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Lead emission from the cadmium Suzuki phase in NaCl: CdCl₂: Pb²⁺

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Abstract. The system NaCl: CdCl₂: Pb²⁺ has been studied by the photoluminescence technique. The results for quenched crystals consist of the usual emission bands of Pb²⁺ in a NaCl matrix: at room temperature, one intense band centred at 314 nm; at liquid-nitrogen temperature, two bands, one peaking at 312 nm and one weak band at 380 nm. The aging of these crystals at 355 K produces a cadmium Suzuki phase precipitate in which the minor impurity Pb²⁺ ions are incorporated. The emission of these incorporated lead ions into the Suzuki phase consist of two emission bands. These are centred at 388 and 460 nm; the latter is very intense even at room temperature. The temperature behaviour of these bands suggests that the former can be assigned to the A_X band, while the latter to the A_T emission band. This might be the result of a large coupling to the T_{2g} vibrational modes of the Cd²⁺ Suzuki phase. In crystals annealed at higher temperatures the cadmium ions precipitate into the CdCl₂ phase. For this case the lead emission consists of the usual high-energy A_T band (390 nm) and the low-energy A_X band (458 nm).

1. Introduction

The optical properties of alkali halides doped with Tl⁺-like ions, with the ns² electronic configuration in their ground state, have been extensively studied since the pioneering work of Hilsch (1927). The presence of these types of impurity induces several absorption bands designated as A, B, C and D, in increasing order of energy. These absorption bands are due to transitions from the (a_{1g})² ground state to terms arising from the (a_{1g}) (t_{1u}) excited configuration. Band A is due to the ¹A_{1g} → ³T_{1u}(³P₁) transition, allowed by spin-orbit interaction; band B corresponds to a transition from ¹A_{1g} to ³E_u and ³T_{2u}(³P₂), partially allowed by vibronic spin-orbit coupling; band C is attributed to the dipole-allowed transition ¹A_{1g}(¹S₀) → ¹T_{1u}(¹P₁); band D is due to charge transfer from ligand halide orbitals into vacant cation p orbitals (Jacobs (1991), and references therein). These absorption bands are in general very broad because of the coupling between the electronic states and the lattice vibrations. On the other hand, their luminescence usually presents a large Stokes shift, suggesting a considerable relaxation of the neighbouring ions for these excited states. The excitation in band A produces two emission bands, usually designated A_X and A_T in increasing order of energy. These emission bands have been interpreted in terms of the Jahn-Teller effect (Fukuda 1970, Kamishina *et al* 1980, Ranfagni *et al* 1983). This produces two kinds of minimum (one of tetragonal and one of orthorhombic symmetry) on the ³T_{1u} and ³A_{1u} adiabatic potential energy surface (APES) in the space of normal coordinates. The coexistence of these two minima is a consequence of the quadratic Jahn-Teller effect and/or anharmonicity, or strong spin-orbit mixing between ³T_{1u} and ¹T_{1u} states.

The characteristics of the luminescence bands are determined by the relative magnitudes of the Jahn–Teller and spin–orbit interactions, and the symmetry of the vibrational modes involved (Bersuker 1984).

The Pb^{2+} ion is a typical example of the above-discussed characteristics and many experimental studies dealing with absorption and emission spectroscopy of this ion have been published (see, e.g., Marculescu and Ghita (1976), Benci *et al* (1982), Kang *et al* (1985), Capelletti *et al* (1983), Zaldo and Agulló-López (1983) and Jaque *et al* (1982). On the other hand, the emission bands of this ion are very sensitive to the state of aggregation (Pascual *et al* 1978) and have been used as an optical probe to monitor clustering processes in several divalent-cation-doped alkali halides (García Solé *et al* 1981).

The aggregates of divalent impurity ions produce certain structures that are not naturally stable outside the host matrix; for example Cd^{2+} in NaCl produces under suitable thermal treatments the so-called Suzuki (1961) phase. This phase possesses a cubic structure with a lattice parameter double that of the sodium chloride matrix.

In NaCl crystals the lead ion enters substitutionally with a cation vacancy associated at near-neighbour positions, decreasing the local symmetry. Nevertheless, the emission spectra consists of two bands whose characteristics depend on the relative magnitude of the Jahn–Teller coupling constants and spin–orbit interaction. On the other hand, when incorporated into precipitates such as the Suzuki phase mentioned above, it is expected to be located in a cubic symmetry site, a fact that allows study of the importance of the vibrational coupling modes.

In this paper we present the experimental results obtained for divalent-lead-doped $\text{NaCl}:\text{CdCl}_2$, when the Cd^{2+} ions form precipitates, showing the importance of the coupling to the T_{2g} and E_g modes.

