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LETTER TO THE EDITOR

The aggregation pathway of lead impurities in NaCl crystals

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Abstract. Experimental results for NaCl:Pb^{2+} crystals on the luminescence polarisation of lightly doped samples indicate mainly trimer centres with C_3 symmetry and a low concentration of D_{4h} dimer centres. Calculations of the cluster stability performed by Bannon and co-workers for the same systems are in agreement with the aggregation pathway proposed by us.

Aggregation phenomena in alkali halides doped with divalent impurities have been extensively studied. Cook and Dryden (1960), and then Dryden and Harvey (1969), Collins and Crawford (1971), Dryden and Heydon (1983), Capelletti *et al* (1983) and Garcia Solé *et al* (1983), have studied the aggregation of divalent impurity–vacancy complexes by means of dielectric loss and ITC techniques and by studying optical absorption and emission spectra for NaCl:Pb^{2+} and KCl:Pb^{2+} crystals. Such studies have provided useful information on the aggregation processes—for example, providing evidence of a stable trimeric centre in many systems—but cannot verify the structure of the different aggregates.

A direct experimental determination of the nature and of the structure of the clusters can be obtained by analysis of the polarisation properties of the luminescence (Zazubovich *et al* 1969, Collins and Crawford 1972, Benci *et al* 1982, 1986, 1989). Measurements of polarisation spectra and of azimuthal diagrams can supply information on the cluster symmetries. Such analysis is suitable for use in studies of the aggregate symmetries in lightly doped systems, where x-ray diffraction and electron microscopy techniques cannot be used, and it can be useful in investigations of the early stages of the aggregation processes. It is appropriate for systems that present absorption and/or emission bands connected with the aggregates and that show modifications of the optical spectra during the growth of the clusters. Systems such as KCl:Pb^{2+} and NaCl:Pb^{2+} show such features.

In previous work on KCl:Pb^{2+} crystals, Benci *et al* (1989) presented experimental luminescence polarisation results for lightly doped and thermally aged samples. These measurements did not give a clear picture of the aggregate structures, because of the strong overlap of the absorption and emission bands of many emitting centres. However,
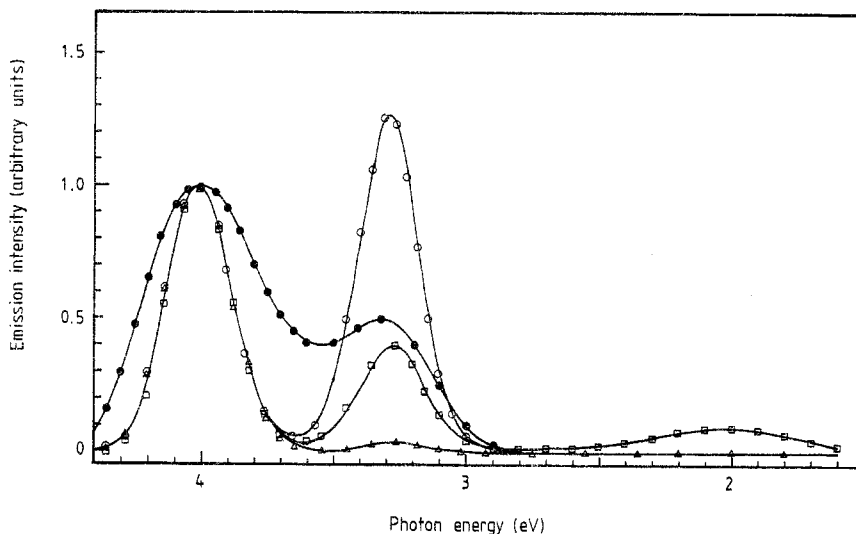
Figure 1. Emission spectra of lightly doped $NaCl:Pb^{2+}$ crystals excited in the A absorption band observed at $T = 80$ K. The curves are normalised at the high-energy emission peak. $\square$, 'as-received' sample; $\triangle$, quenched sample; $\bigcirc$, sample annealed at 300 K after quenching for 1000 h; $\bullet$, emission observed at 300 K for the sample as before. The emission intensities at the high-energy band peak are: $\square$, $I_E = 100$; $\triangle$, $I_E = 730$; $\bigcirc$, $I_E = 113$.

they are in agreement with the results on the types of aggregates obtained by means of calculations of their stability performed by Bannon *et al* (1985) for the same system. We consider that the analysis of the luminescence polarisation, in connection with the results of the calculations of the relative stability of small aggregates (Corish *et al* 1981, Bannon *et al* 1985), looks to be a useful way to clarify what the first steps of the aggregation processes are in many systems.

