

THE EFFECT OF PRESSURE ON THE ABSORPTION SPECTRA OF ALKALI HALIDE PHOSPHORS*

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Abstract—The effect of pressure (over 150,000 atm) has been measured on the spectra of twenty-six alkali halide phosphors, including nine doped with Tl^+ , two doped with In^+ , twelve doped with Pb^{++} , two doped with Cu^{++} and one doped with Bi^{+++} . ν_{max} for the Tl^+ doped phosphors depends very strongly on the crystal structure and very little, if any, on the halide ion involved, which is consistent with the Seitz model. The In^+ doped phosphors behave like the Tl^+ analogs. For the Pb^{++} phosphors, the shift of ν_{max} depends very strongly on the halide ion, and only incidentally on the lattice structure. This is consistent with the complex model.

INTRODUCTION

THIS work is concerned with the effect of pressure on the A absorption band due to the presence of low concentrations of impurities such as thallium and lead in alkali halide crystals. Since irradiation in this band is directly responsible for the occurrence of luminescence in these crystals, this is a study of the effect of pressure on the luminescent center.

Two models have been advanced to explain the nature of the luminescent center in alkali halide phosphors:

One of these, commonly called the Seitz model,⁽¹⁾ pictures the luminescence process as being confined to the internal transition of the valence electron(s) of the impurity ion from the 1S_0 to the 3P_1 states, perturbed by the crystalline field of the lattice. One would expect such a model to be strongly dependent upon the structure of the bulk crystals, but relatively independent of the nature of the nearest neighbor halide ions.

The other model, called the complex ion model,⁽²⁻⁵⁾ pictures the luminescence process as being an electron transition within a tightly bound impurity-halide ion complex. Here one would expect the system to be a strong function of the

nature of the bound halide ions, but relatively independent of the structure of the bulk crystal.

The phosphors studied and the techniques used to synthesize them are shown in Table 1. The melting procedure is a simplified Kyropoulos method.⁽⁶⁾ The grinding technique is similar to that used by dentists for mixing dental filling compounds. Press fusing consists of compressing the sample to around 15,000 atm on the anvil of a cylindrical tube type press.

The high pressure optical system used is that of Fitch *et al.*⁽⁷⁾ At 1 atm, the absorption spectra of impurity ions in alkali halides have been measured by several investigators over the past 25 years. However, the literature in the field is by no means complete, so that for some of the materials studied, it was necessary to measure the 1-atm spectra. In Table 2 are listed the 1-atm peak frequency of the A band for all of the impurity activated alkali halides used in this investigation. Where no reference is given in column four, the 1-atm spectra were first measured here.

The effect of pressure on the spectra of the A band in twenty-six different alkali halide phosphors is shown in Figs. 1-9. Typical sets of experimental points are shown in Figs. 4 and 5. The maximum pressure attained on each phosphor is shown in column five of Table 2. The results, except for $KBr:Bi$ (Fig. 5) are discussed below.

