

## Optical spectroscopy of solute lead in NaCl:Sr crystals

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The optical spectroscopy (absorption and luminescence) of a small concentration of lead ( $\sim 10$  ppm) incorporated into a NaCl:Sr crystal, containing a relatively higher concentration of Sr ( $\sim 350$  ppm), has been investigated. For samples annealed at room temperature after quenching, two overlapping absorption bands at 255 and 260 nm grow at the expenses of the  $A$  band typical of dissolved  $\text{Pb}^{2+}$ . For high-temperature (150 and 300 °C) annealed samples, the 255- and 260-nm bands grow initially, saturate, and finally decrease for the benefit of another band at 249 nm, which becomes prominent after a long time. The same band is observed in as-grown samples. The luminescence emissions for the various bands have been determined. In the light of the available information, it has been concluded that the 249-nm band corresponds to  $\text{Pb}^{2+}$  incorporated into  $\text{SrCl}_2$  precipitates, whereas the 255- and 260-nm bands should be associated to some intermediate phases, whose structure is not currently known.

### I. INTRODUCTION

The optical spectra (absorption and luminescence) of lead-doped alkali halides has been shown to be quite sensitive to the state of aggregation of  $\text{Pb}^{2+}$  ions. Most work has been performed on NaCl and KCl.<sup>1-8</sup> Consequently, it could be expected that lead might be an adequate optical probe to monitor the clustering processes occurring in a divalent cation-doped system, if it becomes incorporated in the aggregates and precipitates formed. One of the systems which has received much attention is NaCl:Sr. A number of techniques has been used to follow its aggregation and precipitation kinetics: ionic thermocurrents,<sup>9,10</sup> dielectric losses,<sup>11</sup> ionic conductivity,<sup>11-13</sup> light scattering,<sup>14,15</sup> and NMR.<sup>11</sup> More direct techniques, such as x-ray diffraction<sup>16</sup> and electron microscopy<sup>17,18</sup> have also been used to detect the occurrence of precipitate phases and determine their structure. The conclusion has been that  $\text{SrCl}_2$  precipitates are definitely formed in slowly cooled samples and during high-temperature annealing ( $T > 100$  °C).<sup>16,17</sup>

In line with the above comments, the aim of the present work has been to use  $\text{Pb}^{2+}$  as an optical probe on NaCl:Sr as the host doped system. The evolution of the absorption spectra has been followed at various annealing temperatures. Moreover the thermal stability of the new bands formed

during annealing as well as their luminescence emissions have been determined. It has been concluded for this system that optical spectroscopy provides a powerful tool to investigate aggregation and precipitation processes. In particular, the optical data obtained on the precipitated phases complement the results of other direct techniques usually applicable to much higher doping levels, such as x-ray diffraction<sup>16</sup> and electron microscopy.<sup>17,18</sup>

### II. EXPERIMENTAL

NaCl:Sr(Pb) crystals were grown in our laboratory by the Czochralski method in an inert atmosphere. Suprapure NaCl powder from Merck was used in all cases. The lead and strontium contents in the crystals were determined by atomic absorption spectrophotometry and are expressed in ppm, referred to atomic concentrations.

Absorption spectra were taken at liquid-nitrogen temperature (LNT), by using a Cary 17 spectrophotometer. Luminescence spectra, also at LNT, have been obtained with a conventional setup. For excitation, a Bausch-Lomb double-grid monochromator (250-nm focal length) has been used. Resolution was  $\sim 5$  Å in all cases. The emitted light was analyzed with a motor-driven high-intensity Bausch-Lomb monochromator followed by an EMI (S-20) 9558 QB photomultiplier and a PAR lock-in amplifier (chopping frequency 750 Hz). Quench-

ing treatments were performed by heating samples up to a 450 °C in air and dropping them, after 15 min, onto a copper block.

### III. EXPERIMENTAL RESULTS

#### A. Optical absorption

##### 1. Quenched and as-grown samples

The absorption spectra, in the wavelength range 220–310 nm, for a NaCl:Sr(Pb) sample before (i.e., as-grown) and after a quenching treatment from 450 °C are shown in Fig. 1(a). The sample was cleaved from a crystal block containing 350 ppm Sr and 11 ppm Pb. For the as-grown sample, two bands are observed in addition to the *A* band

of  $Pb^{2+}$  peaked at 272 nm; more specifically, a prominent band with maximum at 249 nm and half-width of 0.06 eV, and another one at 260 nm, whose height is comparable to that of the *A* band. These additional bands have not been observed in NaCl, exclusively doped with lead.<sup>1,4,5,7</sup> After quenching, they disappear to the benefit of the *A* band, which appears alone, except for a small remaining absorption at 249 nm. The spectra for quenched and as-grown samples of NaCl:Sr(Pb) containing 2100 ppm Sr and 10 ppm Pb are qualitatively as in Fig. 1(a).