Another interesting system from this point of view is that of $NaCl:Pb^{2+}$ crystals. These crystals, as regards ITC and absorption results (Dryden and Harvey 1969, Collins and Crawford 1971, 1972, Capelletti *et al* 1983), present some features very similar to those found for $KCl:Pb^{2+}$ crystals, but their absorption and emission spectra show more significant variation on thermal treatment than those of $KCl:Pb^{2+}$ crystals. Moreover, aggregation processes are already taking place at room temperature, so some complications can arise for optical spectra, but this is mainly for heavily doped samples. In order to avoid the complications due to fast processes of precipitation into large aggregates, very lightly doped crystals must be used. Under these conditions small clusters can be expected and the first step of the impurity aggregation can be controlled.

Single crystals of $NaCl:Pb^{2+}$, lightly doped ($\simeq 5$ ppm) and freshly quenched from 500 °C to room temperature, show an intense emission band at 4.01 eV (figure 1) and a small band at 3.29 eV for excitation at 4.54 eV (absorption band A). The high-energy band decreases during the annealing at RT, while the emission band at 3.29 eV increases and a band at 2.0 eV, detected in the as-received sample, does not appear for annealing durations of up to 40 days (Benci *et al* 1982). The polarisation measurements have been carried out at LNT and RT and they have been interpreted on the basis of the Feofilov's theory (Feofilov 1961). The results for luminescence polarisation have shown that the emission at 4.01 eV can be attributed to isolated Pb vacancy dipoles, according to Dryden and Harvey (1969) and Collins and Crawford (1972), and indicate the C_3 and C_4
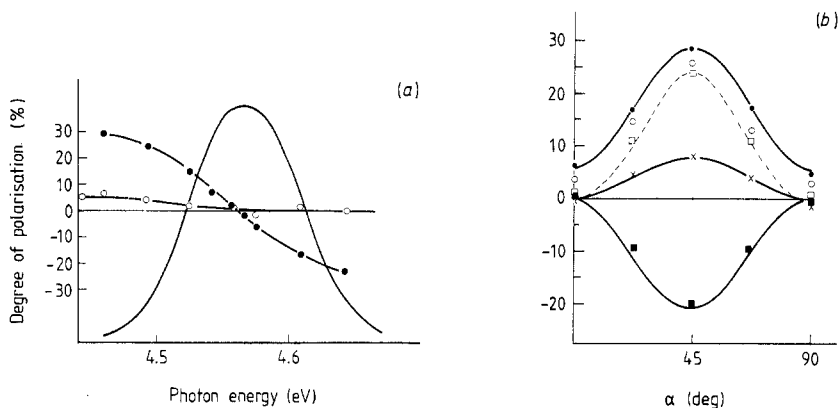
Figure 2. (*a*) Polarisation spectra observed at 80 K for the 3.30 eV emission excited in the A absorption band region of a NaCl: Pb^{2+} sample annealed at 300 K for 318 h after quenching. The azimuthal angles are $\alpha = 0°$ (O) and $\alpha = 45°$ (●). The polarisation was measured with the parallel arrangement. (*b*) Polarisation diagrams of the 3.30 eV emission excited in the A absorption band of a NaCl: Pb^{2+} sample observed at 80 K (■, □, O, ●) and at 300 K (×). The excitation energies are 4.47 eV (×, □, O, ●) and 4.64 eV (■). The annealing times at 300 K after quenching were: 30 min (□), 14 h (O) and 318 h (■, ×, ●).

symmetries of the emitting centres, which are attributed to the Jahn–Teller effect (Benci *et al* 1982). For the emission band at about 3.29 eV our results indicate aggregates with C_3 symmetry, as proposed by Dryden and Harvey (1969) and Collins and Crawford (1972).

Figure 2 shows the azimuthal polarisation spectra and the azimuthal degree of polarisation of a sample annealed at RT for different lengths of time. The azimuthal diagrams for excitation at high energy (4.64 eV) show independence of the thermal history of the sample, while for excitation at low energy (4.47 eV) a shift on the vertical axis to higher positive values occurs during the annealing. This shift is of the order of 5% after an anneal of 14 h. After 300 h of annealing, the shift is of the order of 6%, showing that these effects become stable during the thermal clustering process. This behaviour can be explained by the presence of centres with C_4 or C_2 symmetries.

The high values of the degree of polarisation at RT also in figure 2 suggest the static structure of the emitting centre with C_3 symmetry, and measurements with perpendicular geometry have indicated that C_4 and C_2 centres are not present for excitation at high energies (Benci *et al* 1982). On the whole, these results show that for high-energy excitation the emitting centre is a small aggregate with C_3 symmetry and suggest that it can be a trimer of impurity vacancy dipoles with [111] symmetry axes. For low-energy excitation of a moderately annealed sample, a low concentration of centres with C_4 or C_2 symmetry appears. The equilibrium for these centres is reached after relatively fast annealing. Their optical absorption and emission bands overlap the optical bands of trimers. Such results suggest that these centres can be dimer centres (Collins and Crawford 1971), different from the precursor dimer of C_3 trimers. These dimers can be detected after a relatively lengthy annealing owing to the low concentration of impurities, but their equilibrium with dipoles appears to be established rapidly.

