## SOME OPTICAL PROPERTIES AND DEHYDRATION BEHAVIOUR OF CRYSTALLINE ZEOLITES

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Captions of the figures
CHAPTER - 8

SOME OPTICAL PROPERTIES AND DEHYDRATION BEHAVIOUR OF CRYSTALLINE ZEOLITES

8.1 Introduction

Potential applications of both natural and synthetic zeolites are related to their fundamental physical and chemical properties which in turn are related to their chemical composition and crystal structure. Results on studies of some of the optical properties of zeolite crystals, such as colour, refractive index, luminescence and also studies on dehydration behaviour are discussed in this chapter.

8.2 Colour

Zeolite crystals in pure state are colourless. Crystals of some natural zeolites, like natrolite and thin flakes of scolecite, are colourless and so transparent that it is difficult to see them in a matrix rock. However, in many cases impurities account for the colour of the crystal. Iron is a common impurity observed in zeolites of the present
study, viz. natrolite, scolecite, thomsonite, stilbite and heulandite. The author has established that iron impurity does affect the transparency of natrolite and scolecite crystals appreciably. From electron microprobe analysis, the author concludes that, pinkish or brownish colouration of thomsonite, stilbite and heulandite is due to presence of iron in them. Transparency of zeolite crystals varies with the degree of hydration. For example, transparency of natrolite and scolecite reduces when dehydrated above 300°C.

8.3 Refractive Index

Zeolite crystals can be reversibly dehydrated without any apparent change in their transparency or morphology. This is possible up to a particular temperature beyond which — due to structural change, or structural breaking — this reversibility of dehydration does not exist. This temperature limit is different for different zeolites. This particular property of hydration and dehydration was used to study the variation of refractive indices of zeolite crystals when intra-crystalline pore and channels, after
dehydration were occluded by different liquids such as alcohol, benzene and chloroform. A few transparent crystals of natrolite and scolecite were used for this study. On account of occlusion of intracrystalline pores and channels by different liquids, by qualitative measurements it is found that refractive indices of host crystals bear a definite relationship with the refractive indices of occluded liquids. Refractive index of the crystal increases in accordance with the refractive index of the occluded liquid.

8.4 Luminescence Studies

8.4.1 General

Luminescence and related electrical properties of crystals are some of the striking effects that are brought about by the introduction of impurities. During last three decades considerable amount of work has been carried out in the field of luminescence\(^1\)\(^-\)\(^5\) Methods and concepts of the luminescence process in solid phosphors occupy a key position in the study of solid state physics. Since results obtained with crystals of simple structure and known properties in pure state are more amenable
to interpretation, alkali halides have been widely used as host crystals for fundamental researches on phosphors. Alkali halides do not luminesce strongly in the pure state. Various attempts\textsuperscript{6-10} have been made to investigate the nature of the centres responsible for intrinsic luminescence of the alkali halides. A small amount of thallium introduced in an alkali halide, produces a luminescent material of considerable fundamental interest. To explain its experimental features, Seitz\textsuperscript{11} proposed a model in which activator ions enter the lattice substitutionally at cation sites. According to Seitz, Tl\textsuperscript{+} ions replace alkali ions in alkali halide lattices.

Substances which exhibit the property of luminescence are called phosphors. In those materials whose luminescence depends on impurities or defects in structure, the imperfections responsible for the characteristic of the luminescent emission are termed activators. Other imperfections that are essential to the luminescence of certain classes of inorganic solids, but have little influence on the spectral distribution of emission, are called coactivators.
Though alkali halides are still the predominant subjects for study in the present day luminescence research, luminescence studies have been carried out on many different types of crystals. In the present investigation, luminescence studies on few zeolite crystals are reported.

8.4.2 Luminescence in zeolites

Many natural zeolites were found to fluoresce in blue, blue-green, yellow-green, white-yellow and blue-white when illuminated by 365nm radiation\textsuperscript{12}. Activator elements such as manganese, lead, silver and copper can be introduced into the zeolite by cation exchange. Although zeolites exchanged with these activator ions do not exhibit photoluminescence when fully dehydrated, dehydration was found to develop cathodoluminescence in the manganese exchanged forms of chabazite and other zeolites. Copper and silver exchanged forms respond to ultraviolet excitation whereas on rehydration they do not. Kost et al\textsuperscript{14} reported low temperature luminescence spectra of napthalene adsorbed on crystalline zeolites.
Under uv excitation, silver exchanged zeolite X shows six emission bands with three peaks in the blue region ($B_1$, $B_2$, and $B_3$) and one each in green, yellow and red regions. Narita\textsuperscript{15} pointed out that the $B_1$ green and red bands are due to Ag\textsuperscript{+} centers, while $B_2$, $B_3$ and yellow bands are due to Ag centres. Kononov\textsuperscript{16} published his work on natural and structural types of stationary luminescent centres in zeolites by studying the excitation and emission spectra of natural zeolites. Spectroscopic studies of zeolite synthesis were carried out by McNicol et al\textsuperscript{17} in which they had shown that trace amounts of Fe\textsuperscript{3+} ions substituted for Al\textsuperscript{3+} in the tetrahedral aluminosilicate gel framework exhibit characteristic phosphorescence spectra, which had been used to follow the buildup of the zeolite framework. Recently, Bogomolov et al\textsuperscript{18} studied luminescence of tin-activated NaX zeolite. Studies on thermal fluorescent material for the manufacture of cathode-ray tube screens by the thermal decomposition of zeolites (in the presence of an alkali halide or with Na\textsubscript{2}SO\textsubscript{4}) are reported by Galves et al\textsuperscript{19}

