

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

R. A. EPPLER and H. G. DRICKAMER

Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois

(Received 18 November 1959; revised 10 December 1959).

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.

* This work was supported in part by AEC Contract AT(11-1)-67, Ch.E. Project 5.