2. Experimental details

Single crystals of NaCl doubly doped with Cd^{2+} and Pb^{2+} were grown from the melt by the Czochralski method under a controlled atmosphere of dry argon, the crystals being slowly cooled to room temperature (RT) in the furnace. Thermal quenching was performed by heating the samples at 800 K for 1 h and then dropping them onto a copper block at RT. Aging treatments at 355 and 480 K of previously quenched crystals were carried out in a standard furnace with temperature control in the range ± 3 K.

The absorption spectra were obtained with a Milton–Roy spectrometer model Spectronic 3000 diode array. The emission and excitation spectra were detected with Perkin–Elmer spectrofluorimeter models 650–10S and MPF-44B. The excitation source was a 150 W xenon lamp. All excitation spectra have been corrected for lamp intensity and photomultiplier response, using a differential-spectra-corrected unit (DCSU-2). The spectral width is 2 nm. Low-temperature spectra in the range 10–300 K were obtained using an Air Products liquid-helium refrigerator and in the range 77–300 K with a home-made cryostat.

The lead concentration, in the range 40–60 ppm, was obtained by means of the absorption spectra. The cadmium concentration was determined by atomic absorption; the result was 200 ppm.

3. Results and discussion

The fluorescence spectrum obtained at RT from a $\text{NaCl}:\text{CdCl}_2:\text{Pb}^{2+}$ quenched crystal using an excitation wavelength of 272 nm consists of a broad band peaking at 314 nm. At 77 K

the spectrum consists of one emission band (the A_T band) peaking at 312 nm and one weak intensity emission band peaking at 380 nm (the A_X band). These agree with previous results and have been attributed to Pb^{2+} ions in solid solution in the NaCl matrix (Pascual *et al* 1978). Ionic thermocurrent experiments were also performed in quenched doubly doped cadmium and lead NaCl single crystals to probe dissociation of the impurities. While as-grown crystals show a single peak at 220 K, which can be ascribed to isolated Cd-cation-vacancy dipoles (Capelletti and De Benedetti 1968) in excess over Pb-vacancy dipoles, two well defined peaks can be observed in freshly quenched samples. The temperature difference between the depolarization peaks is over 30 K for the heating rates used. They correspond to isolated Cd^{2+} - and Pb^{2+} -cation-vacancy dipoles in increasing values of temperature, respectively. Concentration measurements using the ionic thermocurrent spectrum are in good agreement with the values previously mentioned.

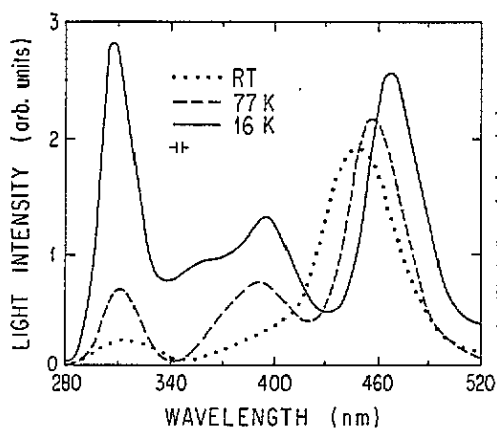


Figure 1. Emission spectra of NaCl:CdCl₂:Pb²⁺ samples annealed for 3 h at 355 K. The spectra were obtained at different sample temperatures and the excitation wavelength was 274 nm in all cases.

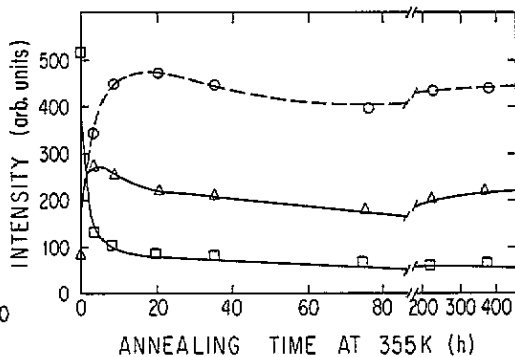


Figure 2. Evolution of the emission band integrated intensity (area under the band of the intensity versus wavelength spectrum) as a function of the time of annealing at 355 K of a NaCl:CdCl₂:Pb²⁺ crystal: □, 312 nm, Δ, 388 nm; ○, 460 nm. The spectra were obtained at 77 K after quenching from the annealing to room temperature.

