"Mechanical Doping" of Polycrystalline Alkali Halides with Pb²⁺ Ions

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It is shown that Pb²⁺ ions can be introduced into polycrystalline matrices of NaCl, KCl, KBr, KI, and $KCl_{0.5}Br_{0.5}$ by mechanical treatment of powder mixtures of the relevant alkali halides (AH) with small quantities of $PbCl_2$ or PbO (up to a few dozens of molar ppm). The comparison of the adsorption spectra of the above materials pressed into transparent pellets with those of conventionally Pb²⁺-doped AH single crystals proves that due to mechanical stimulation the dopant enters into the AH matrix in the form of isolated Pb²⁺ ions substituting for the original lattice cations. It is shown that mechanical treatment is also effective in preparing polycrystalline samples of some mixed alkali halides like $KCl_{0.5}Br_{0.5}$.   © 1996 Academic Press, Inc.

1. INTRODUCTION

The first paper dealing with grinding effects in mixtures of an alkali halide (AH) with an appropriate luminescent activator appeared in 1948 (1). Further papers describing the phosphors prepared by the same technology were published, e.g., Refs. (2–4). In the early 1950s, AHs were found to have applications in IR spectroscopy as chemically neutral, or nearly neutral solid solvents, mostly in the examination of some organic species (5, 6). Particularly useful proved to be KBr, which is rather easily compressed into transparent polycrystalline pellets. It should be emphasized, however, that in some ground and compressed mixtures of AH and the substance examined, numerous authors have observed various "anomalies" which they ascribed, to possible metathesis or formation of mixed crystals, among other causes; e.g., see (7, 8).

Some time ago we found that mechanical treatment (e.g., grinding) of the powder mixture of AH and a small quantity of divalent metal halide (MeX_2) results in the introduction of Me^{2+} ions into the cationic sites of the AH lattice. In this paper we describe the effects induced by mechanical treatment of polycrystalline AH samples containing $PbCl_2$ or PbO as the admixture.

2. EXPERIMENTAL

The powder mixtures of the matrix material and the admixture (dopant) were prepared from high-purity alkali halides (NaCl, KCl, KBr, and KI) and $PbCl_2$ or PbO. Because of weighing accuracy, the dopant-rich mixtures containing 10,000 mole ppm (molar fraction $\times 10^6$) were prepared first. Subsequently, they will diluted with the matrix material in a few steps to desired Pb²⁺ contents as low as 10 ppm. Small portions (about 0.2 g) of each final mixture were ground in an agate mortar, always in a similar way. After that treatment each mixture was placed in a special device (of our own construction) permitting us to compress the samples in a vacuum of 0.5 hPa. All pellets thus obtained ($\phi = 10$ mm, $d \sim 1$ mm) were transparent in the visible and ultraviolet range for a long time (up to a few months). We have also prepared lead-doped mixed-phase samples of composition $KCl_{0.5}Br_{0.5}$ using an appropriate mixture of pure KCl and KBr with a small amount of Pb²⁺, treated in the same way as described above. The particle size of the samples obtained both by the procedure described above and by applying a conventional mill or Wig-L-Bug grinding mill are roughly the same, in the range from 10 to 20 μm. We have also examined a few monocrystalline samples obtained from Pb²⁺-doped single KCl and KBr crystals grown according to (9) from the melt in sealed quartz ampoules. The absorption spectra of all samples were taken at room temperature in a Specord M40 (Zeiss–Jena) spectrophotometer.

