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$Pb^{2+} \rightarrow Mn^{2+}$ nonradiative energy transfer in KBr

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The analysis of optical emission and excitation spectra of KBr single crystals doubly doped with Pb^{2+} and Mn^{2+} ions has been accomplished for different sample conditions. The results show that highly efficient nonradiative energy transfer occurs from Pb^{2+} to Mn^{2+} ions which then decay by giving orange-red (640 nm) emission. A comparison of excitation spectra for manganese emission of as-grown and annealed samples shows that Mn^{2+} excitation is associated with the aggregated phase of Pb^{2+} ions. The 640-nm emission has been explained on the basis of a model which proposes trapping of Mn^{2+} ions in the Suzuki phase of Pb^{2+} dipoles. The electron-paramagnetic-resonance results also support this model. The results for annealed and subsequently aged samples are further in conformity with the model. Finally, the observed 520-nm emission band in as-grown samples has been attributed to a Suzuki-type aggregated phase of Mn^{2+} ions.

I. INTRODUCTION

The alkali-halide crystals doped with divalent impurities have been extensively studied by optical,[1-5] electron paramagnetic resonance (EPR),[6] ionic thermoconductivity (ITC),[7] and ionic conductivity[8] techniques. Particularly, the optical properties of Pb^{2+} ions in alkali-halide crystals are fairly well understood.[2,9-11] The alkali-halide crystals doped with Pb^{2+} ions have four absorption bands labeled[10] A, B, C, and D. Of these the most intense A band arises due to a dipole-allowed transition with oscillator strength of the order of 10^{-1} and has been extensively studied in many systems. Freshly quenched crystals of Pb^{2+}-doped KBr show a well-resolved A absorption band peaking[12] at 298 nm. Thus, this system is an efficient absorber of uv light. The optical spectra of Pb^{2+} ions in alkali-halide crystals are quite sensitive[5] to the state of aggregation. On aging the A band broadens on both wavelength sides due to the growth of various absorption bands associated with aggregates and precipitates of Pb^{2+} ions. Zaldo and Lopez[12] have identified 295–338 nm broadening of such a band associated with various aggregates and precipitates of Pb^{2+} ions in a KBr host. The Pb^{2+}-doped alkali-halide crystals also yield broad band (366–555)-nm emission,[12] when illuminated with uv radiation.

The optical spectra of Mn^{2+} ions doped in alkali-halide crystals are also studied[13,14] quite extensively. The optical absorption and excitation studies in Mn^{2+}-doped systems by Mehra[13] and Rodriguez *et al.*[14] have established that the absorption bands arise through spin- and parity-forbidden transitions with low oscillator strength $\sim 10^{-7}$. Thus, a Mn^{2+}-doped system is a very weak absorber of uv light. The EPR of Mn^{2+}-doped alkali-halide crystals has been reported by Watkins[6] and isolated ions, nearest-neighbor (NN) and next-nearest-neighbor (NNN) ion-vacancy pairs and even aggregates of manganese have been identified through their characteristic spectra.

The various stable and metastable aggregates and precipitates of divalent impurities in alkali-halide crystals[15,16] have been identified. However, the precipitation or aggregation depends on aging, annealing temperature and time, rate of cooling, and also on the composition[15,16] of the crystal. At times aggregates and/or precipitates may be present even in an as-grown sample. The ordered metastable arrangement of (I-V) dipoles with low activation energy, called the Suzuki phase, has been investigated by x rays,[17] electron microscopy,[18] EPR,[19] optical[3,14,16,20] dielectric loss, and ITC measurements.[21] More recently, it has been identified through Raman spectroscopy.[22] Rodriguez *et al.*[14] and Moreno *et al.*[19] have identified the Suzuki phase in as-grown NaCl:Mn^{2+} crystals by photoluminescence and ascertained its emission at 633 nm with 231-nm excitation. Bortoldi *et al.*[5] have identified the Suzuki phase of Pb^{2+} dipoles in KCl host giving characteristic orange-red emission at 580 nm with 280-nm excitation.

Recently, detailed optical spectroscopic studies in NaCl crystals doubly doped with Eu^{2+} and Mn^{2+} ions have been undertaken,[23] and the interesting phenomenon of energy transfer from Eu^{2+} to Mn^{2+} has been reported. Zaldo *et al.*[24] have subsequently reported energy transfer from Eu^{2+} to Pb^{2+} in NaCl host. The energy transfer between Eu^{2+} and Mn^{2+} ions has further been reported in fluoroperovskite crystals by Garcia and Sibley.[25] It may thus be rather interesting to explore the possibility of such an energy transfer in other crystals with different impurities.

The radiationless transfer of optical excitation energy is very useful for developing materials which can be used for laser and phosphor applications and for optical wavelength conversion. The Mn^{2+} ions could make an important phosphor but have the disadvantage that $d \rightarrow d$ transitions are difficult to pump due to their strongly forbidden character (oscillator strength $\sim 10^{-7}$). However, excitation of Pb^{2+} ions through strong ultraviolet allowed transitions, followed by an energy transfer from Pb^{2+} ions as a sensitizer (donor) to Mn^{2+} ion as an activator (acceptor) could provide an efficient mechanism for improving the efficiency of pumping the manganese ions.