The aging of NaCl:Cd²⁺ at 355 K produces the cadmium Suzuki (1961) phase. Now, since cadmium is the dominant impurity, it is expected to produce the same phase in the doubly doped crystals NaCl:CdCl₂:Pb²⁺, aged at this temperature. Short aging times produce important changes in the emission spectrum of lead ions. For example, for 3 h there is a reduction in the intensity of the A_T emission peaking at 314 nm and the appearance of a new band whose maximum lies at about 452 nm at RT. These results are portrayed in figure 1. This figure also shows the emission spectra obtained at low temperatures from other crystals aged for the same period at 355 K. As can be seen, at 77 K the spectrum consists of three bands peaking at 312 nm, 388 nm and around 460 nm with band-widths at half the maximum intensities of 2390 cm⁻¹, 3160 cm⁻¹ and 1890 cm⁻¹, respectively; the band-width and asymmetry of the 388 nm band suggest a double-band structure that might be due to the superposition of the A_X lead dipole band peaking at about 380 nm (Pascual *et al* 1978; Marculescu 1977) and another band at lower energies. At 16 K there are four bands at around 310, 360, 395 and 465 nm (see figure 1). Aging the crystals for longer

periods of time at 355 K produces only changes in the relative intensity of these bands; the evolution of the integrated intensity under wavelength as a function of the aging time at this temperature is shown in figure 2. These results were obtained from the same sample, aged for different periods and measured at 77 K. One must note the decrease in the intensity of the 312 nm band to the benefit of the 460 nm band. On the other hand, the weak band at 360 nm, which can only be detected below 77 K (see figure 1), might be due to lead dimers according to Marculescu (1977). The bands at 395 and 465 nm correspond to Pb^{2+} ions incorporated into the cadmium precipitates, since these are the bands which are stabilized at long aging times (figure 2), although they peak at 388 and 460 nm at 77 K, i.e. below liquid-nitrogen temperature there is a red shift. These results are summarized in table 1.

Table 1. Emission bands observed under excitation in band A of lead ions in the $\text{NaCl}:\text{CdCl}_2:\text{Pb}^{2+}$ system under different thermal treatments.

Emission band (nm)	Thermal treatment	Assignment
314 (RT)	Quenched	A_T dipoles
312 (77 K)	Quenched	A_T dipoles
380		A_X
388 (77 K)	Aged at 355 K	A_X Cadmium
460		A_T Suzuki phase
395 (20 K)	Aged at 355 K	A_X cadmium
465		A_T Suzuki phase
390 (77 K)	Aged at 480 K	A_T CdCl_2
458		A_X phase

The striking fact about these results is the large intensity of the band peaking at about 460 nm even at room temperature, and that the band at 388 nm presents a structure of two bands at low temperatures. We have also determined the integral intensity variation of each band as a function of the sample temperature, and the results are given in figure 3; as can be seen, the intensity of both bands (388 and 460 nm) increases as the temperature is lowered from RT to 77 K. We have also observed that at temperatures below 50 K the band at 388 nm decreases in intensity, while that at around 460 nm remains almost constant in intensity down to 16 K, this being the characteristic behaviour of the A_X and A_T bands, respectively (Capelletti *et al* 1983, Kang *et al* 1985). The data were obtained from a crystal aged for 72 h.

The excitation spectrum for the three emission bands observed at 77 K consists of a broad band peaking at around 274 nm. Spectra with a better resolution were obtained at 20 K. Figure 4 shows these spectra and we can observe that the emission bands at 312 and 460 nm show a single asymmetrical excitation band peaking at about 272 nm; this asymmetrical lineshape is a characteristic of the absorption band A and it is ascribed to a dynamical Jahn-Teller effect (Bersuker 1984). The structured emission band at 388 nm is excited by a double asymmetrical structured band peaking at 272 and 284 nm. Excitation

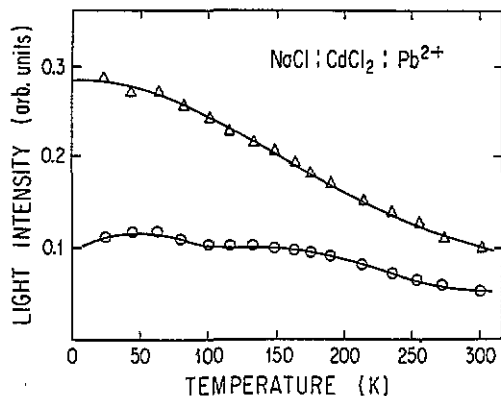


Figure 3. Integrated emission band light intensity as a function of the measured sample temperature of a NaCl:CdCl₂:Pb²⁺ crystal, annealed for 35 h at 355 K: Δ , 460 nm; \circ , 388 nm; \square , line guides.

