm. On the other hand, a plot of the amount of first-stage coloration ( $n_{F0}$ ) as a function of the square root of the total concentration of lead in the samples ( $C$ ) gives a quite good linear dependence as shown in the inset of Fig. 4(b). The values for  $n_{F0}$  were obtained by extrapolating the linear part of each  $F$ -center growth curve to meet the ordinate. This result is in very good agreement with the

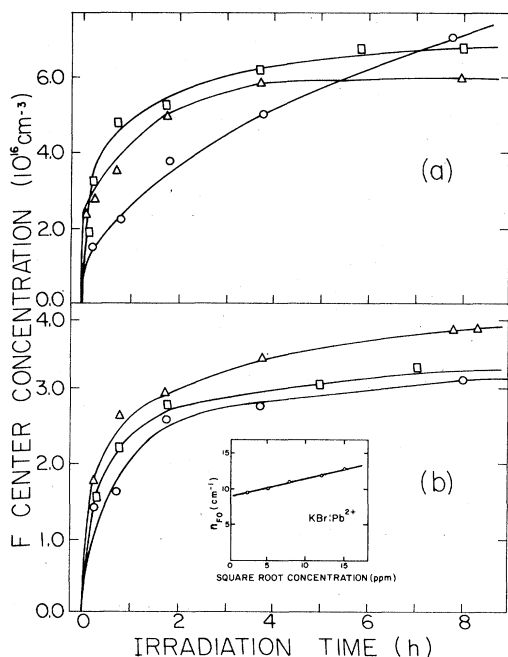


FIG. 4. (a) Room-temperature  $F$ -center growth curves as a function of lead concentration for quenched samples irradiated at a radiation intensity of 50 R/min:  $\circ$ , 7 ppm;  $\square$ , 66 ppm;  $\triangle$ , 155 ppm. (b) The same, but obtained at a radiation intensity of 10 R/min. The inset in this figure displays the relationship between the amount of first-stage coloration ( $n_{F0}$ ) and impurity concentration ( $C$ ).

predictions of the theoretical model proposed by our group<sup>10</sup> to account for  $F$ -center production in alkali halides doped with  $M^{2+}$  impurities that change their valence state by irradiation. It is obvious that a similar linear dependence between  $n_{F0}$  and  $C^{1/2}$  is not obeyed for the coloring curves shown in Fig. 4(a).

It was found that radiation causes the  $A$  band to diminish. The decrease is particularly fast during the initial stage of  $F$ -center growth and its relative decrease is higher the lower the lead concentration. The intensity of the ITC peak was also found to decrease as the irradiation time increases, its decrease being much faster than that of the absorption  $A$  band. In fact, irradiation of the 155-ppm-doped crystal for  $\approx 30$  min at the higher radiation intensity brings about the decay of the ITC peak down to its total disappearance, while the  $A$  band remains with an intensity of about 60% of its original value. On the other hand, a marked widening of the  $A$  band, preferentially on the low-energy side, was found to occur in the absorption spectrum of the irradiated specimens. This fact suggested the growth of an additional band peaking at  $\approx 325$  nm during irradiation.

As illustrated in Fig. 5, the amount of  $Pb^{+}$  grows initially with the irradiation time reaching a maximum value and then experiences a monotonic decay. The results obtained in an "as-grown" crystal are also included in Fig. 5 for the sake of comparison. In this latter case a similar behavior for  $Pb^{+}$  creation was found although the amount of  $Pb^{+}$  ions produced under the same irradiation dose is considerably smaller.

In order to investigate the effect of the initial concentration of  $Pb^{2+}$ -cation vacancy dipoles on the efficiency of production of  $F$  and  $Pb^{+}$  centers, the number produced by a fixed dose of irradiation after a variable time after quenching was measured in a 120-ppm-doped sample. To do this, samples were cleaved from the same crystal block, heated for 1 h at 900 K and quenched to room temperature. They were then annealed at 300 K for different periods of time. The results of these measurements are portrayed in Fig. 6. Each point in the figure corresponds to a different sample irradiated 30 min after the annealing treatment. The irradiation time employed brings the coloring to an intermediate point on stage I of the  $F$ -