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Table 1. Phosphor crystals

Phosphor	Starting materials		Source		Preparative procedure(s)
	Host crystal	Impurity	Host	Impurity	
Low impurity KI:Tl for concentration study 0.8KI/0.2KBr:Tl 0.6KI/0.4KBr:Tl 0.4KI/0.6KBr:Tl 0.2KI/0.8KBr:Tl	Single crystal KI:Tl (0.1-0.2%)		Harshaw Chemical Co.		Melting (impurity dilution) and press fusing Melting, press fusing
	Single crystal KI:Tl and KBr:Tl		Harshaw Chemical Co.		
	Single crystal KI:Tl and KBr:Tl		Harshaw Chemical Co.		Melting, press fusing
	Single crystal KI:Tl and KBr:Tl		Harshaw Chemical Co.		Melting, press fusing
	Single crystal KI:Tl and KBr:Tl		Harshaw Chemical Co.		Melting, press fusing
NaCl:Tl	Single crystal NaCl	Chemically pure TlCl	Harshaw Chem. Co.	Fairmount Chem. Co.	Grinding press fusing
NaBr:Tl	Chemically pure NaBr	Chemically pure TlCl	Schaar Co.	Fairmount Chem. Co.	Melting, press fusing
CsBr:Tl	Single crystal CsBr	Chemically pure TlCl	Harshaw Chemical Co.		None
RbBr:Tl	Chemically pure RbBr	Chemically pure TlCl	A. D. Mackay, Inc.	Fairmount Chem. Co.	Melting, press fusing
RbI:Tl	Chemically pure RbI	Chemically pure TlCl	A. D. Mackay, Inc.	Fairmount Chem. Co.	Melting, press fusing
NaCl:Pb	Single crystal NaCl	Chemically pure PbCl ₂	Harshaw Chem. Co.	Allied Chem. and Dye	Melting, press fusing
NaBr:Pb	Chemically pure NaBr	Chemically pure PbCl ₂	Schaar Co.	Allied Chem. and Dye	Melting, press fusing
NaI:Pb	Single crystal NaI	Chemically pure PbCl ₂	Harshaw Chem. Co.	Allied Chem. and Dye	Grind together, press fusing
	Single crystal KCl:Pb		Dr. A. B. Scott, Oregon State College		None
KCl:Pb	Single crystal KCl	Chemically pure PbCl ₂	Harshaw Chem. Co.	Allied Chem. and Dye	Melting, press fusing
KBr:Pb	Single crystal KBr	Chemically pure PbCl ₂	Harshaw Chem. Co.	Allied Chem. and Dye	Melting, press fusing
KI:Pb	Single crystal KI	Chemically pure PbCl ₂	Harshaw Chem. Co.	Allied Chem. and Dye	Melting, press fusing
RbCl:Pb	Chemically pure RbCl	Chemically pure PbCl ₂	A. D. Mackay, Inc.	Allied Chem. and Dye	Grind together, press fusing
RbBr:Pb	Chemically pure RbBr	Chemically pure PbCl ₂	A. D. Mackay, Inc.	Allied Chem. and Dye	Melting, press fusing
RbI:Pb	Chemically pure RbI	Chemically pure PbCl ₂	A. D. Mackay, Inc.	Allied Chem. and Dye	Melting, press fusing Grind together, press fusing

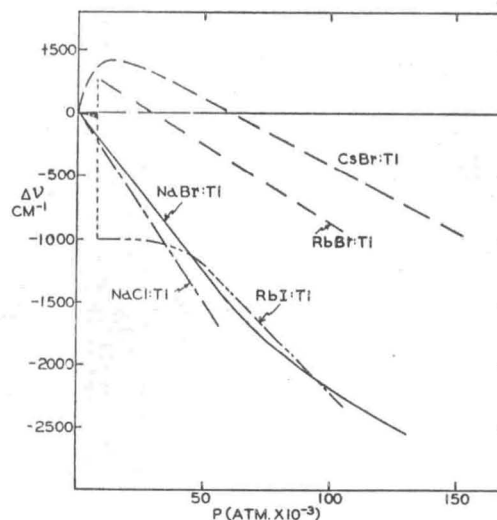
Table 1. Phosphor crystals—(continued)

Phosphor	Starting materials		Source		Preparative procedure(s)
	Host Crystal	Impurity	Host	Impurity	
CsI:Pb	Single crystal CsI	Chemically pure PbCl ₂	Harshaw Chem. Co.	Allied Chem. and Dye	Melting, press fusing
CsCl:Pb	Chemically pure CsCl	Chemically pure PbCl ₂	Fisher Scientific Co.	Allied Chem. and Dye	Melting, press fusing
NH ₄ Br:Pb	Chemically pure NH ₄ Br	Chemically pure PbCl ₂	Allied Chem. and Dye	Allied Chem. and Dye	Melting, press fusing
KCl:In	Single crystal KCl:In		Dr. F. E. Williams, General Electric Co.		None
KBr:In	Single crystal KBr	Chemically pure In	Harshaw Chem. Co.	A. D. Mackay, Inc.	Melting, press fusing
KBr:Bi	Single crystal KBr	Chemically pure BiCl ₃	Harshaw Chem. Co.	Allied Chem. and Dye	Melting, press fusing
KCl:Cu	Single crystal KCl	Chemically pure CuCl ₂	Harshaw Chem. Co.	Mallinkrodt Chem. Co.	Melting, press fusing
KBr:Cu	Single crystal KBr	Chemically pure CuCl ₂	Harshaw Chem. Co.	Mallinkrodt Chem. Co.	Melting, press fusing