Accordingly, in this work we report the results concerning optical emission and excitation of KBr crystals doubly doped with Pb^{2+} and Mn^{2+} ions. The emission from the aggregated and/or precipitated phase of Mn^{2+} ions is identified and further nonradiative energy transfer from Pb^{2+} to Mn^{2+} has been obtained. The parallel EPR measurements indicate that Mn^{2+} ions are trapped in the Suzuki-phase aggregates of Pb^{2+} dipoles.

II. EXPERIMENT

Single crystals of KBr doubly doped with lead chloride and manganese chloride were grown by the Stockbarger technique. The average impurity concentration of lead and manganese ions in the crystal, as determined by atomic absorption spectroscopic technique, was 50 and 95 ppm, respectively. The samples of suitable thickness were easily cleaved from the as-grown crystals and polished.

Optical emission and excitation spectra were recorded with Spex model 1902 Fluorolog, the excitation source being a 150-W xenon lamp. The luminescence was observed at 90° to the direction of excitation. For better resolution the slit widths of exciting and detecting monochromators were kept narrow. The excitation and emission spectra were corrected for lamp intensity and photomultiplier sensitivity, respectively. The excitation spectra were recorded in the *E/R* mode. For annealing, the sample was vacuum sealed in a quartz tube and heated at 240 °C for 2.5 h and then quenched into acetone. The EPR spectra were recorded on a Varian E-109 X-band spectrometer with 100-KHz field modulation.

III. RESULTS

The results of optical and EPR studies in $KBr:Pb^{2+},Mn^{2+}$ crystals at various sample conditions are given below. The various optical spectra reported in the following pertain to a fixed arbitrary intensity scale, and for comparison of various intensities a multiplying factor is indicated in the figures.

A. emission and excitation spectra of as-grown samples at RT

The absorption spectra of Pb^{2+}-doped KBr system have been studied by Zaldo and Lopez.[12] They have reported three absorption bands associated with free dipoles, aggregates, and precipitates of lead in KBr host. This system has been found to get excited by different wavelengths between 295 and 338 nm. In our samples we could get appreciable excitation with 300-, 323-, and 345-nm wavelengths. Figure 1 shows the RT emission spectrum of as-grown sample excited with 300-nm light. It has a strong band at 395 nm, a weak band at 520 nm, and, further, a composite band which gets resolved into two very weak bands peaking at 557 and 640 nm on magnification. Of these, the 395-nm emission has been attributed to small aggregates of Pb^{2+} dipoles and 557-nm emission to lead precipitates by Zaldo and Lopez.[12]

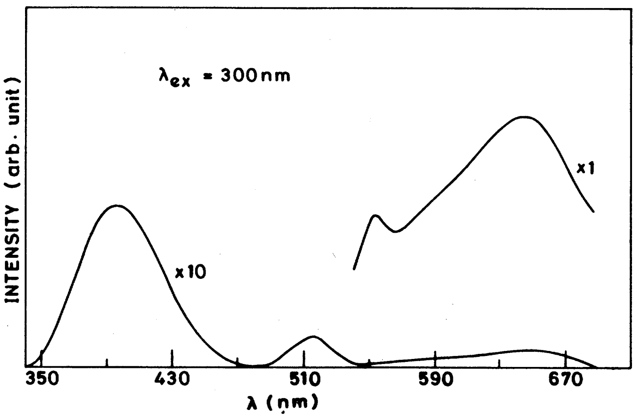

FIG. 1. The emission spectrum at RT of an as-grown $KBr:Pb^{2+},Mn^{2+}$ sample with 300-nm excitation.

Appreciable 640-nm emission of manganese was observed with both 323- and 345-nm excitations. However, the latter excitation gave stronger emission of 640 nm and, further, a 520-nm emission missing with the 323-nm excitation. Accordingly, in Fig. 2 we report the RT emission spectrum of as-grown sample with 345-nm excitation. The resolution of the composite emission band of this figure shows that it is simply a combination of two bands—one of moderate intensity peaking at 520 nm and the other strong at 640 nm.

