CHAPTER III
MECHANOLUMINESCENCE SPECTRA OF X-RAY IRRADIATED ALKALI
HALIDE CRYSTALS

3.1. INTRODUCTION

Spectroscopy plays a significant role in understanding and elucidating the mechanism of luminescence. In the beginning, it was believed that the spectroscopy may be useful in ascertaining whether the ML emission is incandescent, or gas discharge or is solid state luminescence from the excited states of the molecules comprising the crystals. However, the very weak intensity of ML and its short duration ruled out the use of conventional spectrograph for recording the ML spectra. Initially many workers tried to understand the nature of the ML by the visual observations of the colour of the ML emission, and by using the colour filters. (Trautz 1909, Levison 1904, Waggoner 1917, Burke 1898, Weiser 1918, Wick 1937). Longchambon (1922) first succeeded in taking the photograph of the ML spectra of a few substances by giving exposures of many hours duration and by using a large amount of the materials. Nelson (1926) was successful in photographing the ML spectra of a number of substances such as sphalerite (zinc sulphide ore), chlorophane (calcium fluoride ore) and artificial zinc sulphide. Inoue et al (1939) were successful in recording spectrographically the ML spectra of sugar and tartaric acid crystals.
Stranski et al (1955) were successful in photographing the ML spectra of arsenolite crystals. The ML spectra of only a limited number of substances could be investigated before the present day devices described below, were available.

The two best devices for recording the ML spectra are: (i) Monochromator based spectrometer, and (II) image intensifier spectrometer. Belyaev and Martyshev (1969) have used a monochromator to measure the ML spectra. In this device the ML emission is collimated by a quartz lens and then passed through a quartz window. The beam is further divided by a quartz plate in two parts. One part of the beam passes directly to the first photomultiplier tube, the remainder falls on a monochromator and through it to the second photomultiplier tube. The output pulses from the two photomultiplier tubes are compared directly on a double beam oscilloscope or more conveniently, a ratiometer is used. By rotating the drum of the monochromator, it can be set for any wavelength. The ML spectra can be determined by measuring the ratio of the intensity of the output pulses of the two photomultiplier tubes, at different wavelengths. Butler (1966) and Hardy and Zink (1976) have also used the monochromator based spectrometer for the determination of the ML spectra.

The other device for recording the ML spectra is an image intensifier spectrometer (Walton and Botos 1978). In this system the input photo-cathode of a four stage image intensifier (EMI Type 1964) is located in the place,
that would be occupied by the plate in a conventional spectrograph. The dispersion of the spectrometer is such that a spectrum extending from 400 to 620 nm will fill the input photo-cathode. The output phosphor of the intensifier is photographed with a conventional camera. Overall photon gain of the system is such that even a single electron leaving the first photo-cathode will give rise to a visible spot on the developed emulsion. It takes only about $10^4$ to $10^5$ photons incident on the photo-cathode to produce a visible line on the emulsion.

A few workers have studied the ML spectra of coloured alkali halide crystals. Butler (1966) has taken the ML spectra during the plastic deformation of eight alkali halide crystals irradiated with γ-rays. Leider (1958) have recorded the ML spectra of X-ray coloured KBr crystals. Zenchukov and Shmurak (1970) have reported the ML spectra of γ and X-rays irradiated KCl, and KCl : Sc crystals. It has been described in the Chapter II, that ML appears in X-ray irradiated alkali halide crystals during the application as well as release of pressure. In this chapter we described the ML spectra of coloured KBr, KCl, KI, LiF and NaCl crystals produced during the application as well as release of pressure, and compared them with the spectra of other types of luminescence.

3.2. EXPERIMENTAL

For the ML measurements, the crystals of small size were cleaved from the central lower portion of the
large size single crystals supplied by the National Physical Laboratory, New Delhi. The small size crystals were annealed at 450°C for about two hours and cooled very slowly. The X-ray irradiation was carried out at room temperature by X-ray tube having tungsten target operating at 40 kV with 20 mA filament current. The ray irradiation was carried out from a $^{60}$Co source (1.25 Mev). A uniaxial pressure was applied to the specimen by placing heavy load with almost zero velocity following the technique described in our earlier investigation (Chandra and Alyas 1976, also described in Chapter II). The ML spectra during the application and release of pressure from the crystals were recorded by placing band pass filters (Schott Mainz) between the crystal mounting platform and the photomultiplier tube (RCA 1P28) housing as shown in Fig. 3.1. The output of the photomultiplier tube was fed to the amplifier and monitored by a strip chart recorder. At least three crystals were used at each wavelength for determining the ML spectra. The ML intensities of the first pressing and first release were used for determining the ML spectra. The ML intensity was normalized with respect to mass of the crystals and for the different transmission coefficients of the filters. The irradiated specimens wrapped in aluminium foil were kept in dark for about an hour to allow the after glow to decay to a value well below that expected in the ML measurements. All the measurements were carried out in a dark cell.
Fig. 3-1- A schematic diagram of the device used for the determination of the mechanoluminescence spectra. (1) Vertical stand; (2) Platform; (3) cylinder with uniform bore; (4) Just fitting cylinder spring; (5) exactly fitting solid rod passing through the central hole of the platform; (6) axial for supporting hanger; (7) load and adjustable hanger; (8) Clamp for lever; (9) lever rod; (10) mount of the PM tube; (11) Glass plate for mounting the crystal; (12) PM tube IP28; (13) Adjustable rod; (14) Guiding rod for lever; (15) guide for central rod; (16) crystal; (17) filter.
For studying the ML spectra at different temperatures, the device described in Chapter VI (Fig. 6-1) was used.