It is worthwhile noting that the absorption spectra for as-grown samples present an increasing background towards short wavelengths suggesting light-scattering by agglomerates, as observed for NaCl:Pb containing  $PbCl_2$  precipitates.<sup>4</sup> In fact, as-grown samples have a translucent appearance, which completely disappears after quenching.

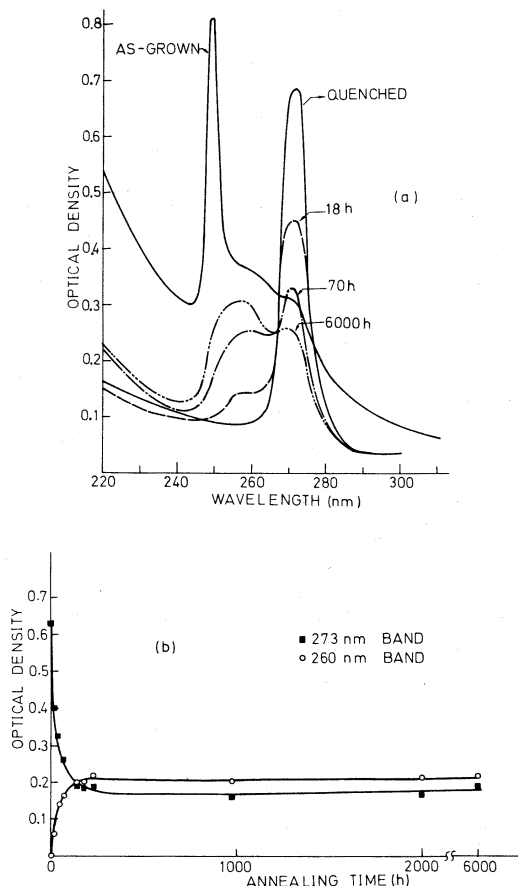


FIG. 1. (a) LNT absorption spectra after various annealing times (*h*) at RT for NaCl:Sr(Pb). Spectra for the quenched and as-grown sample are also included (solid lines). (b) Evolution with time of the optical absorption at 260 and 273 nm (*A* band). Sr concentration 350 ppm; Pb concentration 11 ppm.

##### 2. Evolution of the absorption spectra after quenching (annealing)

(a) *Room-temperature (RT)*. An annealing treatment at RT induces a decrease of the *A* band with a corresponding increase of the optical absorption in the 250–270-nm region as illustrated in Fig. 1(a). After 6000 h annealing, the spectrum consists of a complex absorption with peak at ~258 nm, together with the rest of the *A* absorption at 272 nm. The evolution with time of the absorption at two significant wavelengths (260 and 272 nm) is given in Fig. 1(b). A rapid increase in the absorption at 260 nm occurs during the first 100 h, in correlation with a decrease of the *A* band. After that stage, a stationary or saturating absorption level is reached. It is to be remarked that no indication of a growth of the 249-nm band, appearing in the as-grown samples, has been observed even after 6000 h annealing.

(b) *150 °C*. Absorption spectra taken after various annealing times at 150 °C are shown in Fig. 2(a). There is a first stage of the process, wherein the *A* band experiences a fast decrease to the benefit of a band at 260 nm, which reaches a maximum height at ~200 h. After this time a stationary region or “plateau” sets in. This spectral evolution appears similar to, although faster than that observed for RT annealing. After the plateau a second stage appears where the 260-nm and *A* bands decrease, whereas a new band at 249 nm very rapidly grows. This behavior is more clearly