To ascertain proper excitations of 395-, 520-, 557-, and 640-nm emissions, corresponding excitation spectra were recorded. Figure 3(a) shows the RT excitation spectra of as-grown sample for 395- and 520-nm emissions. The excitation spectrum for 395-nm emission has a peak at 305 nm, whereas the excitation spectrum for 520 nm shows a peak at 360 nm. Figure 3(b) shows the excitation spectra for 557- and 640-nm emissions. The two excitation spectra clearly overlap around 345 nm. Further, the excita-

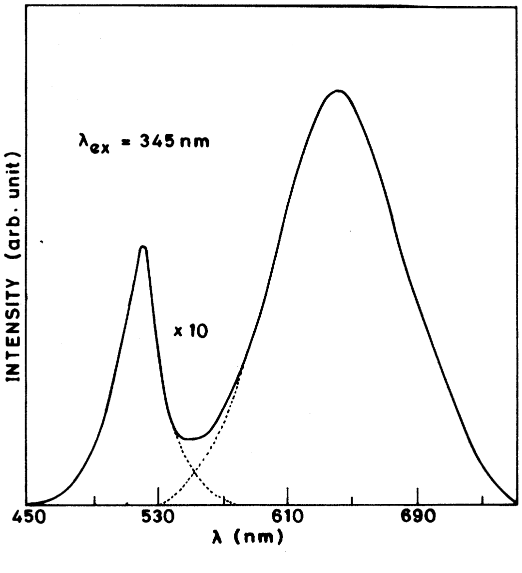

FIG. 2. The emission spectrum at RT of an as-grown $KBr:Pb^{2+},Mn^{2+}$ sample with 345-nm excitation.

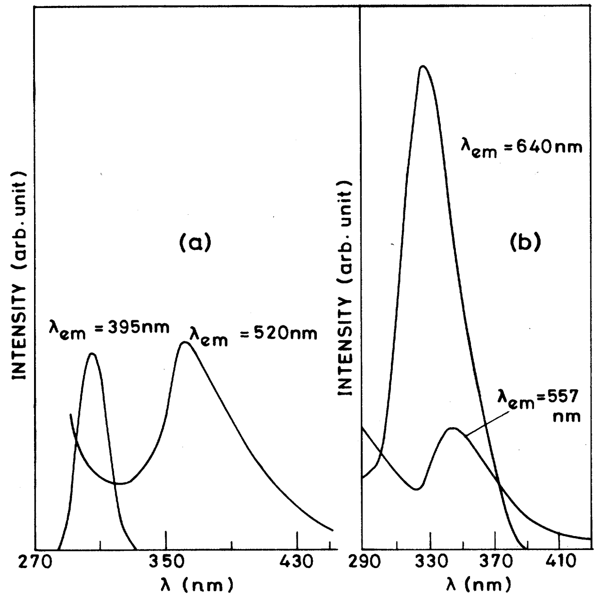

FIG. 3. Excitation spectra at RT of an as-grown KBr:Pb^{2+},Mn^{2+} sample. (a) Spectra for 395- and 520-nm emissions. (b) Spectra for 557- and 640-nm emissions.

tion for 640-nm emission is more pronounced than for 557-nm emission.

B. Emission and excitation spectra of as-grown samples at liquid-nitrogen temperature (LNT)

The emission spectrum of an as-grown sample at 80 K with 300-nm excitation is shown in Fig. 4. It shows three quite strong bands peaking at 370, 465, and 530 nm, and a weak broad band at 660 nm. The 465-nm band has arisen on cooling the sample and is associated with $PbCl_2$-type precipitates.[10–12] The 370- and 530-nm bands are due to blue and red shift, respectively, of RT 395- and 520-nm bands. The 640-nm band seems to have also suffered a red shift of 20 nm.

The emission spectrum under 345-nm excitation of the as-grown sample, cooled in liquid nitrogen for 40 min, is shown in Fig. 5. It shows three distinct bands—a strong band at 660 nm, a medium-intensity band at 536 nm, and a weak band at 465 nm. The 465-nm emission band was not seen in the emission spectrum of the as-grown sample at RT under similar excitation and is attributed as above to the $PbCl_2$ precipitates formed[10–12] in the lattice. The 660- and 536-nm emission bands appear slightly red shifted with respect to the 640- and 520-nm emission bands obtained in the as-grown sample at RT under identical excitation.

The inset of Fig. 5 shows the excitation spectra for 640-nm emission. The intense excitation band at 345 nm is due to Pb^{2+} absorption, but even weak Mn^{2+} bands are also seen.

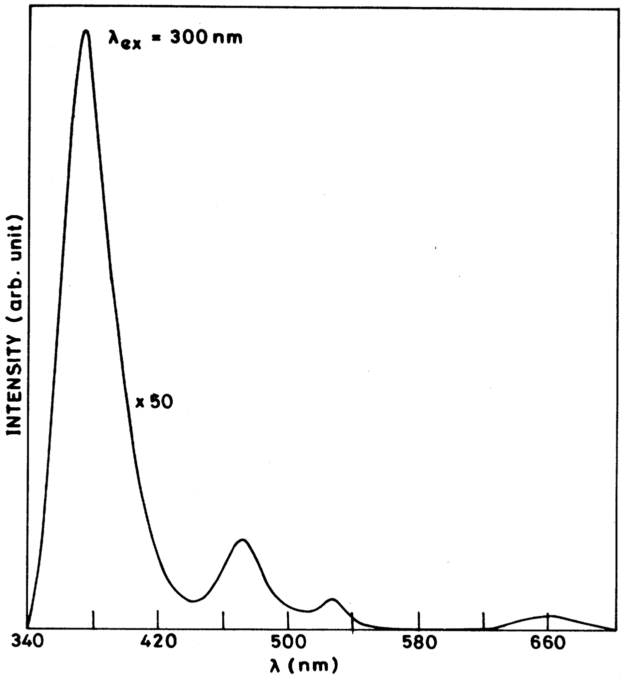

FIG. 4. The emission spectrum at 80 K of an as-grown KBr:Pb^{2+},Mn^{2+} sample with 300-nm excitation.