If we assume that in our samples the trimer with C_3 symmetry gives rise to a more stable configuration, we can take it that the NN configuration dipole is prevailing over

the NNN configuration (Corish *et al* 1981). On this hypothesis, the proposed dimer centre may consist of two NN dipoles and have D_{4h} symmetry.

Let us discuss our results in comparison with those obtained for the same system, from the calculations of Bannon *et al* (1985). The binding energies calculated by Bannon and co-workers (BCJ) for Pb^{2+} impurity in NaCl crystals suggested that mainly NN coordination dipoles may be expected in our samples at 300 K ($dipole_{NNN}/dipole_{NN}$ = 4×10^{-4}). The annealing treatment at RT yields the aggregation processes. In our annealed samples, on the basis of the stabilisation energies of the aggregates estimated by BCJ, we can expect two aggregation pathways:

$$D_a + dipole_{NN} \rightleftarrows T_g \qquad D_d + dipole_{NN} \rightarrow T_e$$

where D_a, D_d, T_g and T_e are dimers and trimers with the structures presented in figure 2 of BCJ (1985) and D_a and D_d dimers can be expected with about the same concentration because their stabilisation energies are similar. The formation of T_g trimers is not very probable owing to its low stabilisation energy, while T_e is the most stable aggregate— much more stable than its precursor dimer.

Hence, in $NaCl:Pb^{2+}$, as underlined by BCJ and widely experimentally observed, Suzuki phase formation would not be expected, while for dipoles in the NN configuration the trimer T_e is the most stable complex. If dimer interconversion between the two configurations is assumed not to occur as expected from the stabilisation energy values, the estimated pathways indicate that in our samples mainly T_e trimer centres having C_3 symmetry will be present, together with D_d dimers as precursors of T_e centres and D_a (D_{4h} symmetry) dimers that are much more stable than the T_g trimer. The D_a and D_d dimers appear less strongly bound that T_e centres.

The same conclusions have been drawn from our polarisation measurements; these have also provided some useful information on the cluster symmetries.

In summary, the experimental results on luminescence polarisation in lightly doped $NaCl:Pb^{2+}$ crystals indicate that in the first aggregation step a centre with C_3 symmetry, whose stability is good when the temperature is varied, is emitting at 380 nm, with an intensity increasing with the annealing time.

For excitation at low energies of the absorption band A, a small concentration of new centres, probably D_{4h} dimer centres, is detected after 14 h of annealing at RT, but their contribution does not increase significantly for longer annealing times. These D_{4h} centres may be the D_a dimer of BCJ—that is, a dimer more stable than the T_g trimer. For lightly doped crystals this picture is unchanged for annealing durations of up to 40 days,
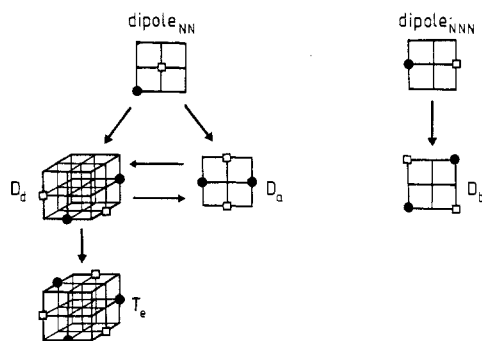

Figure 3. The aggregation pathway of the impurity vacancy dipoles in a $NaCl:Pb^{2+}$ sample annealed at 300 K. The aggregation pathway, starting from dipoles in NNN configurations, appears to be much less important, owing to the low concentration of NNN dipoles ($dipole_{NNN}/dipole_{NN}$ = 4×10^{-4} at 300 K).

and no Suzuki phase or other precipitate phase is detected. The D_d dimer, which can be present as a precursor of the trimer T_e, does not contribute to the luminescence polarisation owing to its low symmetry.

The experimental results and the calculations of the cluster stability provide evidence that the NN dipole configuration is the more stable configuration and the T_e trimer can be considered the end-point of the aggregation process. In figure 3 the aggregation pathway proposed for lightly doped $NaCl:Pb^{2+}$ crystals is summarised. In conclusion, the lightly doped samples are found to be suitable for studies of small clusters and the experimental results compare well with the calculations of BCJ. Further work on samples with increasing concentrations of impurities and higher annealing temperature could be performed in order to analyse the emission bands detected for these samples by Dryden and Harvey (1969), Collins and Crawford (1972), Marculescu (1977) and Capelletti *et al* (1983), and to verify whether an interconversion between the NN and NNN configurations may take place.

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