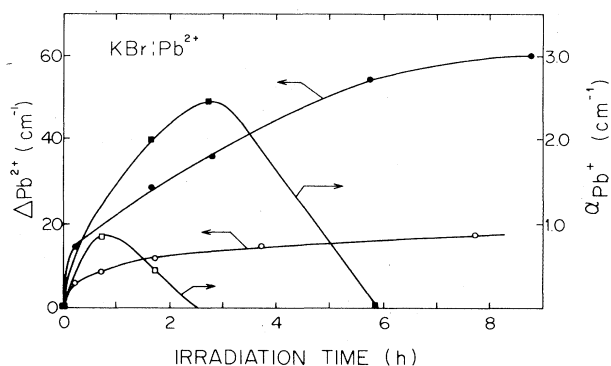


FIG. 5. Data for  $Pb^{+}$  production and valence change [ $\Delta(Pb^{2+})$ ] for a quenched sample (solid symbols) and for an "as-grown" sample (open symbols) as a function of irradiation time.

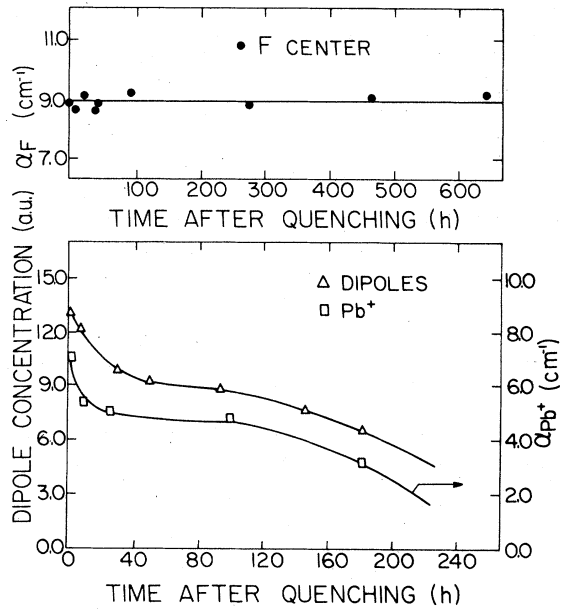


FIG. 6. *F*-center production and  $Pb^{+}$ -center formation induced by 30 min irradiation as a function of the time elapsed between quenching and irradiation. Dipole evolution is also shown in the figure for the sake of comparison.

center growth curve. The evolution of dipole concentration (as measured by ITC) as a function of the annealing time at this particular temperature after quenching is also included in Fig. 6.

At this point, it is enlightening to compare the coloring curves for a crystal which had been aged at 473 K for three months and for one quenched under the same conditions of lead concentration and radiation intensity. An ITC measurement performed on the well-aged crystal established that isolated  $Pb^{2+}$ -cation vacancy dipoles were not present at the start of irradiation. Rather, almost all lead ions were found to have precipitated into the phase responsible for the emission band peaking at 550 nm, as revealed from the emission and excitation spectra of this crystal. The curves obtained which are not shown for the sake of brevity revealed that the amount of coloring produced in the aged sample during both stages I and II is quite less than that produced in the quenched one.

The thermal stability of the *F* centers was also analyzed in quenched samples which were irradiated with the two radiation intensities employed. To do this, the decay in intensity of the *F* band during linear heating (rate of 4 K min<sup>-1</sup>) was determined. It was found that the *F* centers were more stable in the samples irradiated at the lowest radiation intensity than when they are produced through the use of the highest radiation intensity. On the other hand, the *F* centers produced in the aged crystal at 473 K for three months were found to be quite less thermally stable than those in quenched ones.

In order to obtain additional information which would promote a better understanding of the effects reported above, the emission and excitation spectra of the irradiated samples were carefully analyzed. It was found that the intensity of the emission band peaking at 366 nm, due to

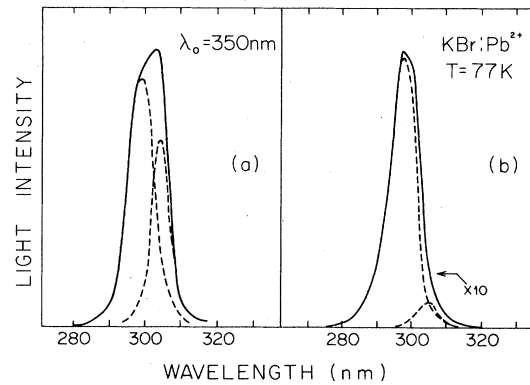


FIG. 7. Excitation spectra corresponding to the left-hand side of the 369-nm emission band: (a) after quenching; (b) after 30 min irradiation at the highest radiation intensity.