C. Emission and excitation spectra of annealed sample at RT

When the sample, annealed at 240 °C for 2.5 h and then quenched in acetone was excited with 300-nm radiation, within 10 min of quenching, a luminescence was observed [as shown in Fig. 6(a)]. It comprises two bands—one peaking at 370 nm and other broad band peaking at 640 nm. The intensity of the 640-nm band is stronger in the present case than for the as-grown sample (Fig. 1) under

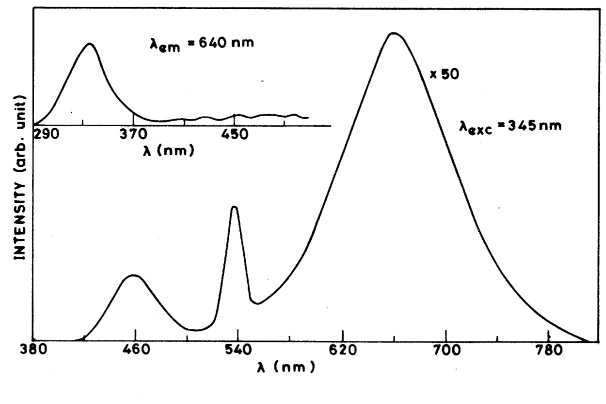

FIG. 5. The emission spectrum at 80 K of an as-grown KBr:Pb^{2+},Mn^{2+} sample with 345-nm excitation. Inset: The excitation spectrum at 80 K of an as-grown KBr:Pb^{2+},Mn^{2+} sample for 640-nm emission.

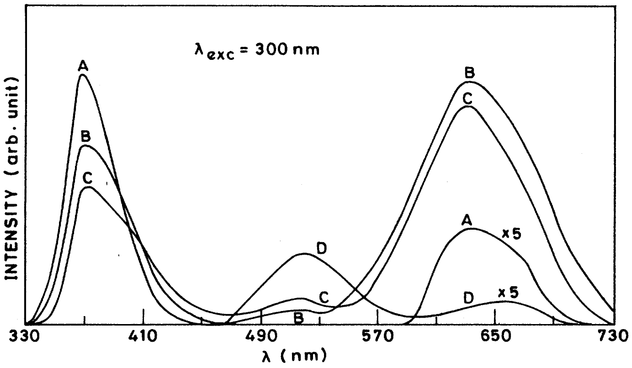

FIG. 6. RT emission spectra with 300-nm excitation of sample annealed at 240 °C for 2.5 h and then quenched into acetone. (*A*) Spectrum recorded after 10 min of quenching. (*B*) Spectrum recorded after 2 h of quenching. (*C*) Spectrum recorded after 21 h of quenching. (*D*) Spectrum recorded after 72 h of quenching.

similar excitation. Further, the intensity of 640-nm band is more than that of the 370-nm band. The 520-nm emission band which was present in the spectrum (Fig. 1) for the as-grown sample is missing here, suggesting that this emission was associated with some metastable aggregates of manganese ions. Subsequent experimentation has revealed that 520-nm band comes up again on aging of the annealed sample at RT for 21 h [Fig. 6(c)]. The intensity of the 640-nm band has been found to depend strongly on aging time after quenching and decreases as shown in Fig. 6 (*A*,*B*,*C*,*D*). A quick fall in intensity is observed in the first 2 h.

The RT emission spectrum of the annealed sample, excited by 345-nm radiation, is shown in Fig. 7. This shows a broad band peaking at 640 nm with intensity lower than that of the corresponding band for as-grown sample under similar excitation. It is also evident from this figure that the 520-nm band emission did not exist immediately after quenching. The intensity variation of 640-nm band with time for 345-nm excitation can be assessed from contours (*a*,*b*,*c*) of Fig. 7, which show that the intensity decreases at a slow rate initially but starts increasing after ~21 h. After 72 h of quenching, however, the intensity of 640-nm band increases considerably and the 520-nm band also reappears.

To ascertain the origin of 640-nm emission in the annealed samples corresponding excitation spectra were recorded. The RT excitation spectra of annealed samples for 640- and 370-nm emissions are shown in Fig. 8. The spectrum for 370-nm emission shows a single sharp band at 300 nm. For 640-nm emission the excitation shows two clear bands—one sharp and intense at 300 nm and the other broad at 365 nm. Further, few other weak bands are seen at higher wavelengths due to absorption of Mn^{2+} ions. The strong excitation observed at 345 nm in as-grown sample for 640-nm emission [Fig. 3(b)] gets annihilated on heat treatment. The excitation spectrum for 640-nm emission of the annealed sample aged at RT for 72 h is also shown in Fig. 8 and is seen to be similar to the corresponding spectrum for as-grown sample.