3.3 RESULTS AND DISCUSSION

Figures 3.2 and Fig. 3.3 show the ML spectra of X-ray irradiated KBr, KCl, KI, LiF and NaCl crystals recorded during the application and release of pressure. It is seen that the ML spectra recorded during the release of pressure are almost the same as those recorded during the application of the pressure. The error bars on the ML spectra show the standard deviation. The peak of ML spectra are found to be at 435, 420, 460, 300 and 380 nm for the X-ray irradiated KBr, KCl, KI, LiF and NaCl crystals. Butler has found the peak of ML spectra at 450, 430, 475, 365 and 295 nm for γ-irradiated KBr, KCl, KI, LiF and NaCl crystals. The difference in the ML spectra between our studies and those of Butler may be primarily due to measuring devices particularly the monochromators and the photomultiplier tubes.

The ML spectra of the γ-ray irradiated KBr, KCl, KI, LiF and NaCl crystals are also similar to those obtained from the X-ray irradiated crystals. The spectra were taken for the load of 1 Kg, 12.5 Kg and 25 Kg, but no appreciable effect of the load on the ML spectra were found. The spectra do not change also with the irradiation time of the crystals. The ML spectra do not change with
FIG. 3.2 ML SPECTRA AT THE RELEASE AND APPLICATION OF PRESSURE.
FIG. 3-3 ML SPECTRA AT THE RELEASE AND APPLICATION OF PRESSURE.
the successive number of pressings and releases of pressure. The ML spectra of X-ray irradiated KBr, KI, and KI crystals do not change, when they were taken during the fracture of the crystals. However, the ML spectra of irradiated LiF and NaCl crystals possess additional emissions between 300 to 400 nm, when the ML spectra were taken during the fracture of the crystal. Thus, the ML related to the colour centres and the ML related to the nitrogen emission, both are excited during the fracture of the X-ray irradiated LiF and NaCl crystals. The unirradiated KBr, KI, and KI crystals do not exhibit ML. However, the unirradiated LiF and NaCl crystals exhibit ML during their fracture. The test with the filters suggests that the ML emission from unirradiated LiF and NaCl crystals lies between 300 to 400 nm. This additional emission in both the cases are due to the adsorbed or absorbed nitrogen molecules (Chandra and Zink 1981).

The ML spectra of the X-ray irradiated KBr, KI, KI, LiF and NaCl crystals were determined at different temperatures (from 35 to 100°C). No appreciable effect of temperature was found on the ML spectra. However, the ML intensity changes considerably with the increasing temperature of the crystals as described in Chapter VI.

Table 3-1 shows the wavelength of the peak of the spectra corresponding to the ML, aqualuminescence (AL), Laser-induced luminescence (LL×), thermoluminescence (TL) and luminescence excited by high energy radiation (L₂LL×). It is seen that the \( \lambda_{max} \) of the ML emission is closer to
the \( \lambda_{\text{max}} \) of the luminescence excited by high energy radiations. Except LiF, the peak of the ML spectra is also closer to the peak of TI spectra.

Figure 3-4 shows that the wavelength \( \lambda_{\text{max}} \) corresponding to the peak of the ML spectra is directly proportional to the square of the lattice constant of the crystals. The values of the lattice constants were taken from the reference (Krishnam et al 1951). Such relation has also been found by Butler (1966). The plot between \( \lambda_{\text{max}} \) and the square of the lattice constants is known as Hollwe-ivey plot (Ivey 1947). The systematic correlation between the \( \lambda_{\text{max}} \) of the ML and the square of lattice constants indicates that the mechanism of the ML excitation should be the same in the X-ray irradiated alkali halide crystals.

The studies of the ML spectra indicate that the light emission during the mechanical deformation of coloured alkali halide crystals is not an incandescent phenomenon. The similarity between the spectra of ML and the luminescence excited by the high energy radiations suggests that some of the traps in the coloured alkali halide crystals are ionized during the mechanical deformation of the crystals. The MI emission may be due to the recombination of the electrons released from the trap to the holes present in the crystal. The similarity between the spectra of MI produced during release of the pressure and the spectra of MI produced during application of the pressure may be helpful in understanding the mechanism of MI emission during the release of the pressure.
Fig. 3-4 Dependence of the peak of ML spectra of X-ray irradiated KBr, KCl, KI, LiF, NaCl crystals on the square of their lattice constant.
Comparision of peaks of the Kα spectra with the peaks of the spectra of other types of luminescence of coloured KBr, KCl, KI, NaI and NaCl crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Lattice constant in Å</th>
<th>Wavelength related to the peak of the spectra in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBr</td>
<td>3.29</td>
<td>435, 450, 505, 430, 470, 540, 575 (from our studies)</td>
</tr>
<tr>
<td>KI</td>
<td>3.53</td>
<td>460, 475, 478, 540, 575, 430, 480, 500 (from our studies)</td>
</tr>
<tr>
<td>LiF</td>
<td>2.01 (TLJ-100)</td>
<td>300, 295, 398, 390, 390, 360, 360, 500 (at 140°C)</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.81</td>
<td>380, 385, 555, 600, 390, 490, 360, 500, 400 (at 150°C)</td>
</tr>
</tbody>
</table>
REFERENCES