isolated  $Pb^{2+}$ -cation vacancy dipoles, decreased with irradiation, while the intensity of the 390-nm band ascribed to small lead aggregates increased. Figures 7 and 8 illustrate, as an example, the evolution of the excitation spectra corresponding to the emission bands peaking at 366 and 390 nm, respectively, as a function of the irradiation time for the same sample as that mentioned above. The intensities of the excitation bands peaking at 298 and 305 nm decreased with irradiation. However, new bands peaking at 308, 323, and 338 nm grew in the excitation spectrum of both the 390- and 467-nm emission bands. Moreover, excitation with light at either 308, 323, or 338 nm produced lead emission at 550 nm, as shown in Fig. 9. The 77-K excitation spectrum of this latter band is also

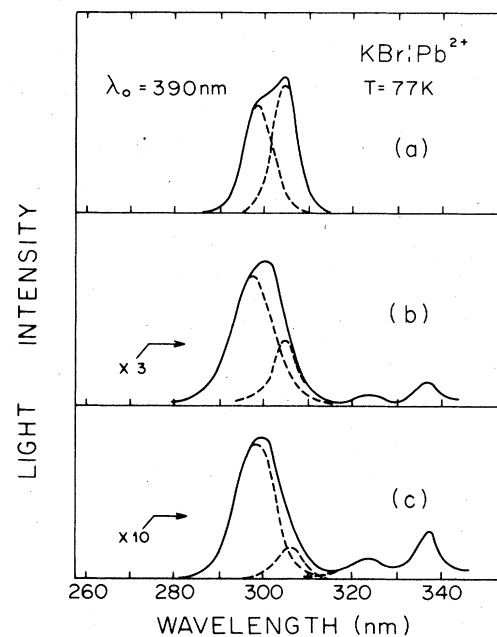


FIG. 8. Excitation spectra corresponding to the right-hand side of the 369-nm emission band: (a) after quenching; (b) after 30 min irradiation; (c) after 2 h irradiation at the highest radiation intensity.

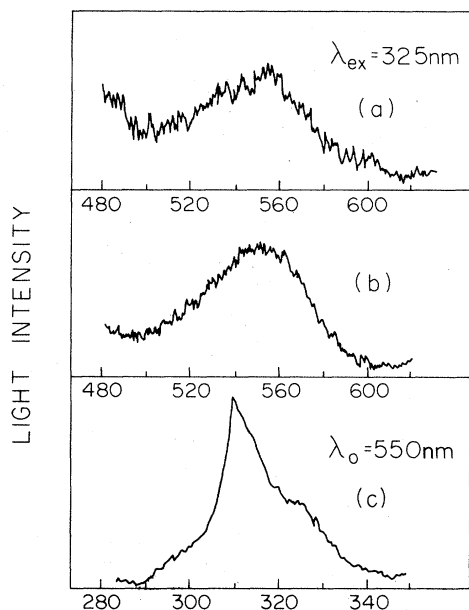


FIG. 9. Liquid-nitrogen emission spectrum when excitation was performed at 325 nm; (a) after 30 min and (b) after 2 h irradiation at the highest radiation intensity; (c) excitation spectrum of the 550-nm emission band.

given in the latter figure. It consists mainly of the 308-, 323-, and 338-nm bands mentioned above. Similar results were obtained in the 66-ppm-doped sample.

#### IV. DISCUSSION

The lack of correlation between the production rate of  $F$  centers and the concentration of nonaggregated dipoles appears to be a quite general phenomenon in alkali halides doped with  $M^{2+}$  impurity ions. This behavior suggests that the isolated dipoles are as equally efficient as small aggregates in enhancing coloring. In contrast with this result, the coloring obtained from the annealed sample at 473 K, in which almost all lead ions were precipitated into the phase responsible for the emission band peaking at 550 nm, is much lower than that of a quenched one during both stages I and II of the  $F$ -center growth curve. It is inferred from this result that these precipitates are less efficient than the isolated dipoles or small aggregates for enhancing coloring. Moreover, since the thermal stability of  $F$  centers in the well-aged crystal is lower than that in a quenched one, it appears that the backreactions involving the annihilation of thermally liberated interstitials with  $F$  centers are more active in the 473-K annealed sample than in the quenched one.