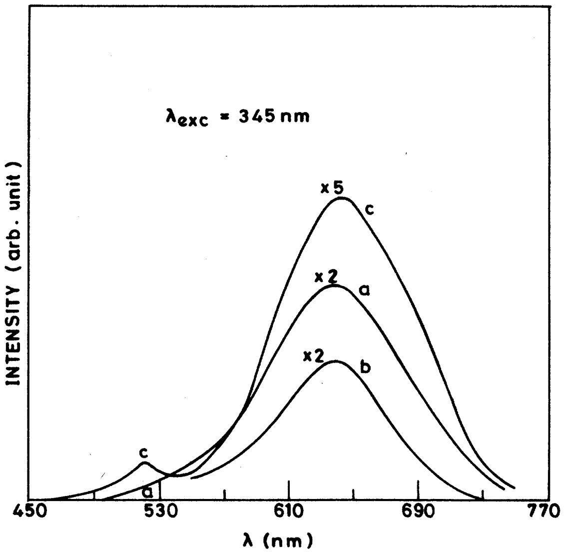

FIG. 7. RT emission spectra with 345-nm excitation of sample annealed at 240 °C for 2.5 h, then quenched into acetone. (*a*) Spectrum recorded after 30 min of quenching. (*b*) Spectrum recorded after 2 h of quenching. (*c*) Spectrum recorded after 72 h of quenching.

D. EPR studies

Figure 9(a) shows the EPR spectrum of an as-grown sample. This represents a six-line spectrum, with a very small crystal-field parameter "*a*," characteristic of Mn^{2+} ions in isolation[6] or in cubic environment. The EPR spectrum of the sample annealed at 240 °C for 2.5 h, recorded immediately after quenching is shown in Fig. 9(b). It shows a single line which is characteristic of aggregates[6] of Mn^{2+} ions. The EPR spectra were also

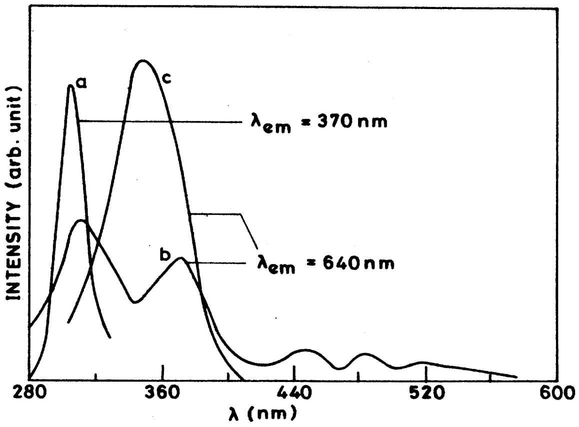

FIG. 8. Excitation spectra at RT of the sample annealed at 240 °C for 2.5 h then quenched into acetone. (*a*) Spectrum for 370-nm emission recorded after 20 min of quenching. (*b*) Spectrum for 640-nm emission recorded after 30 min of quenching. (*c*) Spectrum for 640-nm emission recorded after 72 h of quenching.

