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Emission spectra in KI:Tl and RbI:Tl phosphors with CsCl-type structure

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KI:Tl crystal shows a drastic change in the emission and excitation spectra upon the phase transition from the NaCl phase to the CsCl phase under hydrostatic pressure. There appears two sets of the *A*-like emission and their corresponding excitation bands. It seems that in the CsCl phase, there exist two similar excited states with the *A*-like adiabatic-potential-energy surface having two kinds of minimum points, that is, in the CsCl phase the one corresponding to the *A* state in the NaCl phase and another new one like the *A* state. The measurement of the pressure effects is carried out at 1.5 K to avoid thermal quenching.

I. INTRODUCTION

Tl^+-like-ion doped alkali-halide phosphors have been studied by many authors, and their absorption and emission spectra have been interpreted by the ionic model of the impurity ion, though there are some questions. On the other hand, cesium-halide phosphors (especially cesium-iodide phosphor) show very complicated absorption and emission spectra which cannot be interpreted by the simple ionic model. However, it is not clear whether the above situation is due to the CsCl-type structure or to the character of the cesium ion. The measurement of the pressure effects of the absorption and emission spectra is a useful method to answer the above questions because we can change alkali halides of NaCl phase to those of CsCl phase by applying pressure, that is, we can investigate crystals with the same composition in different crystal structures.

There is much literature on the pressure effects of the emission of Tl^+-like-ion doped alkali-halide phosphors, Masunaga *et al.*[1] have investigated the pressure effects on the competition between the A_T and A_X emissions of several phosphors in the NaCl phase. Drotning and Drickamer,[2] and Klick and Drickamer[3] have also investigated the same subject under higher hydrostatic pressure, i.e., both in the NaCl and in the CsCl phase. Their studies, however, have been carried out at room temperature or at lower temperatures down to 100 K, within the framework of the *A* emission in the NaCl phase (a single set of *A* emission bands and their corresponding excitation band). In the present work, we have carried out a pressure-effect experiment at liquid-helium temperature to get more detailed data on the emission and excitation spectra, with particular concern for the characteristic aspect of the *A*-like emission and excitation spectra in the CsCl phase. The reason why we are mainly concerned with the *A*-like emission has to do with the following facts: (i) Contrary to the *B* and *C* emission bands, the *A* emission in the NaCl phase is a characteristic which consists of two emission bands, A_T and A_X. (ii) Upon the phase transition from the NaCl phase to the CsCl phase there appears two sets of *A*-like emission, i.e., the one corresponding to the *A* emission in the NaCl phase and another new *A*-like emission. (iii) On the other hand, in the *B* and *C* emission, or in their wavelength region, there does not occur any drastic change following phase transition.

II. EXPERIMENTAL

Figure 1 shows the pressure cell used for the optical measurement which is held in a cryostat made of fused quartz and stainless steel, and cooled with liquid helium. A pair of WC anvil-type pistons and a WC cylinder constitute the main part of the cell. The sample (2 mm in diameter, 0.5–1 mm in thickness) sandwiched with sapphire spacers, are inserted in the WC cylinder. The sapphire spacers also serve as optical windows. The pressure is supplied by a 0.7-ton oil press and transmitted to the pressure cell by a stainless-steel rod. A 40-W hydrogen lamp is used as a light source for absorption and a 200-W deuterium lamp is used for emission. The exciting light monochromated by a prism monochromator is focused on the sample. The emission light from the sample is detected by means of an arrangement consisting of a quartz lens, a CT-100 type grating monochromator, a HTV-*R*376 photomultiplier, and a lock-in amplifier. Since the emission is observed in the direction of incidence, the incident light is appropriately scattered by the specimen which is prepared to be somewhat opaque in order to prevent mixing with the emission

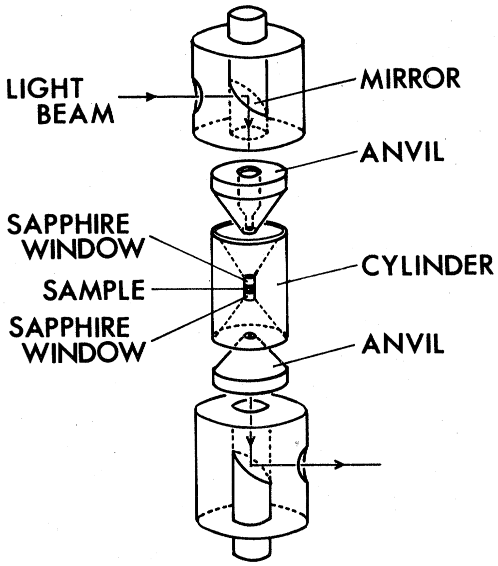

FIG. 1. High-pressure cell.

light. The samples of KI:Tl and RbI:Tl are obtained by cleaving single crystals grown by the Kyropolous method, adding TlI to the melt.