3. RESULTS AND DISCUSSION

In Figs. 1a–1c the absorption spectra of polycrystalline samples of KCl, KBr, KI, and $KCl_{0.5}Br_{0.5}$ mechanically doped with $PbCl_2$ or PbO are presented. The wavelength range of the spectra is restricted to comprise *A* bands (transition $^1S_0$–$^3P_1$ in free ion) only (e.g., Refs. (10–12)). For comparison, in Fig. 1c we also show the adsorption spectrum characteristic of $PbCl_2$, taken from (13), and the adsorption spectra of KCl : Pb²⁺, KBr : Pb²⁺, and KI : Pb²⁺
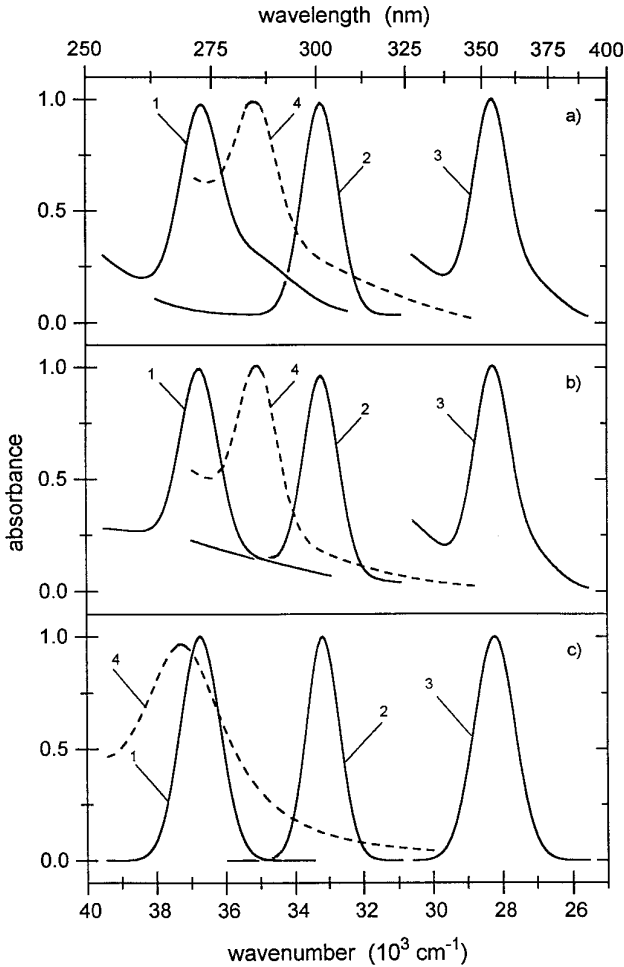
FIG. 1. Absorption spectra of (a) KCl (1), KBr (2), KI (3), and KCl$_{0.5}$Br$_{0.5}$ (4) samples mechanically doped with PbCl$_2$; (b) KCl (1), KBr (2), KI (3), and KCl$_{0.5}$Br$_{0.5}$ (4) samples mechanically doped with PbO; (c) KCl (1), KBr (2), and KI (3) monocrystalline samples from conventionally Pb^{2+} doped crystals, PbCl$_2$ thin layer (4) taken from Ref. (13).

samples taken from Pb^{2+}-doped single crystals. It should be emphasized that the positions and the half-widths of the A bands characteristic of isolated Pb^{2+} ions are the same, within accuracy limits, in mechanically doped samples (Figs. 1a and 1b) and in our conventionally doped single crystals (Fig. 1c). The above facts unambiguously prove that during grinding of the powder mixture of AH and PbCl$_2$ or PbO, the lead enters the host matrix of small crystallites in the form of single (isolated) Pb^{2+} ions substituting for the original lattice cations, while a cation vacancy is created for charge compensation.

It should be noticed that heavy grinding applied in mechanical doping is equivalent to extremely drastic plastic deformation of the matrix grains, generating huge numbers of new dislocations and causing their motion as well as generating hosts of new over-equilibrium lattice vacancies.

Under such circumstances one should expect an enhanced (deformation stimulated) diffusion of the dopant ions from the grain surface into the matrix.

A monotonic increase in absorbance toward the high energy portion of the spectrum in mechanically doped samples (Figs. 1a and 1b) is possibly due to Rayleigh dispersion on the grain boundaries of the polycrystalline material.