DISCUSSION

The effect of pressure on the Tl⁺ ion in alkali halide lattices

The effect of pressure on the spectra of the *A* band in ten alkali halides activated with thallium has been measured to as high as 158,000 atm. In five cases (NaI:Tl, KCl:Tl, KBr:Tl, KI:Tl and CsI:Tl) the data have been reported previously.⁽¹³⁾ The data on the other five phosphors (NaCl:Tl, NaBr:Tl, RbBr:Tl, RbI:Tl and CsBr:Tl) are shown in Fig. 1. For those phosphors which crystallize in the sodium chloride structure (face-centred cubic), the shift with increasing pressure is to lower energy. On the other hand, for those which crystallize in the cesium chloride structure (simple cubic), up to 15,000 atm a shift to higher energy is observed. At higher pressures the shift is to lower energy. A plot of the initial frequency shift vs. pressure for these crystals (see Fig. 2) reveals two important facts. In the first place, the shift is strongly dependent upon the crystal structure, or in other words, the impurity center is dependent upon the bulk crystalline field. On the other hand, no significant

FIG. 1. "A" peak frequency vs. pressure—five alkali halides activated by Tl⁺.

dependence upon the nearest neighbor halides is observed. For example, similar shifts are observed for KI:Tl, KBr:Tl and KCl:Tl. Thus the halide

Table 2. Sp
tion

Crystal
NaCl
NaBr
NaI
KCl
KBr
KI
RbBr
RbI
CsBr
CsI
0.8KI/0.2K
0.6KI/0.4K
0.4KI/0.6K
0.2KI/0.8K
KCl
KBr
KBr
NaCl
NaBr
NaI
KCl
KBr
KI
RbCl
RbBr
RbI
CsCl
CsI
NH ₄ Br
NH ₄ I
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Approximate location of the "A" band absorption due to impurities in alkali halide crystals

Crystal	Impurity	Peak (Å)	Ref. No.	Max. pressure (atm.)
KCl	Thallium	2540	8	50000
RbCl	Thallium	2670	8	127000
NaCl	Thallium	2930	8	50000
KBr	Thallium	2475	8	50000
RbBr	Thallium	2610	8	130000
KI	Thallium	2870	8	129500
RbI	Thallium	2590	8	94000
NaBr	Thallium	2860	8	110000
NaI	Thallium	2630	8	158000
KCl	Thallium	2990	8	118000
.2KI/.2KBr	Thallium	2858	—	124000
.4KI/.4KBr	Thallium	2836	—	50000
.4KI/.6KBr	Thallium	2810	—	50000
.2KI/.8KBr	Thallium	2708	—	50000
KCl	Indium	2815	9	120500
KBr	Indium	2930	10	131000
KBr	Bismuth	3712	—	114000
NaCl	Lead	2740	11	131000
NaBr	Lead	3040	11	111500
NaI	Lead	3578	—	50000
KCl	Lead	2730	11	140000
KBr	Lead	3020	11	170000
KI	Lead	3542	—	130500
RbCl	Lead	2720	11	50000
RbBr	Lead	3004	—	120000
RbI	Lead	3541	—	5000
CsCl	Lead	2849	—	89000
CsI	Lead	3705	—	50000
NH ₄ Br	Lead	3077	—	143000
NH ₄ I	Lead	3580	—	1
KCl	Copper (ic)	2650	12	50000
KBr	Copper (ic)	2650	12	117000

ions next to the impurity produce at most a perturbation on the system, but not a first-order effect. This is consistent with the Seitz model, but inconsistent with the complex ion model.