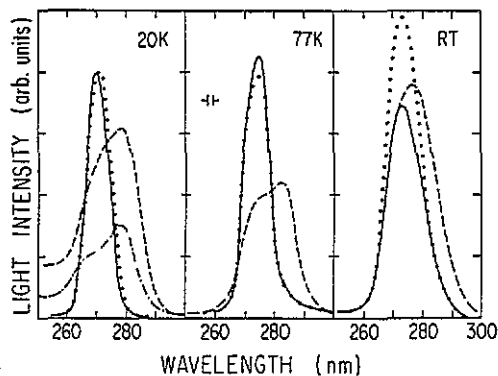


Figure 4. Excitation spectra at three temperature values for selected wavelengths of the emission bands of NaCl:CdCl₂:Pb²⁺ samples: —, 314 nm; - - -, 380 nm; - · - ·, 400 nm; · · · ·, 460 nm.

on the low-energy side of this band produces an increase in the relative emission intensity of each component. In particular, excitation light of 284 nm produces an intense structured 388 nm emission. All these results on the behaviour of the divalent Pb ion emission at 460 nm and the corresponding structured band at 388 nm suggest that lead ions have been incorporated in a precipitated phase in the NaCl host crystals, since the positions of the emission bands strongly depend on the thermal history (Pascual *et al* 1978) of the crystal.

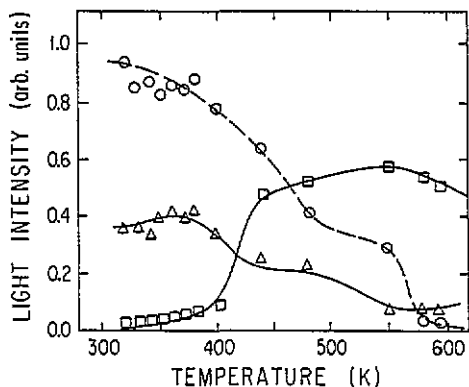


Figure 5. Variation in the integrated light intensity of the emission bands as a function of the temperature of the furnace in which the NaCl:CdCl₂:Pb²⁺ crystals were maintained for 30 min: \square , 312 nm; Δ , 388 nm; \circ , 460 nm.

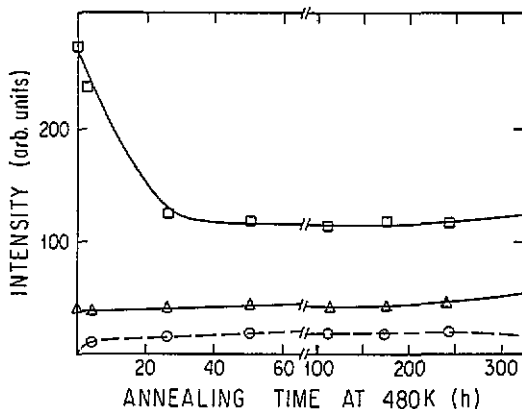


Figure 6. Evolution of the emission band integrated intensity as a function of the time of annealing at 480 K for a NaCl:CdCl₂:Pb²⁺ crystal: \square , 312 nm, Δ , 380 nm; \circ , 460 nm. The spectra were obtained at 77 K after quenching from annealing to room temperature.

The data portrayed in figure 5 represent the dissolution of the precipitates that have been previously formed by annealing the samples at 355 K. Here lead emission obtained by excitation with light of 272 nm was measured at 77 K after thermal treatment for $\frac{1}{2}$ h at different temperatures. According to Suzuki, two kinds of precipitate can be produced

in NaCl:Cd²⁺, depending on the annealing temperature: below 370 K, the so-called Suzuki metastable phase and above 470 K the CdCl₂ phase. In addition, the cadmium metastable precipitate in the NaCl matrix is dissolved at around 550 K in agreement with the present results, where the bands peaking at 460 and 388 nm decrease and the Pb-dipole emission at 312 nm reaches the highest value, suggesting therefore that the lead ions were incorporated into the Suzuki phase precipitate.