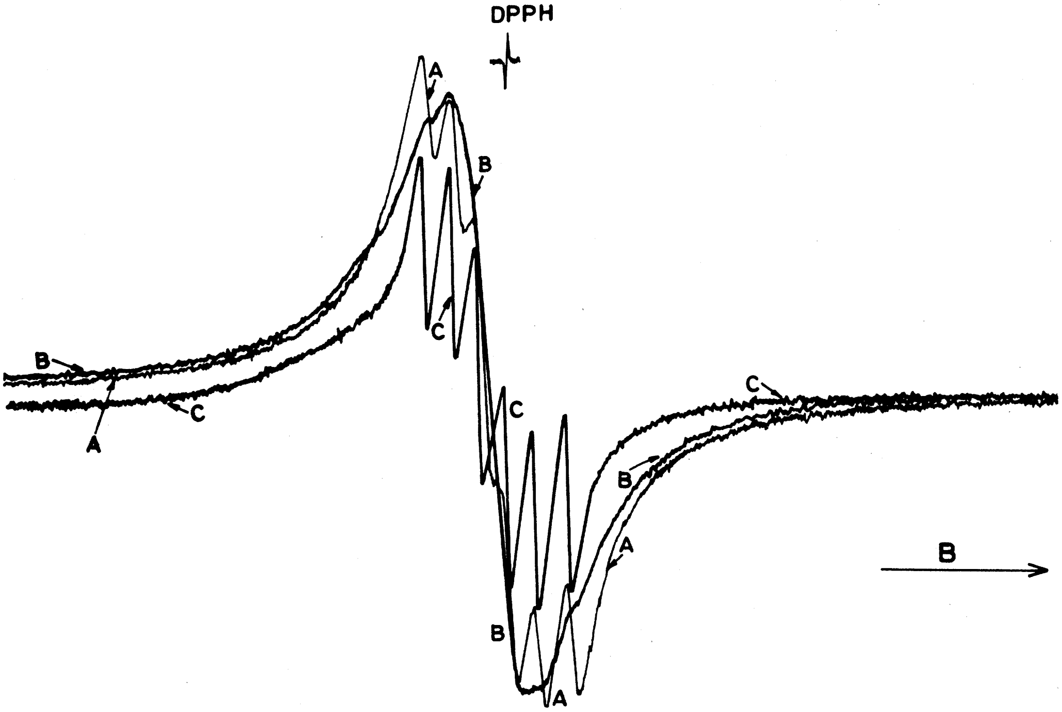

FIG. 9. EPR spectra at RT of KBr:Pb^{2+},Mn^{2+} samples. (A) As-grown sample. (B) Sample annealed at 240 °C, then quenched into acetone spectrum recorded after 15 min of quenching. (C) Spectrum recorded for the above annealed sample after 72 h of quenching.

recorded with aging time after quenching. The spectrum recorded after 72 h of quenching is shown in Fig. 9(c). This again represents the six-line spectrum of separated Mn^{2+} ions and suggests that the sample is coming back to its as-grown condition after 72 h.

IV. DISCUSSION

An emission around 640 nm observed by Dryden and Heydon[2] and further by Zaldo and Lopez[12] in Pb^{2+}-doped alkali-halide crystals could not be attributed to Pb^{2+} ions. The 520-nm emission obtained by us in as-grown crystals also cannot be assigned to Pb^{2+} ions.[12] The above two emissions observed in the present system are thus attributable to Mn^{2+} ions.

The 520-nm emission band matches exactly with the energy difference for ${}^4T_1(G) \rightarrow {}^6A_1(S)$ transition in a manganese ion under octahedral field. This band can be attributed to manganese emission without any involvement of lattice and thus be a zero-phonon band. Suzuki[17] has reported a superlattice to exist in manganese-doped NaCl crystals. This phase has further been extensively studied by x rays,[17] EPR,[19] optical spectroscopy,[3,14,16,20] and has been reported to be a metastable aggregate of Mn^{2+}-vacancy dipoles. A small size microcrystal of Suzuki phase possesses a crystal structure entirely different from the main lattice. The phonons of the main crystal are thus not likely to enter freely into the Suzuki phase and observance of zero-phonon band is quite probable.

The parallel EPR investigations of as-grown crystals [Fig. 9(a)] indicate a single line spectrum due to Mn^{2+} aggregates superimposed on the six lines of isolated Mn^{2+} ions. This suggests that aggregates of Mn^{2+} ions are present in our as-grown crystal along with isolated Mn^{2+} ions. The EPR study thus supports the formation of Suzuki-type aggregated phase of Mn^{2+} ions. It would be worth mentioning here that an emission similar to 520 nm has been observed recently in a CsCl host.[26] Further, Garcia and Sibley[25] have also reported simple ${}^4T_1(G) \rightarrow {}^6A_1(S)$ manganese emission in doped fluoroperovskite crystals.

The drop in emission energy to 640 nm could be due to Mn^{2+} ions strongly linked to the KBr lattice. Such an emission would thus be due to ${}^4T_1(G) \rightarrow {}^6A_1(S)$ Mn^{2+} transition[13] with accompanied transfer of a portion of the energy to the host.

Zaldo and Lopez[12] have observed lead emission at 555 nm with 338-nm excitation. In our as-grown sample, however, there is no emission around this wavelength with 345-nm excitation. It therefore appears that Pb^{2+} ions transfer their excitation energy efficiently to Mn^{2+} ions through a nonradiative process.[27] Figure 3(b) shows the RT excitation spectra of as-grown sample for 557- and 640-nm emissions. The two excitation spectra clearly overlap and the excitation for 640-nm emission is more pronounced than for 557-nm emission. Though Pb^{2+} ions are efficient absorbers of uv light (oscillator strength $\sim 10^{-1}$) and Mn^{2+} ions are quite weak absorbers (oscillator strength $\sim 10^{-7}$), yet in the present case Mn^{2+} excitation is stronger than the Pb^{2+} excitation [Fig. 3(b)]. This is possible if excited Pb^{2+} centers transfer their energy to Mn^{2+} centers. The absence of 557-nm excitation for 640-nm emission of Mn^2 ions further supports such a transfer of energy from Pb^{2+} to Mn^{2+} ion. Since Pb^{2+} emission[12] and Mn^{2+} absorption[13] overlap, an efficient[23] energy transfer is possible here.