With regard to the production of  $Pb^+$  ions observed in our samples, several comments should be made. In particular, the shape of the  $Pb^+$  growth curve portrayed in Fig. 5 is quite similar to those previously reported by Pascual and Agulló-López<sup>1</sup> in lead-doped NaCl and KCl. According to these authors the shape of this curve suggests that two competing processes contribute to the kinetics of

$Pb^+$  formation under irradiation. One of them is a saturation of the  $Pb^{2+} \rightarrow Pb^+$  conversion, while the other is a destruction mechanism of the type  $Pb^+ \rightarrow Pb^0$ . Unfortunately, absorption bands which could be unambiguously associated with  $Pb^0$  ions in the spectrum of the irradiated specimens were not identified. However, it appears reasonable to consider that the mechanisms proposed by Pascual and Agulló-López are also operative in lead-doped KBr. On the other hand, from the data portrayed in Fig. 6 it is inferred that the production of  $Pb^+$  centers decreases in close parallel with dipole concentration. This result indicates that the  $Pb^{2+} \rightarrow Pb^+$  conversion only involves nonaggregated  $Pb^{2+}$  ions. This conclusion is supported by the fact that  $Pb^+$  ions were only minimally produced in samples aged at 473 K for a long time, in which a relatively small number of isolated dipoles was present at the start of irradiation.

On the other hand, one of the main conclusions of this work can be obtained from the analyses of the emission and excitation spectra of the irradiated crystals. These spectra give evidence that second-phase precipitates were formed in our samples when they were irradiated at the highest radiation intensity employed in this work. These precipitates were really induced by ionizing radiation and not by the room-temperature aging of the crystal during the time in which the irradiations were performed, since neither the emission nor the excitation spectra of a twin unirradiated quenched sample which was annealed at 300 K for times up to  $\approx 50$  h revealed the presence of second-phase precipitates.

From the obtained optical data it appears that the pathway for the formation of these precipitates is as follows: At the start of the irradiation the small aggregates act as important nucleation centers for the lead dipoles, the rate of aggregation of the latter being considerably enhanced by ionizing radiation. As a result of this fact, the size of the small aggregates increases upon irradiation. These somewhat larger aggregates still produce emission bands peaking at 390 and 467 nm or slightly shifted. Their structure appears to be similar to that of the precipitated phase responsible for the emission band peaking at 550 nm observed in the nonirradiated specimens since the excitation spectrum of the latter band is quite similar to those of the 390- and 467-nm emission bands. As the irradiation time proceeds, a net flow of solute from the smaller to the larger aggregates takes place until the latter give rise to the precipitated phase associated with the emission band peaking at 550 nm. Under irradiation the diffusion is enhanced and the ripening accelerated.

Similar results were obtained when the samples were irradiated at the lowest radiation intensity. More relevant is the fact that the bands peaking at 308, 325, and 338 nm also grew in the excitation spectra of the 390- and 467-nm bands. However, lead emission at 550 nm was not found to be produced in the irradiated specimens for the times up to  $\approx 10$  h. These results suggest that the exposure of the crystals to the lowest radiation intensity produced that the small aggregates grew during irradiation. Their growth, however, appears to be smaller than in the case of higher radiation intensities since they did not give rise to second-phase precipitates. These results indicate that the

phenomenon of lead precipitation in KBr induced by ionizing radiation is very dependent on radiation intensity.

Since lead precipitation was found to occur simultaneously with color-center formation in the samples which were exposed to the highest radiation intensity but not with the use of the lowest one, we are tempted to suggest, following Rubio *et al.*, that the formation of lead precipitates during irradiation is the effect responsible for the differences observed in the coloring curves shown in Fig. 4. In order to support this conclusion some of the most relevant information obtained for the 66- and 150-ppm-doped samples with the two radiation intensities employed will be discussed below. It was ascertained that the exposure of the 150-ppm-doped sample to  $\approx 20$  min irradiation at the highest radiation intensity produced the almost total disappearance of the  $\text{Pb}^{2+}$ -cation vacancy dipoles which were originally present in the sample at the beginning of irradiation. Simultaneously, the rate of  $F$ -center growth slows down and the transformation of stage I into II in the  $F$ -coloring curve starts. Moreover, lead precipitation into the phase responsible for the emission band peaking at 550 nm has already occurred as a consequence of the enhanced rate of impurity precipitation by irradiation. The total disappearance of the  $\text{Pb}^{2+}$ -cation vacancy dipoles is due mainly to the following facts: (a) the dipoles act as efficient traps for the radiation-induced interstitials, (b) the  $\text{Pb}^{2+}$  ions forming the dipoles capture electrons in such a way that they reduce their valence state, and (c) the dipoles form aggregates as a result of the fact that their diffusion is enhanced by irradiation. Although all these processes can produce the disappearance of the lead dipoles, the latter two appear to be the more important since the number of  $F$  centers produced after  $\approx 20$  min of irradiation ( $\approx 1.0 \times 10^{17} \text{ cm}^{-3}$ ) is only a small fraction of the concentration of dipoles ( $7 \times 10^{17} \text{ cm}^{-3}$ ) at the start of irradiation. Therefore, the number of dipoles destroyed as a consequence of interstitial trapping is too small to explain the total disappearance of the  $\text{Pb}^{2+}$ -cation vacancy dipoles after 20 min irradiation and suggests that the valence-change and aggregation-precipitation processes induced by irradiation are the main mechanisms involved in the destruction of lead dipoles during stage I of the  $F$ -center growth curve. A similar situation was found to occur in the 66-ppm-doped sample when it was exposed to the lower radiation intensity. However, the irradiation time needed to produce the effects mentioned above was somewhat larger, i.e.,  $\approx 2$  h.