8.4.3 Experimental

In the present investigation the emission
and excitation spectra of the zeolite crystals were studied at room temperature. Samples used for the study were some natural zeolites, viz. natrolite, scolecite, thomsonite, stilbite and heulandite. The phosphors were taken in the form of microcrystalline powder. Their chemical composition and impurity contents, were detected, and their approximate estimate was obtained by electron microprobe analysis.

In the present work excitation and emission spectra were examined and recorded by means of Aminco-Bowman spectrophotofluorometer manufactured by American Instruments Co. For most of the samples, the peak positions in excitation and emission spectra were determined by manual operation whereas in the case of a few samples of natrolite, scolecite and thomsonite, these spectra were recorded on the chart.

It was observed that the peak position of an excitation or emission band read from strip-chart was found to coincide with the position of the corresponding peak observed by the manual operation of the graduated disc.

3.4.4 Observations

Photoluminescence is observable in
some natural zeolites, viz. natrolite, stilbite, heulandite, scolecite and thomsonite. The peak positions of the bands in excitation and emission spectra observed are summarized in Tables 8.1, 8.2 and 8.3. The representative excitation and emission spectra, as recorded on strip-chart recorder in the case of natrolite, scolecite and thomsonite, are presented in Figs. 8.1, 8.2 and 8.3 respectively. Intensities recorded in the Tables 8.1, 8.2 and 8.3 are of emitted radiations. These were calculated by multiplying the intensity values (in arbitrary units) on chart by meter multiplying factor.

It is observed that iron (Fe) is the main impurity present in these samples, but very minute traces of K are also detected. Sodium traces exist with calcium zeolites (scolecite and heulandite), whereas calcium exists in the form of small traces in sodium zeolites (natrolite).

Further, it is observed that in the case of sodium zeolite - natrolite - and in the case of calcium zeolite heulandite, the intensity of principal emission band around 360 nm increases with...
<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Exciting radiation (nm)</th>
<th>Emitted radiation (nm)</th>
<th>Intensity (emitted radiation)</th>
<th>Si/Al</th>
<th>Impurities</th>
<th>Remarks</th>
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<tr>
<td>Natrolite-1</td>
<td>256</td>
<td>360</td>
<td>390</td>
<td>1.24</td>
<td>Mainly Fe</td>
<td>Traces of Ca and K.</td>
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<tr>
<td>Natrolite-2</td>
<td>254</td>
<td>360</td>
<td>400</td>
<td>1.26</td>
<td>-do-</td>
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<tr>
<td>Natrolite-3</td>
<td>250-260</td>
<td>360</td>
<td>430</td>
<td>1.47</td>
<td>-do-</td>
<td></td>
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<tr>
<td>Natrolite-4</td>
<td>236,258</td>
<td>364</td>
<td>450</td>
<td>1.54</td>
<td>-do-</td>
<td></td>
</tr>
<tr>
<td>Natrolite-5</td>
<td>264</td>
<td>360</td>
<td>550</td>
<td>1.72</td>
<td>-do-</td>
<td>Fe percentage increases...</td>
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Table 8.2 Photoluminescence study of stilbite

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Exciting radiation (nm)</th>
<th>Emitted radiation (nm)</th>
<th>Intensity (emitted radiation) (arb.units)</th>
<th>Si/Al</th>
<th>Impurities</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stilbite-1</td>
<td>250-260</td>
<td>358</td>
<td>440</td>
<td>2.53</td>
<td>Mainly Fe</td>
<td>Traces of K</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-do-</td>
<td>Fe percentage increases</td>
</tr>
<tr>
<td>Stilbite-2</td>
<td>230-240</td>
<td>358</td>
<td>300</td>
<td>2.94</td>
<td>-do-</td>
<td></td>
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<tr>
<td>Stilbite-3</td>
<td>230</td>
<td>350</td>
<td>500</td>
<td>2.98</td>
<td>-do-</td>
<td></td>
</tr>
<tr>
<td>Stilbite-4</td>
<td>232</td>
<td>358</td>
<td>300</td>
<td>3.13</td>
<td>-do-</td>
<td></td>
</tr>
<tr>
<td>Stilbite-5</td>
<td>232</td>
<td>356</td>
<td>300</td>
<td>3.60</td>
<td>-do-</td>
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Table 8.3 Photoluminescence study of heulandite, scolecite and thomsonite