III. RESULTS AND DISCUSSION

When hydrostatic pressure is applied over 15.6 kbars (as expected from Clausius-Clapeyron's equation; the phase-transition pressure at 1.5 K is somewhat reduced with respect to that at room temperature), the KI:Tl crystal shows the phase transition from NaCl phase to CsCl phase, accompanying a drastic change in the emission spectra.[4] There appears two emission sets having features similar to those of the A emission of the NaCl phase which consists of the A_T and A_X emission bands, upon the phase transition. These emission sets have their own excitation bands peaking near the A absorption band.

Figure 2 shows the emission and excitation spectra of KI:Tl crystal: (a) shows the A emission band and its excitation band at atmospheric pressure, (b) shows those at 9.6 kilobars, and (c) shows the aspect upon phase transition, where we can see two sets of emission and excitation spectra, i.e., the A_T, and A_X, and A set, and the A'_T, and A'_X, and A' set. The A_T and A_X emission bands appear by irradiation in the A band, and A'_T and A'_X appear by irradiation in the A' band. The excitation spectrum (solid line A and A') is observed by excitation for the A_T emission band (336 nm), and the excitation spectrum (dashed line A and A') by excitation for the A'_X emission band (410 nm). Figure 3 shows the case for RbI:Tl crystal: (a) shows the A emission band and its excitation band at atmospheric pressure, (b) shows the aspect upon phase transition where we can see two sets of emission and excitation spectra similar to those of KI:Tl phosphor, and (c) shows the spectra at 12 kbars. The emission spectra are not corrected for the transmission function of the monochromator and the wavelength dependence of the detector in all figures. These emission bands, A_T and A'_T, and A_X and A'_X, clearly have a different peak position, though they appear in the same wavelength region. It is interesting to note that in A emission, the A_X band is weaker than the A_T band, in the NaCl phase at 1.5 K, and vice versa in A' emission, for both KI:Tl and RbI:Tl.

In KI:Tl phosphor, we could not observe the absorption bands corresponding to the excitation bands A and A'. At room temperature the sapphire window breaks before the phase transition because of the

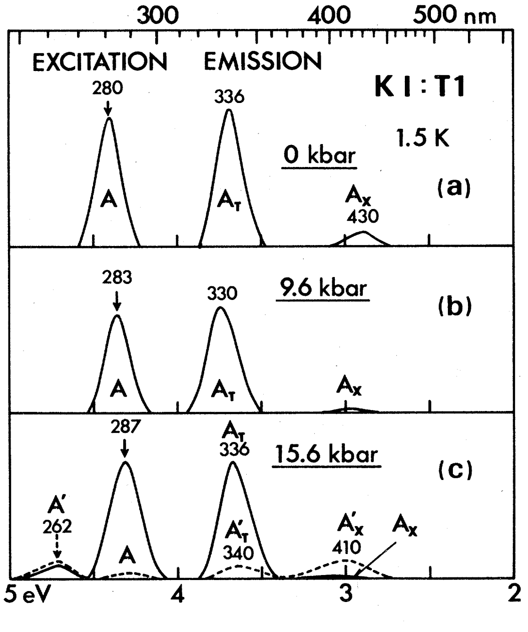

FIG. 2. Emission and excitation spectra of KI:Tl for several pressures at 1.5 K. (a) Emission spectra excited in the A band and excitation spectra for 336-nm emission (A_T) at 1 atm. (b) The same spectra at 9.6 kbar. (a) and (b) show the spectra for the NaCl phase. (c) Spectra for the CsCl phase at 15.6 kbar. Upon the phase transition, two A-type bands, A and A' appear. The emission spectrum excited in the A band (287 nm) is shown by the solid line A_T and A_X, and the spectrum excited in the A' band (262 nm) is shown by the dashed line A_T' and A_X'. The excitation spectrum for the A_T or A_T' emission band is shown by the solid line A and A', and the one for the A_X' or A_X emission band is shown by the dashed line A and A'. Emission and excitation spectra shown by dashed lines are so weak that they are drawn enlarged by a factor of 3.

high-transition pressure of this phosphor. While at low temperature the sapphire window becomes strong and does not break upon phase transition, but the crystals become so opaque that we cannot measure the absorption spectra, though the emission and excitation spectra can be observed anyway. (The crystals become that opaque upon the phase transition at low temperature.) It may be reliable that there exist absorption bands peaking at the wavelength of the *A* and *A'* excitation bands. Actually, we can find the corresponding absorption bands in the data at room temperature of the earlier experiment by Eppler and Drickamer[5] where they were not so much concerned with this absorption. In RbI:Tl phosphor, we can observe the absorption bands corresponding to the *A* and *A'* excitation bands at low temperature. In this case, we can cause a phase transition at room temperature without breakdown of the sapphire window because of the low transition pressure of this crystal, and can measure the absorption spectra after cooling the crystal without inducing opacity in the sample. Here, we see that the absorption band corresponding to the *A* excitation band has a comparable bandwidth to that of the *A* band in the NaCl phase, while the absorption band corresponding to the *A'* excitation band has a far broader width than the former. Therefore, we might say that the former corresponds to the *A* band in the NaCl phase and the latter to another *A*-like band which appears newly in the CsCl phase. The above conclusion is also derived from the characteristics of the pressure or temperature peak shift of these absorption bands.

