LASER-INDUCED FLUORESCENCE IN POTASSIUM MANGANESE SULPHATE SINGLE CRYSTAL

N. MANICKAM, P. CHANDRA SEKHAR, P. S. NARAYANAN, H. L. BHAT and C. K. SUBRAMANIAN
Department of Physics, Indian Institute of Science, Bangalore 560 012, India.

A study of the absorption and fluorescence of ions in different crystals provides information not only about the impurity atoms but also on the lattice phonons and their interaction with the electronic energy levels of the impurity ions\(^1,^2\). Therefore a laser-induced fluorescence study of Mn\(^{2+}\) ions in a potassium manganese sulphate \(\text{K}_2\text{Mn}_2(\text{SO}_4)_3\) crystal was made.

Potassium manganese sulphate (KMS) belongs to the Langbeinite family\(^3\), some of which are ferroelectric. KMS is not ferroelectric but undergoes a structural phase transition from the space group \(P2_13\) at room temperature (RT) to \(P2_12_12\) at low temperature (191 K). In the high temperature phase Mn\(^{2+}\) ions are on the three fold axes\(^4\). At low temperature they lose this symmetry and are situated in a general position. Raman spectroscopic studies of this phase transition have been made in this laboratory\(^5\) and in this connection its absorption spectrum was recorded but not studied in detail. There is no information in the literature on the absorption and fluorescence spectra of potassium manganese sulphate. The absorption spectrum of KMS was taken for the present sample at RT. It showed features similar to those of Mn\(^{2+}\) ion in MnF\(_2\) and RbMnF\(_3\) crystals\(^6,^7\).

The fluorescence spectrum was excited with the 337.1 nm line of a home made pulsed nitrogen laser (pulse length 8 ns, repetition rate 10 Hz, peak power 100 kW). The crystal was kept in a low temperature optical cryostat, whose temperature could be varied from liquid nitrogen temperature (LNT) to RT. The fluorescence collected at 90° to the incident nitrogen laser beam was collimated, filtered and focussed on the slit of a three prism glass spectrograph. The dispersed fluorescence spectrum of KMS at LNT showed a wide band extending from the red (\(\approx 6200 \text{ Å}\)) into the green region (\(\approx 5000 \text{ Å}\)). The fluorescence was considerably weaker at room temperature. Similar red fluorescence is reported by others\(^8,^9,^10\). By using a slit in the focal plane of the spectrograph, the red fluorescence portion of the dispersed spectrum centred around 6100 Å was focussed on a photomultiplier tube (RCA C31034) whose output was given to a digital storage oscilloscope (DMS6430).

The decay of the red fluorescence recorded at RT and LNT is shown in figure 1. It is clear from the figure that the fluorescence decay times are widely different at LNT and RT. Assuming a single exponential decay, the decay times are found to be

\[ \tau_{\text{LNT}} = 30 \text{ ms}, \quad \tau_{\text{RT}} = 0.8 \text{ ms}. \]

Further work is in progress to measure the fluorescence decay times at various temperatures from LNT to RT and close to the phase transition.

The authors thank Dr Vikram Kumar for the use of the digital storage oscilloscope and Dr B. Raghunathachary for the sample.

30 July 1987

5. Raghunathachary, B., Bhat, H. L., Narayanan, P. S. and European, V., Meeting on Ferroelec-
Two categories of phosphorites viz. (i) bedded phosphates, and (ii) white clayey phosphates are reported. The bedded phosphates are composed of microsparite, consisting of iron oxides and authigenic aphanic quartz (10–15 μm). The microsparite is composed of very fine randomly arranged crystallites of apatite (10–15 μm) (figure 1). The interstitial spaces and voids are filled with authigenic quartz and micritic calcite.

White clayey phosphorites are composed of apatite (7–10 μm) embedded in discrete clayey, siliceous matrix (figure 2).

About 10 specimens of both bedded and clayey phosphates were scanned for mineral identification using a X-ray diffractometer (Phillips), which indicates carbonate fluorapatite as the major constituent in bedded phosphates, whereas in clayey phosphates, quartz is the major and carbonate fluorapatite is the minor constituent (table 1).

Petrographic studies indicate that both the types of phosphates originated in euxinic basal condition developing in shallow cratonic Chattisgarh basin. The pyrite nodules in the underlying limestones indicate reducing conditions, whereas iron oxides in the voids of bedded phosphate were formed during early stages of diagenesis under oxidizing conditions.

The authors thank CSIR, New Delhi for financial assistance.

### Table 1 X-ray diffraction data of phosphorites of Lohara area

<table>
<thead>
<tr>
<th></th>
<th>Sp. No.</th>
<th>dA° Highest</th>
<th>II Highest</th>
<th>a°</th>
<th>c°</th>
<th>% CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bedded phosphate</td>
<td>NEB-14</td>
<td>2.803</td>
<td>2.703</td>
<td>9.376</td>
<td>6.917</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>SEB-9</td>
<td>2.798</td>
<td>2.699</td>
<td>9.357</td>
<td>6.906</td>
<td>3.85</td>
</tr>
<tr>
<td></td>
<td>NWB-6</td>
<td>2.800</td>
<td>2.702</td>
<td>9.359</td>
<td>6.894</td>
<td>4.30</td>
</tr>
<tr>
<td>Clayey phosphates</td>
<td>SWA'-15</td>
<td>2.805</td>
<td>2.707</td>
<td>9.377</td>
<td>6.913</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>SWB-9</td>
<td>2.806</td>
<td>2.708</td>
<td>9.378</td>
<td>6.919</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>NWA'-15</td>
<td>2.806</td>
<td>2.706</td>
<td>9.379</td>
<td>6.910</td>
<td>2.28</td>
</tr>
</tbody>
</table>

* % CO₂ based on Gulbrandsen’s* Peak pair method 2θ (004) – (410) values; N.D. Not determined.