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Exciting radiation (nm)</th>
<th>Emitted radiation (nm)</th>
<th>Intensity (emitted radiation)</th>
<th>Si/Al</th>
<th>Impurities</th>
<th>Remarks</th>
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<tr>
<td>Heulandite-1</td>
<td>250-270</td>
<td>359</td>
<td>270</td>
<td>3.13</td>
<td></td>
<td>Mainly Fe traces of Na, K and Sr</td>
</tr>
<tr>
<td>Heulandite-2</td>
<td>230-240</td>
<td>360</td>
<td>300</td>
<td>3.23</td>
<td></td>
<td>-do-</td>
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<td>Heulandite-3</td>
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<td>358</td>
<td>400</td>
<td>3.50</td>
<td></td>
<td>-do-</td>
</tr>
<tr>
<td>Scolecite</td>
<td>234, 238</td>
<td>360, 392</td>
<td>340, 300</td>
<td>1.80</td>
<td></td>
<td>Traces of Fe, Na and K</td>
</tr>
<tr>
<td>Thomsonite</td>
<td>258</td>
<td>315, 364</td>
<td>335, 450</td>
<td>-</td>
<td></td>
<td>-do-</td>
</tr>
</tbody>
</table>

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Note: Si/Al ratio indicates the presence of silicon and aluminum in the zeolites, which can affect their luminescence properties. The intensity values suggest the strength of emitted radiation, with higher values indicating stronger luminescence. Remarks highlight the presence of main impurities such as Fe, Na, K, and Sr.
the increasing Fe percentage. This relationship between iron impurity and intensity of the emission band does not exist in the case of stilbite which is a sodium-calcium zeolite.

8.4.5 Discussion

Luminescent properties are very much dependent on imperfections (or defects) in crystals. Generally imperfections responsible for luminescence are phonons, electrons and holes excitons, vacant lattice sites, interstitial atoms or ions, foreign atoms or ions in either interstitial or substitutional positions and dislocations.

Structural defects in zeolites are generally introduced by

(a) decationization and dehydroxylation,
(b) hydrothermal stabilization,
(c) metal cation reduction,
(d) dealumination, that is the removal of framework aluminium atoms.

The last type of defect may be responsible for the luminescent properties of zeolites in the present case. The possible substitution
of Fe ions for Al ions in the framework structure can cause dealumination of zeolite crystals.

Survey of the literature indicates that the presence of an iron impurity in zeolite crystals has an important bearing on their luminescent properties. The results obtained in the present investigation show that with the increase in the iron content of the specimen, there is consistent increase in the intensity of the principal emission band around 360 nm particularly in the case of natrolite and heulandite (Tables 8.1 and 8.3). This happens when Fe$^{3+}$ ions substitute Al$^{3+}$ ions in the tetrahedral aluminosilicate framework. If Fe$^{3+}$ ions replace Al$^{3+}$ ions substitutionally, then with the increasing Fe percentage, Al percentage must decrease or the Si/Al ratio must increase accordingly. In fact this has actually been observed. Aluminosilicate gels of definite composition but with deliberately added impurities in different proportions (particularly iron) were used by Mc Nicol et al.\textsuperscript{17} to study the effect of impurities on their characteristic phosphorescence spectra. It is therefore inferred that substitutional Fe$^{3+}$ ions either singly or in association with other
ions form the centres responsible for luminescence.

The consistent enhancement in the emission intensity with the increase in Fe concentration is conspicuously absent in stilbite. This characteristic can be explained on the basis of the fact that Na\(^{+}\) and Ca\(^{2+}\) ions present together in stilbite are more numerous than the number of Na\(^{+}\) ions alone in a natrolite or Ca\(^{2+}\) ions alone in heulandite. Statistically, therefore, there is a large probability for either Na\(^{+}\) or Ca\(^{2+}\) ions to be in the proximity of the luminescence centres. It is believed that the presence of Na\(^{+}\) or Ca\(^{2+}\) ion in the close vicinity of the luminescence centre gives rise to luminescence quenching. In other words, Na\(^{+}\) or Ca\(^{2+}\) ions act as "killer" centres.

8.5 Dehydration Behaviour of Crystalline Zeolites

8.5.1 General

Most of the zeolites can be dehydrated to some degree without major changes in their crystal structure and, they may be rehydrated with the absorption of water from the vapour or liquid phase. Some zeolites, when completely dehydrated, undergo irreversible structural changes and later suffer total
structural collapse on further heating. Studies on the dehydration behaviour of zeolites are based upon observations of the loss in weight with increasing temperature. Interpretations are based on computations from the dehydration isobars and the ability of the dehydrated zeolite to completely rehydrate or absorb other gases or vapours.

