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Effect of Grinding on the Low Temperature Photoluminescence of Certain Molecular Crystals

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Effect of Grinding on the Low Temperature Photoluminescence of Certain Molecular Crystals

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The wavelengths of the vibronic peaks of the low temperature photoluminescence of anthracene, phenanthrene, benzophenone and phthalic acid crystals do not change considerably, but their relative intensity changes significantly with grinding. The dislocations may change both the absorption coefficient and absorption spectra of the crystals, hence the photoluminescence emission may be affected by the grinding.

INTRODUCTION

It is well known that the presence of impurities can strongly influence the physical properties of the crystals. In many cases, the presence of dislocations and other defects is determined from the physical properties of crystals that depend on the defect themselves. Photoluminescence (PL) is chiefly a phenomenon related to the surface property of the crystals. The surface of the crystals can be highly deformed during their grinding. Hence, it will be interesting to check how the grinding affects the PL of the crystals. The present paper reports the effect of grinding on the low temperature PL of certain molecular crystals. The effect of grinding on the PL of molecular crystals is least understood.

EXPERIMENTAL

The crystals of phenanthrene were grown from the melt using Bridgman technique. The crystals of benzophenone and phthalic acid were grown from the slow evaporation of their solution in acetone. The crystals of anthracene were obtained from the slow evaporation of their solution in ethanol. The PL spectra were determined using a Spex spectrofluorometer. For the determination of PL at low temperature, the sample in a quartz tube was placed inside a Dewar filled with liquid nitrogen. For the determination of the PL in powder form, the samples used for the PL determination in crystal form, were ground to a powder form. Narrow slits were used for exciting and detecting the PL, so that the sensitivity of the device was ± 1 nm.

RESULTS AND DISCUSSION

Figure 1 shows the low temperature PL spectra of anthracene, phenanthrene, benzophenone and phthalic acid crystals. It is seen that the

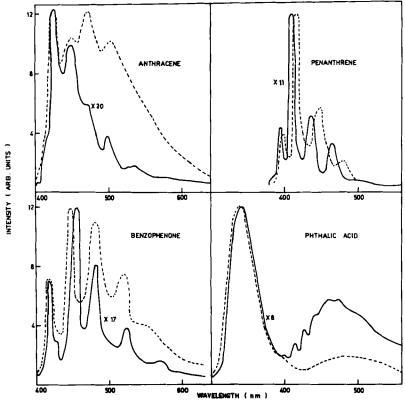


FIGURE 1 Effect of pressure on the low temperature photoluminescence of certain molecular crystals. (——— crystals, ———— powders)

grinding changes considerably the PL of anthracene, phenanthrene, benzophenone and phthalic acid crystals. In anthracene, the PL emission in the crystalline form possesses a main peak at 426 nm and five other vibronic peaks of low intensity at 449, 468, 497, 534 and 580 nm. After the grinding, no considerable change is found in the wavelength of the vibronic peaks. The main peak after grinding occurs at 468 nm and the relative intensity of the vibronic peaks changes significantly. The vibronic peaks of phenanthrene crystals shift towards longer wavelengths with grinding of the crystals. The change in the relative intensity of vibronic peaks is less as compared to that in anthracene crystals. The main PL peak in phenanthrene crystals does not change with grinding. The vibronic peaks shift towards shorter wavelengths with grinding of benzophenone crystals. There is change in the relative intensity of the vibronic peaks, but the main PL peak does not change with grinding. In phthalic acid, the grinding suppresses significantly the peaks at the higher wavelength side of the PL spectra. The overall PL intensity decreases many times after the grinding of the crystals. The PL emission in anthracene and benzophenone crystals may be assigned to $(\pi^* \to \pi)$ and $(T \to S)$ transitions respectively. The emission in phenanthrene crystals has been assigned to ¹L_b florescence. It is known that the phthalic acid exhibit PL, but the responsible states have not been assigned.

It is well known that the grinding affects the PL of phosphors. The decrease in the PL intensity has been explained to be due to the creation of new traps, increased scattering of exciting and luminescent radiation, change of wurtzite into sphalerite, decomposition of luminescent centers and increase in the probability of non-radiative transitions, or by simultaneous influence of some of these factors. 1-5 It is known that the hydrostatic pressure affects the PL emission of the crystals. High local pressure may exist at the dislocations on the surface of the crystals, hence the change in the PL may be speculated to be due to the creation of dislocations during the process of grinding. Since no considerable shift of vibronic peaks occurs with the grinding of the crystals, the local pressure at the dislocations should be less and, as a matter of the fact, the large changes in the relative intensity of the PL emission due to grinding should not be due to the local pressure near the dislocations. It seems that the dislocation changes both the absorption coefficient as well as absorption spectra of the crystals, hence the PL emission is affected by the grinding. Thus, the present investigation provides an idea of interaction of dislocations with the electron states in the molecular crystals.

In some cases, where the PL spectra have to be compared, the grind-

ing-effect may be of importance. For example, the mechanoluminescence or triboluminescence spectra resemble the PL spectra of powder form but they differ from the PL spectra of crystalline form. In the studies of high pressure PL, fine powders are used. Sometimes, the zero pressure study is made either in crystalline form or in powder form. The present investigation shows that for the better comparison, the zero pressure study of PL should be made in powder form.

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