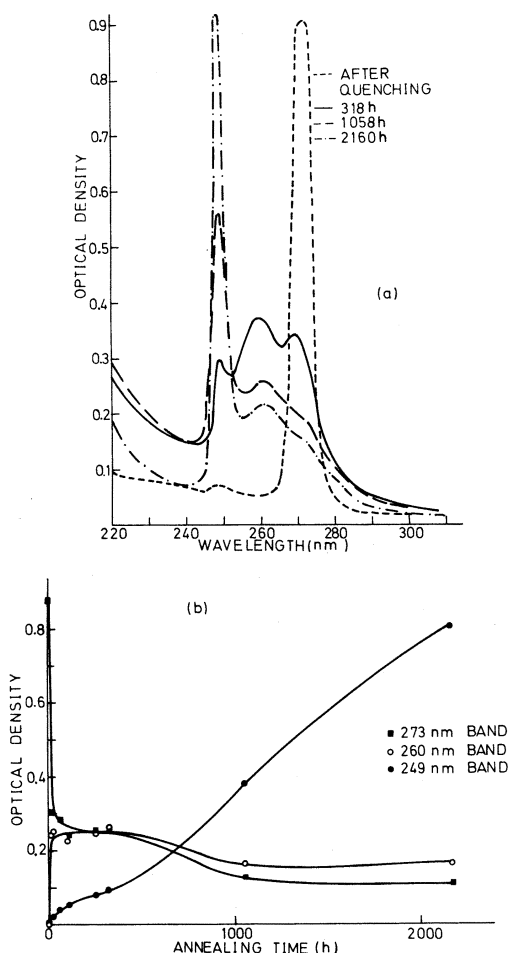


FIG. 2. (a) LNT absorption spectra after various annealing times at 150°C for NaCl:Sr(Pb). (b) Evolution with time of the optical absorption at 249, 260, and 273 nm (*A* band). Concentrations as in Fig. 1.

illustrated in Fig. 2(b), where the plateau following the initial stage, as well as the final stage is clearly apparent. According to these data, the broad band at 260 nm behaves as an intermediate state in the clustering process leading to the formation of the 249-nm band. The band at 260 nm is, presumably, the same developing during RT annealing, although it is, indeed, complex, because the position of the peak shifts slightly to longer wavelengths during the treatment at 150°C. The spectra after ~1000 h annealing are essentially similar to those found in as-grown samples.

(c) 300°C. A sample has also been annealed at 300°C, although the process has not been followed in detail, as for the other temperatures. Similarly to 150°C annealing, a prominent band develops at 249 nm. However, two main differences are now

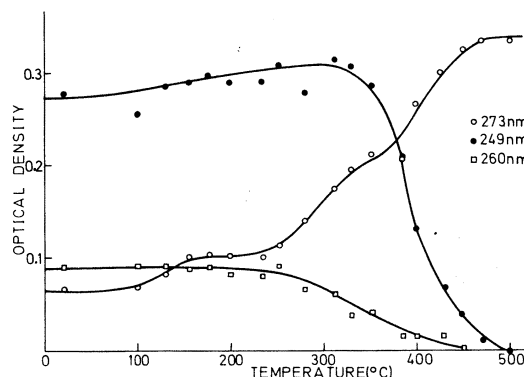


FIG. 3. Evolution with temperature (see text) of the optical absorption at the significant wavelengths 249, 260, and 273 nm. Concentrations as in Fig. 1.

apparent: (i) a quite intense *A* band is present and (ii) the 260-nm band seems to have been markedly reduced to the benefit of another one closer to the 249-nm band and probably peaked at ~255 nm.

### 3. Thermal stability of the absorption bands

The thermal stability of the various bands has been investigated on a sample doped with 350 ppm Sr and 11 ppm Pb. For this experiment, an as-grown sample was kept for 0.5 at each fixed temperature and then rapidly cooled down to RT where the spectra were recorded. The detailed evolution of the height of the various bands is given in Fig. 3. The intermediate band at ~260 nm starts decreasing at ~200°C in correlation with an increase of the *A* band and presumably of the 249-nm band. It also appears that the absorption at 260 nm decreases more markedly than that at 255 nm, suggesting once more that at least two bands are involved in this spectral region. The 249-nm band begins a rapid decay at ~325°C, also resulting in an increase of the *A* band. The temperature for maximum decay rate lies at ~390°C. Finally, at ~500°C only the *A* band remains in the sample. For the crystal containing 2100 ppm of Sr, the thermal annihilation of the various bands occurs over the same temperature range as for the less-doped sample.

### B. Luminescence spectra

In order to obtain additional information on the nature of the centers responsible for the optical ab-

sorption produced during annealing, the luminescence spectra of the various bands have been determined.

### 1. Samples annealed at RT

Immediately after quenching from 450°C, only the *A* band is apparent, except for a small absorption at 250 nm. The emission spectra for *A*-band excitation include the 310- and 380-nm emissions previously observed in lead-doped samples.