On the other hand, it is a well known fact (López *et al* 1980) that the Suzuki phase can only be produced in a limited range of temperatures, and that above the maximum temperature other phases precipitate, e.g. EuCl₂, MnCl₂ and BaCl₂ (Rubio *et al* 1981, Verdigué *et al* 1991). To study the effects on the A_T and A_X lead emission bands the NaCl:CdCl₂:Pb²⁺ crystals were aged at 480 K. At this temperature, as mentioned before, it is expected that CdCl₂ precipitates are produced. Excitation and emission spectra were obtained at 77 K for different aging times. At the start of the process only the 312 and 380 nm (the A_T and A_X) lead emission bands are observed and after about 5 h at 480 K a band peaking at 390 nm starts to develop; this band mixes with the A_X emission of isolated impurity–vacancy dipoles. Simultaneously a small 458 nm band is obtained and both emissions are stabilized after annealing for about 30 h at 480 K. The results are shown in figure 6. Evidently in this aggregation process the intensity of the 312 nm emission band, corresponding to free dipoles, decreases, while those of the 390 and 458 nm bands increase. It should be mentioned here that this latter band can only be observed at low temperatures. On the other hand, as these bands are very broad, decomposition of the bands peaking at 380 and 390 nm was not attempted and the results shown in figure 6 correspond to the total integrated intensity. The excitation spectra of all these bands correspond to the structured absorption band A of divalent lead ions.

The above results present interesting features from the theoretical point of view. The usually observed emission bands of Pb²⁺ correspond to a Jahn–Teller regime where the most important vibrational coupling mode is E_g (besides spin–orbit coupling effects). As is well known (Bacci *et al* 1975), these effects produce the existence of two minima on the adiabatic potential energy surface, each of different symmetry: one of tetragonal and one of orthorhombic symmetry leading to the A_T and A_X emission bands, respectively, in the case of free dipoles. The usual temperature behaviour of the A_X emission is complicated. At very low temperatures (less than 20 K) its intensity is low, and it increases as the temperature is also increased, reaching a maximum (which depends on the alkali halide system (Kang *et al* 1985)), and then decreases until it disappears at around room temperature, while the A_T band intensity remains almost constant over a wide temperature range. Now, in this work the observed intensity decrease in the A_T emission band (312 nm) which benefits the band at 460 nm, as a function of the annealing time at 355 K, is just due to the incorporation of Pb²⁺ ions into the Cd²⁺ precipitates. This conclusion agrees with that of García-Solé *et al* (1983). On the other hand, the temperature behaviour indicates that the emission bands peaking at 395 nm (one component of the structured 388 nm emission band) and 460 nm, once the lead ions have been incorporated into the Cd²⁺ Suzuki phase precipitates, behave as A_X and A_T bands, respectively. From the theoretical point of view this situation has been predicted by Ranfagni *et al* (1983) for a case in which not only the E_g vibrational coupling mode but also, as the main coupling, the T_{2g} mode is present. That this latter mode is the most important in the Suzuki phase has been demonstrated by Calleja *et al* (1980) using Raman spectroscopy in NaCl:CdCl₂. Although a similar study for the NaCl:CdCl₂:Pb²⁺ system has not been performed, the situation seems similar, and one might expect that this type of coupling is also valid here. On the other hand, this assumption can also be supported by the results obtained from the excitation spectra (figure 4); the structured band

obtained for the A_X -type emission resembles the triplet structure that is expected if coupling to a T_{2g} vibrational mode predominates, as has been predicted by Englman *et al* (1970) and Toyozawa and Inoue (1966). In this case the $^1A_{1g} \rightarrow ^3T_{1u}$ absorption curve must have three bumps, the band is split into three components, but the interaction with the A_{1g} vibrational mode smooths the curve (Bersuker 1984). Then it seems to be clear that the emission band peaking at 388 nm (395 nm at 20 K) might be assigned to the A_X orthorhombic minimum and the band at around 460 nm to the A_T tetragonal minimum. As mentioned above, this reversed assignment of the emission bands, i.e. the low-energy band as the A_T band, was predicted by Bacci *et al* for the case in which the T_{2g} vibrational coupling mode is included together with the E_g mode.

For an annealing temperature of 480 K there are only two emission bands peaking at 390 nm and 458 nm, respectively. The behaviour of these two bands is the usual type and can be ascribed to Pb^{2+} ions incorporated into $CdCl_2$ precipitates, the former to the A_T band and the latter to the A_X band. Also the symmetry of the structure is such that the E_g vibrational coupling mode is the principal mode, as contrasted with the previous case of $6NaCl:CdCl_2$ (Suzuki phase).

4. Conclusions

It has been found that the inclusion of Pb^{2+} ions in the cubic Suzuki phase precipitates of Cd^{2+} ions in NaCl produces predominant coupling to T_{2g} vibrational modes, the coupling to E_g vibrational modes also being present; this leads to a situation where the high-energy emission band (395 nm at 16 K and 388 nm at 77 K) is associated with the A_X minimum in the APES while the low-energy emission band (around 460 nm) is assigned to the A_T minimum. In contrast, Pb^{2+} ions incorporated into $CdCl_2$ -type precipitates produce the usual situation in which the high-energy emission band is the A_T band while the low-energy band is assigned to the A_X APES' minimum.

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