The shape of the excitation spectra at 80 K of as-grown crystals for 640-nm emission (inset of Fig. 5) is essentially similar to that of the absorption band in Pb^{2+}-doped KBr, as reported by Zaldo and Lopez.[12] This indicates that total absorption for 640-nm emission is through Pb^{2+} ions. The overlap of RT excitation spectra for 557- and 640-nm emissions in as-grown crystals shown in Fig. 3(b), and observance of a peak at 345 nm in the excitation spectrum at 80 K for 640-nm emission further confirms that only Pb^{2+} ions are absorbing 345-nm radiation and that 640-nm emission of manganese is due to excitation transfer from Pb^{2+} to Mn^{2+} ion.

A comparison of excitation spectra for 640-nm emission of annealed [Fig. 8(b)] and as-grown [Fig. 3(b)] samples clearly indicates that the centers excited are different in the two cases and further possess different excitations. The strong excitation at 345 nm for 640-nm emission in as-grown crystals gets annihilated on heat treatment. The excitation spectra of as-grown samples both at RT and LNT further indicates that only Pb^{2+} ions are absorbing the 345-nm radiation. The disappearance of 345-nm excitation band on annealing the sample at 240 °C suggests that absorbing Pb^{2+} centers are in a metastable phase. The absence of expected 557-nm Pb^{2+} emission on 345-nm excitation suggests that Pb^{2+} ions are transferring their excitation energy efficiently to Mn^{2+} ions. Because of this, Mn^{2+}-ion excitation which is spin- and parity-forbidden,[13,23] becomes intense as shown Fig. 3(b). Further, the fact that the expected emission of Pb^{2+} ions is missing implies that there is a significant overlap between Pb^{2+} emission[12] and Mn^{2+} absorption.[13] This in turn indicates that the two impurities are not randomly distributed, but a considerable fraction of Pb^{2+} ions are coupled to Mn^{2+} ions and essentially all the absorption is due to Pb-Mn coupling.[27] Further, the structure in EPR spectrum of an as-grown crystal [Fig. 9(a)] represents a set of six lines with a very small crystal-field parameter "*a*," characteristic of Mn^{2+} ions in isolation.[6,19] Our above optical measurements thus indicate absorption by metastable phase of Pb^{2+} ions and transfer of excitation energy to Mn^{2+} ions and EPR spectra indicate the occurrence of separated Mn^{2+} ions in cubic environment. One possibility for explaining this type of distribution is to presume the presence of Mn^{2+} ions within a Suzuki-phase region of Pb^{2+} ions, as shown in Fig. 10. The recent conclusion of Garcia and Sibley[25] that divalent europium ions cluster around Mn^{2+} ions in $KCaF_3$ and $RbCaF_3$ crystals clearly supports our proposed model.

The 520-nm emission gets annihilated on annealing the sample at 240 °C [Fig. 7(a)], suggesting thereby that this emission was solely due to a Suzuki-type phase of Mn^{2+} ions and dissolves on heating. The annealing of a Mn^{2+}-doped alkali-halide crystal at 240 °C has been reported to give rise to aggregates of Mn^{2+} ions by Lilley and Newkirk.[15] The aggregation in the present case is supported by continuance of only a single line[6,19] in the EPR spectrum, even on heating the sample, as shown in Fig. 9(b). So far, Pb^{2+} ions are concerned, simultaneous production of free Pb^{2+} dipoles, on annealing as above, is confirmed by the observance of 370-nm emission of Pb^{2+} dipoles.[10-12] Such free dipoles and manganese aggregates are shown in Fig. 10.

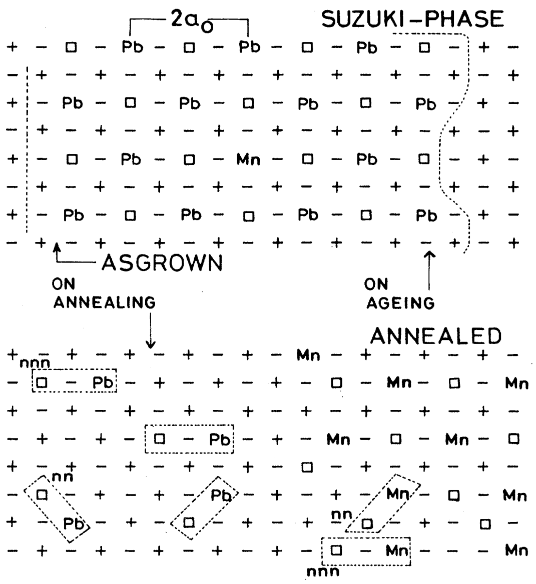

FIG. 10. Illustration of a Mn^{2+} trapped in the Suzuki phase of Pb^{2+},Pb^{2+}-vacancy dipoles and different types of Mn^{2+} aggregates in KBr: lattice.

The excitation spectrum shown in Fig. 8(b) for 640-nm emission of annealed crystal indicates that the aggregates of Mn^{2+} ions are excited appreciably by 300- and 365-nm radiations. The latter incidently matches closely with the emission of Pb^{2+} dipoles, excited by 300 nm [Fig. 8(a)]. This suggests that 640-nm emission, in this case, could be a combined effect of direct excitation of Mn^{2+} aggregates by 300 nm, as well as their indirect excitation through Pb^{2+} dipoles, whose emission at 365 nm is transferred to Mn^{2+} aggregates to finally emit 640 nm, the transfer being radiative.[27] Further, for an annealed sample, our optical emission measurements (Fig. 6) indicate a quick decrease in the number of Pb^{2+} dipoles. Because of this effect, the intensity of the 640-nm band would obviously decrease with time.