We have also checked the effect of grinding time on the quantity of Pb^{2+} introduced into the matrix lattice using KBr containing 10 ppm PbCl$_2$ in the original mixture. As shown in Fig. 2, the optical density under the A band—reflecting the quantity of substitutionally incorporated Pb^{2+} ions—increases with grinding time and after 2 hr approaches saturation. This saturation may be ascribed to the state in which practically all of the PbCl$_2$ added is introduced into the KBr lattice. Hence, we can determine the value of a factor (m) that permits us to evaluate the concentration of introduced Pb^{2+} ions (C_{Pb}^{2+}) from the relevant absorption coefficient ($k_{A band}$). For Pb^{2+}-doped KBr $m = 1.3$ ($C_{Pb}^{2+} = m \cdot k_{A band}$).

For short grinding times only a small fraction of original lead ions enter the AH matrix. The remaining part of PbCl$_2$ or PbO, possibly spread at the surface of the matrix grains, is practically indetectable in the adsorption spectrum (we have not found any traces of the absorption bands in the
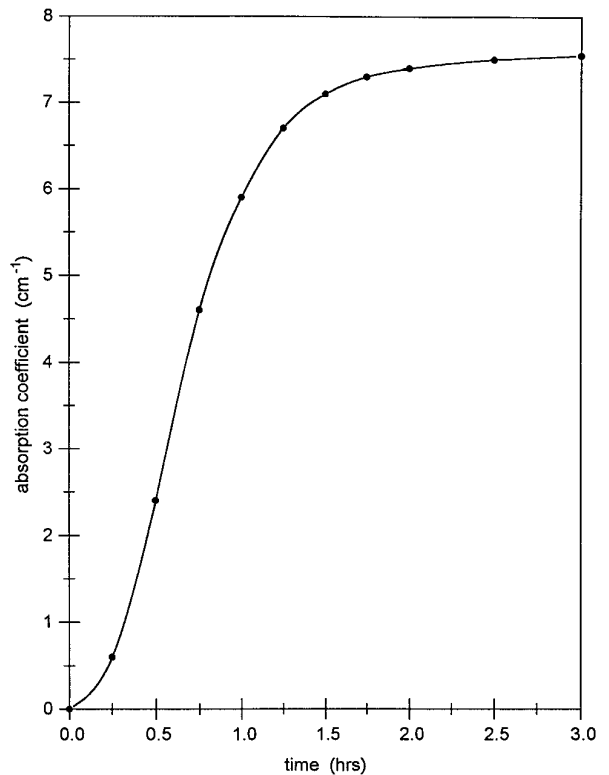

FIG. 2. Relation between absorption coefficient for the A band (at 302 nm) and grinding time of KBr–PbCl$_2$ mixture ($C_{PbCl_2} = 10$ ppm).

vicinity of 32,000 and 37,500 cm^{-1} which might be ascribed to the presence of PbO or PbCl$_2$) and possibly contributes to the Rayleigh dispersion. It should be noted that in all matrices examined, Pb^{2+} ions are more easily introduced into AH lattices when lead oxide (PbO) is used in the original mixtures.

In additional experiments we have found that except for the doping, the mechanical treatment is also effective in preparing polycrystalline samples of some mixed alkali halides like KCl$_{0.5}$Br$_{0.5}$. The existence of such a phase was detected in the absorption spectrum due to the presence of Pb^{2+} ions (see Figs. 1a and 1b, dashed curves). In agreement with (14) the A band characteristic of Pb^{2+} should be, in such material, localized at the half-distance between A bands appearing in simple KCl:Pb^{2+} and KBr:Pb^{2+} species. The examination of the former material by the X-ray powder method has confirmed the presence of a mixed phase of the composition KCl$_{0.5}$Br$_{0.5}$ with the lattice parameter equal to 6.448 Å, in agreement with Vegard's law cf. (15). The above results unambiguously prove that nearly every substitutionally incorporated Pb^{2+} ion is in the nearest neighborhood surrounded by three Cl$^-$ and three Br$^-$ anions.

ACKNOWLEDGMENT

Note added in proof. After sending our article to *J. Solid State Chem.* we have found a paper by Severin *et al.* (16) describing the formation of mixed crystal phases in mechanochemical reactions of some binary alkali halide mixtures.

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