The processes of impurity precipitation and valence change may compete with those leading to the formation of  $F$  centers, and the balance between them could result in a lowering of coloring during stage II as lead concentration increases. However, impurity valence change produced by irradiation does not appear to be the effect responsible for the crossover of the  $F$ -center curves since this effect has been observed in alkali halides doped with impurities that do not change their valence state by irradiation.<sup>14</sup> Therefore, one may consider that the initial  $F$ -center growth in the quenched samples is mainly due to the fact that there exists a large number of available traps (dipoles and small aggregates) at the very beginning of irradiation. These complexes may stabilize the interstitials

created, thereby inhibiting recombination with  $F$  centers. As the irradiation time proceeds, however, the dipolar traps are rapidly destroyed as a result of the valence-change and aggregation-precipitation processes mentioned above. Moreover, the small aggregates originally present in the samples grow during irradiation and give rise to the second-phase precipitates which are not efficient traps for the halogen interstitial defects. As a consequence of the precipitation process, the small aggregates lose their ability to capture interstitials as a function of the irradiation time, and therefore produce a decrease in the coloring efficiency during stage I of the  $F$ -center growth curve. Moreover, since the thermal stability of the  $F$  centers is quite small in samples containing lead precipitates, it is expected that the backreactions involving the annihilation of radiation-induced and thermally liberated interstitials with  $F$  centers will operate more efficiently as lead precipitation occurs during stage I. The occurrence of this process produces an even more pronounced lowering in the rate for coloring. Since these mechanisms that produce a decrease in the rate for coloring will operate at shorter times as the impurity concentration increases, the curves corresponding to very high impurity concentrations must cross those for somewhat lower concentrations after the initial rise, and the saturation level for coloring during stage II must be lower as concentration increases. A quite different situation is expected to occur in the samples when they are irradiated at a radiation intensity which does not produce lead precipitation during stage I of the  $F$ -center growth curve. In this case, since the aggregates originally present in the crystal at the start of irradiation do not grow enough to give rise to the precipitated phase associated with the emission band peaking at 550 nm, it appears to be reasonable to consider that the ability of the small aggregates to capture interstitials and/or the thermal stability of the traps does not change significantly during stage I of the coloring curve. Therefore, it is expected that the coloring must increase as concentration increases. Moreover, since the small aggregates are as equally efficient as the isolated dipoles for enhancing coloring, the amount of first-stage coloration is expected to be proportional to the square root of the total concentration of lead in the sample.

In view of the present results, it would be interesting to reexamine the effects of  $x$  irradiation in  $\text{NaCl:Mn}^{2+}$  and  $\text{KCl:Pb}^{2+}$  as a function of the combined influence of radiation intensity and impurity concentration. It is well known that neither manganese nor lead are very soluble in these types of crystals. Therefore, small aggregates may be present in the samples at the start of irradiation even after a severe quenching from high temperatures. As a consequence, special emphasis must be put on determining whether or not a correlation exists between impurity precipitation induced by irradiation and coloring behavior. This might explain the reported lowering of the saturation value for coloring during stage II of the  $F$ -center growth curve as the concentration increases in these two systems. An investigation of this type would be useful for determining whether or not the explanation given here for the origin of these effects is also appropriate for other systems.

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