At phase transitions, such as occur in the potassium halides at around 20,000 atm, a discontinuous shift in the A-band frequency is observed. These shifts are to lower energies for the alkali iodides and to higher energies for the alkali bromides or chlorides. This is possibly related to the much stronger spin-orbital interaction

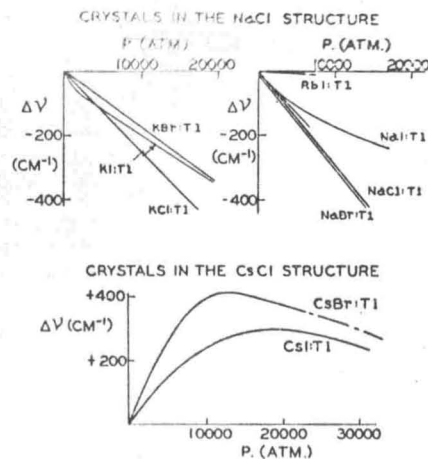


FIG. 2. Initial frequency shift vs. pressure—ten alkali halides activated by Tl⁺.

of the iodide ion, compared to the chloride or bromide.

A study was made to determine if varying the impurity concentration affected the pressure shift of the impurity spectra. Thallium activated potassium iodide, in concentrations from 2×10^{-1} per cent to 4×10^{-3} per cent was used for the study. No dependence on concentration was observed.

Measurements have been made of the spectra of several mixed crystals of potassium bromide and potassium iodide, activated by thallium, and of the effect of pressure on this spectra. The spectral

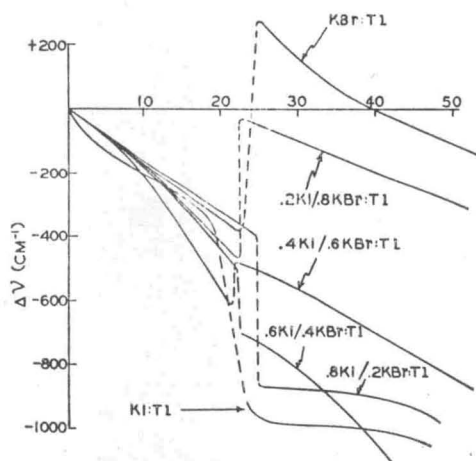


FIG. 3. The effect of pressure on A-band spectra in mixed crystals of KI:Tl and KBr:Tl.

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position of the A band at 1 atm. in these mixed crystals is tabulated in Table 2. It can be seen that in the mixed crystals, the iodide ion is a much stronger perturbing force than the bromide ion, since the mixed crystal spectra are displaced towards KI:Tl. This is to be expected, since the iodide ion is both larger and more polarizable than the bromide ion.

The effect of pressure on these mixed crystals is shown in Fig. 3. A gradual change in the magnitude of the transition discontinuity occurs, proceeding from KI:Tl to KBr:Tl in a regular manner.

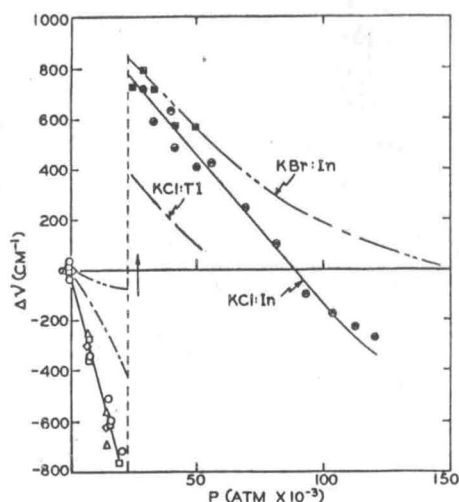


FIG. 4. "A" peak frequency vs. pressure—KCl:In; KBr:In (KCl:Tl shown for comparison); data points are for KCl:In.