As the excitation spectrum for 640-nm emission of annealed crystal, shown in Fig. 8, has a strong band peaking at 365 nm indicating some excitation at 345 nm as well; this sample should give 640-nm emission through 345-nm excitation. This is seen to be true through appreciable intensity of 640-nm emission by such an excitation (Fig. 7). The annealed crystals furnish a single line in EPR [Fig. 9(b)], attributable to aggregates of Mn^{2+} ions. These aggregates cannot be of Suzuki type, as characteristic 520-nm emission is not there. Thus, aggregates of Mn^{2+} ions (other than Suzuki phase) are excited by 345-nm radia-

TABLE I. Summary of the important RT optical and EPR results related to Mn^{2+} ions.

Sample conditions	Optical results	Corresponding EPR results
I. As-grown/long-aged annealed sample.	(i) 520-nm emission associated with Suzuki-like aggregates of Mn^{2+} ions got by direct excitations.	(i) A single broad line.
	(ii) 640-nm emission associated with Mn^{2+} ions trapped in Suzuki phase of Pb^{2+} ions by indirect excitation through Pb^{2+} ions ($Pb^{2+} \rightarrow Mn^{2+}$ nonradiative energy transfer).	(ii) Six lines superimposed on above single broad line.
II. Annealed at 240 °C for 2.5 h.	640-nm emission associated with aggregates of Mn^{2+} ions (other than Suzuki-like phase) through both direct and indirect excitations, latter by $Pb^{2+} \rightarrow Mn^{2+}$ radiative energy transfer.	A single broad line.

tion in annealed samples to give 640-nm emission, which decreases in intensity with time due to decrease in the number of such aggregates.

An important feature in the emission spectrum of annealed crystals by 345-nm excitation (Fig. 7) is that the intensity of 640-nm emission initially decreases and then increases to appreciable strength after 72 h. The initial decrease suggests a decrease in the number of aggregates of Mn^{2+} ions and is probably incited through a fast aggregation of Pb^{2+} dipoles. The aggregation of Pb^{2+} dipoles at RT is known to be very fast.[10–12] When such dipoles aggregate, the resulting crystal lattice with lesser defects would enhance dissolution of existing aggregates of Mn^{2+} ions through their diffusion. This incited dissolution of Mn^{2+} aggregates, due to quick precipitation of Pb^{2+} dipoles is analogous to enhanced dissolution of an electrolyte, when the other is made to precipitate from their common saturated solution.

During aggregation of Pb^{2+} dipoles, few Mn^{2+} ions may be trapped also. The resulting aggregated phase may be a Suzuki phase of Pb^{2+} ions with a few trapped Mn^{2+} ions as shown in Fig. 10. Such a Mn^{2+} ion would exhibit an EPR spectrum with six lines as shown in Fig. 9(c). The trapped Mn^{2+} ions would be coupled further with surrounding Pb^{2+} ions, increasing appreciably the energy transfer from Pb^{2+} to Mn^{2+} ions, the former getting excited by 345 nm and transferring the excitation energy to Mn^{2+} ions to finally give the 640-nm emission. This new state of the system would be similar to its as-grown condition, as evident by the recovery of the six lines in the EPR spectrum [Fig. 9(c)] and appearance of 345-nm excitation band in the excitation spectrum [Fig. 8(c)] after 72 h of quenching. Further, as expected, the intensity of 640-nm emission for a long-aged sample is quite weak under 300-nm excitation.

The important RT optical and EPR results related to Mn^{2+} ions are thus summarized in Table I.

For the doubly doped complex system investigated here, it is not possible to clearly identify the nature of the ion-ion interaction producing the energy transfer. However, for qualitative comparison of transfer properties observed under different sample conditions, it may be useful to assume an electric multipole coupling[27] between Mn^{2+} and Pb^{2+} ions.

V. CONCLUSION

We have used optical and EPR spectroscopy to characterize the defect distribution in KBr:Pb^{2+},Mn^{2+} crystals at different sample conditions. The most important conclusion drawn from the results of this work is the nonradiative energy transfer from $Pb^{2+} \rightarrow Mn^{2+}$. Various sample conditions, viz., as grown, annealed with subsequent quenching have been observed to produce easily observable changes. The thermal annealing does decrease the nonradiative energy transfer, giving rise to a little radiative transfer; however, the former process again recovers after 72 h of aging. The efficient nonradiative energy transfer provides a method for significantly increasing the Mn^{2+} luminescence by enhanced pumping through Pb^{2+} ions. Thus, the system can be used for developing materials which are important for laser and phosphor applications and for optical wavelength conversion.

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