During RT annealing, a broad and presumably complex absorption band develops in the 250–270-nm spectral region [Fig. 1(a)]. Luminescence experiments reveal two main emission bands at ~300 and 345 nm, which are predominantly excited at 255 nm (the one at 300 nm), and 260 nm (the one at 345 nm), as illustrated in Fig. 4(a). The two

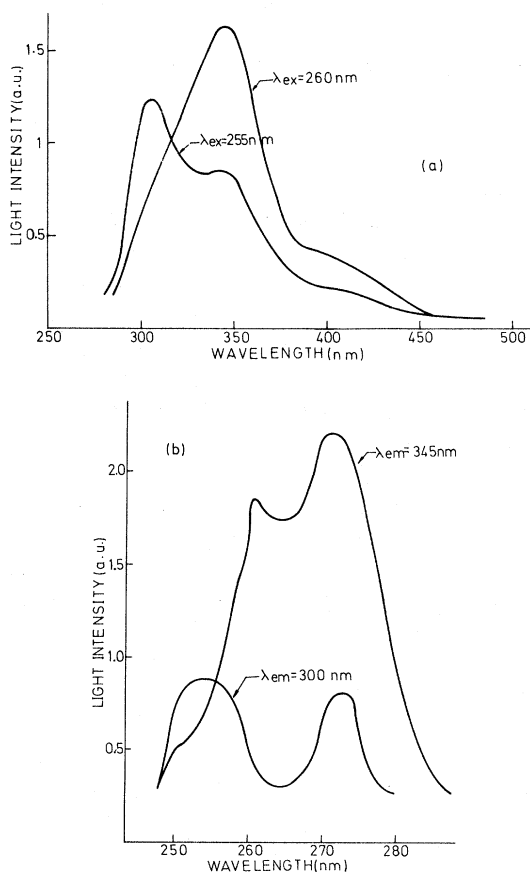


FIG. 4. (a) LNT emission spectra corresponding to excitation at 255 and 260 nm for a sample annealed for 6000 h at RT. (b) LNT excitation spectra for the emissions at 300 and 345 nm. Sr and Pb concentrations as in Fig. 1.

emission bands cannot be well separated because of the strong overlapping between the corresponding excitation bands at 255 and 260 nm. This behavior is confirmed by recouring to the excitation spectra, which are shown in Fig. 4(b). For the 345-nm emission, an excitation band stands out at 261 nm. Unfortunately, in both cases, a marked contribution of the *A* band is apparent, because of the overlapping of the recorded emissions with those at 310 and 380 nm, excited at the *A* band. From Fig. 4, it appears that the excitation band at 260 nm is dominant for the RT annealed samples.

### 2. Samples annealed at high temperature (150 and 300°C)

For these temperatures, a very prominent absorption band develops at 249 nm, apparently at the cost of the absorption in the 250–270-nm region, growing during the first stage of annealing. The emission corresponding to the 249-nm band is shown in Fig. 5, together with those excited at 255 and 260 nm. The crystal used was annealed for one week at 300°C. The 249-nm band presents a well-defined emission peaked at ~290 nm together with some weaker emissions at the 310 and 380-nm bands typical of dissolved  $Pb^{2+}$ .

The intermediate 255- and 260-nm bands emit as reported above for RT annealed samples. It is to be noted that for 150°C as for RT annealing, the dominant emission is at 345 nm, whereas for 300°C annealing, the 300-nm emission is predominant and that at 345 nm has almost completely disappeared. This is in accordance with the reported absorption data.

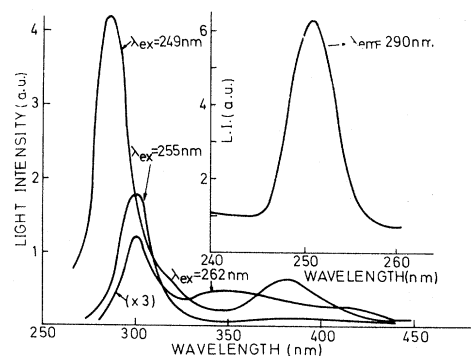


FIG. 5. LNT emission spectra for excitation at 249, 255, and 262 nm. The excitation spectrum for the dominant emission at 290 nm is shown in the inset (compare with the absorption spectra.) Concentrations as in Fig. 1.

### 3. *As-grown samples*

As-grown samples show a luminescence behavior quite similar to that found for 150°C annealed samples. They have a prominent emission at 290 nm (excited at 249 nm) and another emission band at 345 nm, excited at 260 nm. The emission at 300 nm is very weak.