The effect of pressure on the In⁺ ion in alkali halide lattices

Studies have also been made of the effect of pressure on the spectra of the A band in potassium chloride and potassium bromide activated by indium (see Fig. 4). The shifts are similar to those for thallium, but greater in magnitude. This difference can possibly be attributed to the difference in ground state force constant of the two impurity ions.

The effect of pressure on the lead ion in alkali halide lattices

The effect of pressure on the spectra of the A band in twelve alkali halides activated with lead

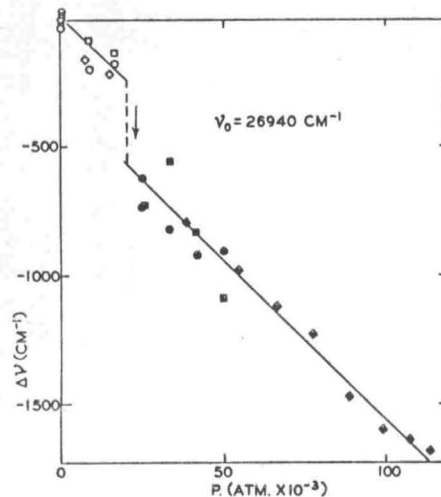


FIG. 5. "A" peak frequency vs. pressure—KBr:Bi.

has been measured to as high as 170,000 atm. The systems studied and the pressure range for each are given in Table 2. The data are shown in Figs. 6-8. In general, the frequency of the band initially shifts to higher energy, except at phase transitions. Then, at very high pressures the shift reverses and moves to lower energy. It is believed that the tendency to shift to higher energy may be connected

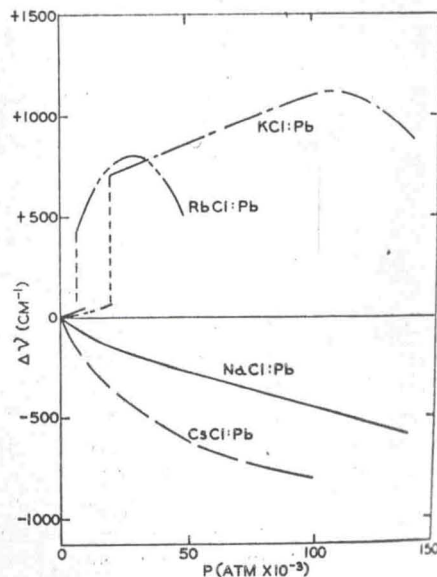


FIG. 6. "A" peak frequency vs. pressure—four alkali chlorides activated by Pb²⁺.

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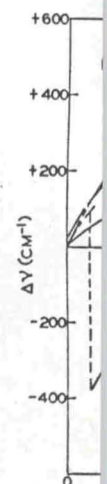


FIG. 7. "A"

halide io sistent th On the o between structure sodium consisten sistent w ment with that the ference r tively ch contain It sho energy o gardless e sufficient pressures where the ant contri

with the presence of a bound vacancy, adjoining the divalent impurity (it has been shown that such vacancies are usually completely bound to the impurity atoms⁽¹⁴⁾).

It can be seen that the initial frequency shift versus pressure for these crystals follows quite a different pattern from the thallium data discussed above. In the first place, the shift is strongly dependent upon the nature of the nearest neighbor

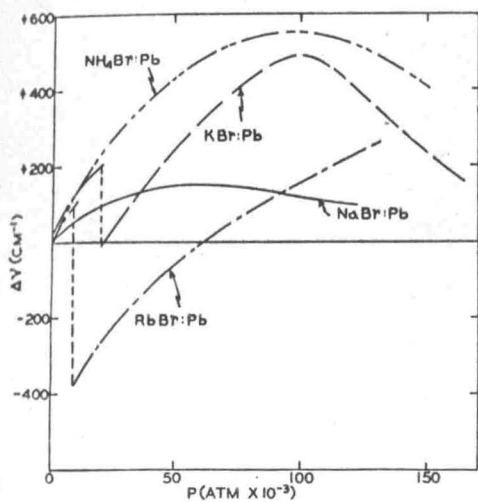


FIG. 7. "A" peak frequency vs. pressure—four alkali bromides activated by Pb^{++} .