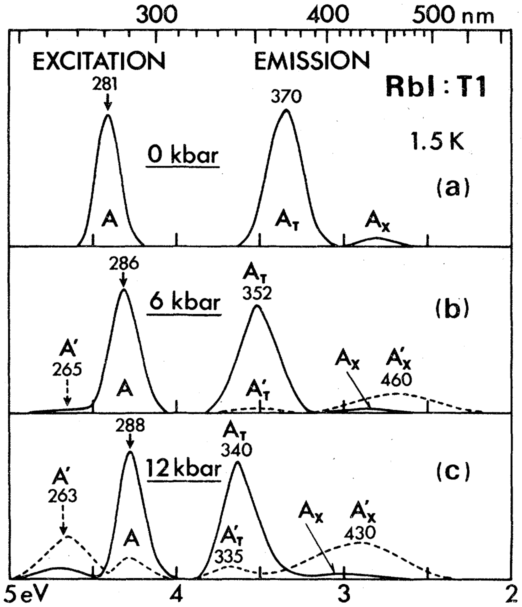

FIG. 3. Emission and excitation spectra of RbI:Tl for several pressures at 1.5 K. (a) Emission spectra excited in the *A* band and excitation spectra for 370 nm emission (A_T) at 1 atm. These are the spectra for the NaCl phase. (b) Spectra for the CsCl phase at 6 kbar. Upon phase transition, two *A*-type bands, *A* and *A'* appear. The emission spectrum excited in the *A* band (286 nm) is shown by the solid line A_T and A_X, and the one excited in the *A'* band (265 nm) is shown by the dashed line A_T' and A_X'. The excitation spectrum for A_T or A_T' is shown by the solid line *A* and *A'*. The observation of the excitation spectra for A_X or A_X' is omitted. (c) The same spectra at 12 kbar. The emission spectrum excited in the *A* band (288 nm) is shown by the solid line, and the one excited in the *A'* band (263 nm) is shown by the dashed line. The excitation spectrum for A_T or A_T' is shown by the solid line *A* and *A'*, and the one for A_X' or A_X is shown by the dashed line *A* and *A'*.

From the above emission, excitation, and absorption spectra, it is unquestionable that there exist two *A*-like adiabatic-potential-energy surfaces (APES) having two kinds of minimum points. This feature is observed in potassium or rubidium iodide crystals, but not the chloride and bromide crystals.

Concerning the origin of the two *A*-like APES, though we cannot say anything decisively at present, it seems to come from the excited state of the thallium ion and the charge-transfer state mutually mixed by the configuration interaction. In alkali-halide thallous phosphors with NaCl-type structure, from the separation between the *C* and *A* bands and the absolute value of the spin-orbit coupling matrix element of the free thallium ion (the minimum splitting condition), Knox[6] proposed a configuration mixing between the excited singlet *P* state of the Tl^+ ion and the charge-transfer state from the neighboring halogen ions to the Tl^+ ion, and estimated the degree of configuration mixing. The *D* band is attributed to the perturbed exciton band (or the transition to the singlet charge-transfer state), and in KI:Tl we can find that a give and take of the intensity between the *C* and *D* bands is caused by applying hydrostatic pressure at low temperature. This situation will support the possibility of configuration mixing between the singlet states described above. It is natural to expect that there also exist the absorption band due to the triplet charge-transfer state and configuration mixing between the triplet charge-transfer state and the triplet excited state ($^3P_1$) of the Tl^+ center. The appearance of the *A* and *A'* bands which correspond to the *C* and *D* bands in the singlet case, respectively, would suggest the above expectation. In alkali-iodide crystals, iodine has a strong tendency to form a covalent bonding with alkali metals, and moreover iodine has a larger spin-orbit coupling than bromine and chlorine (based on the doublet separation of these halogens). This situation would support the appearance of the comparatively strong absorption due to the triplet charge-transfer state which might sometimes be affected by mixing with the triplet excited state of the Tl^+ center.

However, we have not detailed molecular-orbital theory and not enough experimental data on the CsCl phase (for example, data on the exciton band) to explain more precisely the above explicit effect of the host crystals manifested in the energy-level scheme of the Tl^+ center. The question why two *A*-like bands appear only in the CsCl phase remains open.

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