## IV. DISCUSSION

The spectra observed for as-grown or annealed samples of NaCl:Sr(Pb), show a number of bands clearly distinct from those reported for NaCl:Pb.<sup>1,4,5,7</sup> Furthermore, these new bands develop during annealing at the cost of the *A* band typical of dissolved lead. Therefore, they should be ascribed to Pb<sup>2+</sup> ions associated in some way to aggregates or precipitates of strontium. In particular, the most prominent absorption band in as-grown or high-temperature (150–300°C) annealed samples is that one peaked at 249 nm. There are a number of reasons to attribute this band to Pb<sup>2+</sup> embedded into SrCl<sub>2</sub> precipitates. First, Laredo and Dartyge,<sup>16</sup> working on heavily (~10<sup>4</sup> ppm) Sr-doped NaCl, have observed by means of x-ray diffraction that SrCl<sub>2</sub> precipitates occur in slowly cooled samples as well as in those annealed at temperatures higher than 100°C. The formation of the stable dihalide phase SrCl<sub>2</sub> in NaCl has also been reported by Sors and Lilley<sup>17</sup> under similar doping conditions. On the other hand, the annihilation temperature (~390°C) determined for the 249-nm band in our 350 ppm doped samples is in good agreement with the dissolution temperatures of SrCl<sub>2</sub> determined by Brown and Hoodless<sup>12</sup> through ionic conductivity experiments. Finally, the kinetics of growth for that band follows the typical trend expected for a precipitation process [see Fig. 2(b)]. In fact, it involves a nucleation stage or “plateau” region where the strontium ions should be aggregating without efficient formation of the band, followed by the growth stage represented by the rapid final increase in band height.

In addition to the main band at 249 nm, other bands develop at 255 and 260 nm, whose relative importance depends on annealing temperature. From the data at 150 and 300°C it is clear that they grow initially with time and then decrease and even disappear to the benefit of the 249-nm band, attributed to Pb<sup>2+</sup> into SrCl<sub>2</sub>. Therefore, they should correspond to some intermediate phases in the clustering process leading to the stable phase. The intermediate phases are the only ones formed

during RT annealing, at least for periods of several months. In fact, by means of various techniques the occurrence of phases different from SrCl<sub>2</sub> has been confirmed,<sup>13,14,18,19</sup> although their stoichiometry and structure are not clear.

A similar situation to that described here for NaCl:Sr(Pb) has been recently reported for NaCl:Eu.<sup>20</sup> For this material, two metastable intermediate phases have also been apparently observed, in addition to the stable dihalide phase EuCl<sub>2</sub>. They have been ascribed to precipitated plate zones extending parallel to the {111} and {310} planes of the host lattice, as reported by Suzuki<sup>21</sup> for NaCl:Ca. In fact, the behavior of these plate zones during annealing in relation to the stable EuCl<sub>2</sub> or CaCl<sub>2</sub> phases is similar to that described here for the intermediate absorption bands (255 and 260 nm) with regard to the SrCl<sub>2</sub>(Pb) 249-nm band. In particular, only optical bands associated to plate zones are found in two-years annealed NaCl:Eu samples at RT and the growth of the stable phase takes place at the cost of the plate zones. Furthermore, on the basis of this scheme our experimental data on NaCl:Sr(Pb) suggest that the 255-nm band would correspond to the {111} platelets because they are dominant at the higher annealing temperatures<sup>20,21</sup> whereas the 260-nm band should be associated to the {310} platelets mostly present at lower temperatures. However, additional experiments should be performed on NaCl:Sr to propose a reliable assignment of the intermediate bands.

It is not clear how the Pb<sup>2+</sup> can participate in the precipitation process of NaCl:Sr. In fact, although reliable comparative data are not available, it appears that the decay of the *A* band of Pb<sup>2+</sup> in NaCl:Sr(Pb) takes place at a higher rate and reaches a lower value than one would expect on NaCl:Pb from the low lead concentration involved (11 ppm). This suggests that the kinetics of lead may be determined by the trapping of the Pb<sup>2+</sup> ions into the SrCl<sub>2</sub> precipitates during their nucleation and growth.

Finally, it is worth remarking that optical spectroscopy provides very useful information on the aggregation and precipitation kinetics of Sr in NaCl, and permits differentiation among the various precipitates formed under different annealing conditions.

## ACKNOWLEDGMENT

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