halide ions; a dependence, moreover, which is consistent throughout the four cation systems studied. On the other hand, there is no significant difference between those crystals in the cesium chloride structure (the cesium halides) and those in the sodium chloride structure (the others). This is consistent with the complex ion model, but inconsistent with the Seitz model. This is also in agreement with the findings of FREDERICKS and SCOTT⁽¹⁵⁾ that the mobile lead-containing center in transference measurements on these crystals is negatively charged, and must therefore be a complex containing halide ions.

It should be noted here that a shift to lower energy occurs for all alkali halide phosphors, regardless of impurity or of crystal structure, given sufficiently high pressure. At these very high pressures, the system is compressed to the point where the repulsive energy is probably the dominant contribution to the crystal energy in the ground

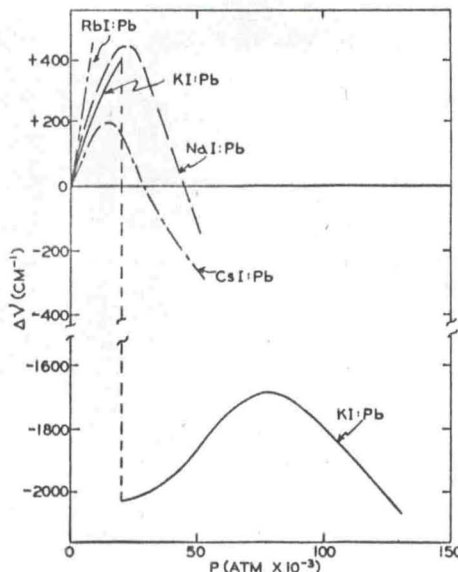


FIG. 8. "A" peak frequency vs. pressure—four alkali iodides activated by Pb^{++} .

state. This repulsive energy is very sensitive to changes in the lattice constant. The excited state probably has a flatter curve of energy vs. lattice constant than the ground state. Thus the energy

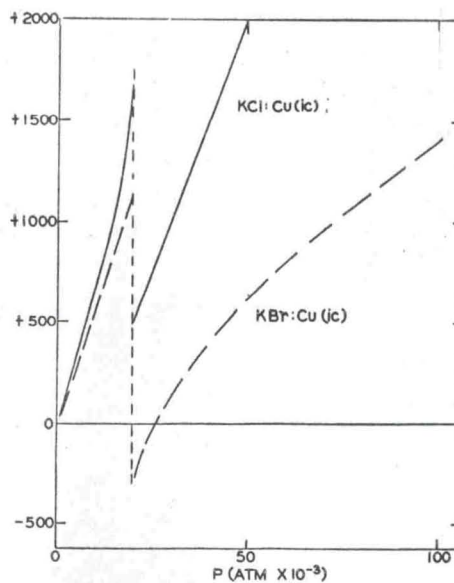


FIG. 9. "2500 Å" peak frequency vs. pressure $\text{KCl}:\text{Cu}(\text{ic})$ and $\text{KBr}:\text{Cu}(\text{ic})$.

of the ground state would increase with pressure more rapidly than the excited state energy, causing a lowering of the transition energy.

The effect of pressure on the copper ion in alkali halide lattices

Experiments with both cuprous and cupric ion impurity in alkali halides confirm the findings of BOESMAN and DEKEYSER⁽¹⁶⁾ to the effect that the absorption band at approximately 2500 Å is caused by copper in the cupric state. This band has been studied as a function of pressure to 117,000 atm in potassium bromide and to 50,000 atm in potassium chloride (see Fig. 9). Very similar shifts occur in the two cases; strongly to higher energy except at phase transitions. This leads to the conclusion that the band results from an almost completely internal transition, probably between *d* electron levels split by the crystal field.

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