In zeolites that undergo dehydration reversibly and continuously, there is no substantial change in the framework structure. Exchangeable cations that are located in the channels coordinated with water molecules may migrate to different sites located on the channel walls or other positions of coordination.

In zeolites which have several cation sites, such as zeolite X with at least five cation sites, the effect of complete dehydration or partial dehydration may be pronounced. The zeolite is referred to as a non-stoichiometric hydrate because the water is present as a guest molecule in the host structure. In fibrous zeolites (natrolite, scolecite, thomsonite) and platy zeolites (such as stilbite), the water molecules are tightly coordinated to the exchangeable cations and the framework oxygen as well as to other
water molecules. In some zeolites complete dehydration results in irreversible changes in the framework due to weaker linkages in the framework structure in certain directions. In such cases cations initially located in the channels may then become trapped.

8.5.2 Thermogravimetric analysis

Thermogravimetric analysis measures loss in weight of a substance as it is heated to elevated temperatures. In the present study specimens were heated continuously, at a constant rate of 10°C/min., while recording simultaneously the loss in weight.

Based on dehydration behaviour, zeolites may be classified as:

(i) Those which do not show major structural changes after dehydration and which exhibit continuous dehydration curves as a function of temperature. This type of dehydration curves is the characteristic of many synthetic zeolites. One such example is given in Fig. 8.4 (curve 4) of synthetic zeolite VSZ.
(ii) Those zeolites which undergo structural changes with dehydration and, which show steps or other discontinuities in dehydration curves.

This second type of dehydration curve is the characteristic property of the natural zeolites of the present study.

Representative TGA curves of stilbite, heulandite, scolecite and VSZ are shown in Fig. 8.4. Summary of the dehydration behaviour of zeolites of the present study, obtained from the curves is given in Table 8.4.

8.5.3 Discussion

Natrolite and scolecite have the same type of framework topology, but exhibit different behaviour upon dehydration. Thermal analysis of these zeolites show that natrolite dehydrates rapidly within a single step, whereas scolecite (Fig. 8.4, curve 3) losses water in two steps. From this it is concluded that there is only one site of water molecule in natrolite, while the water in scolecite occupies two different sites. The natrolite structure becomes amorphous above 800° C, whereas scolecite structure
<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Observations from TGA curves</th>
<th>Structural changes recorded</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Step at (°C)</td>
<td>Percentage weight loss</td>
<td></td>
</tr>
<tr>
<td>Natrolite</td>
<td>240</td>
<td>9.7</td>
<td>New structure above 570°C</td>
</tr>
<tr>
<td>Stilbite</td>
<td>100, 200</td>
<td>17</td>
<td>New structure around 140°C</td>
</tr>
<tr>
<td>Heulandite</td>
<td>100, 240</td>
<td>13</td>
<td>New structure around 200°C</td>
</tr>
<tr>
<td>Scolecite</td>
<td>240, 450</td>
<td>11</td>
<td>New structure around 500°C</td>
</tr>
<tr>
<td>VSZ</td>
<td>-</td>
<td>19</td>
<td>-</td>
</tr>
</tbody>
</table>
collapses above 600° C.

Heulandite is less stable and undergoes a structural change around 200° C. This new structure is generally referred as heulandite "H". Dehydration of stilbite at 350° C results in the loss of most of the water. A step occurs in the dehydration curve for stilbite at 180° C, and an irreversible change of structure is evidenced above 200° C with complete breakdown of the structure at above 400° C.

Structural changes or structural breaking which occur as a result of dehydration, wherever possible, were confirmed by X-ray powder diffraction studies.

8.6 Conclusions

It is shown that colour of zeolites mainly depends upon the type and percentage of impurity. It may vary with the dehydration of crystals.

It is possible to change the refractive index of zeolites if the intracrystalline pores and channels - after dehydration - are occupied by different liquids. The resulting refractive index
varies with the refractive index of occluded liquid.

Luminescence in zeolites occurs mainly due to impurities present as point defects. It is seen that presence and percentage of iron impurity has profound effect on the luminescent properties of zeolites.

TGA curves of different zeolites are helpful for recording the different possible structural changes after dehydration. These changes may later be confirmed by X-ray powder diffraction studies.

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Fig. 8.3(a)

Fig. 8.3(b)

Fig. 8.4
Captions of the figures

Fig. 8.1(a) Excitation spectrum of natrolite
Fig. 8.1(b) Emission spectrum of natrolite
Fig. 8.2(a) Excitation spectrum of scolecite
Fig. 8.2(b) Emission spectrum of scolecite
Fig. 8.3(a) Excitation spectrum of thomsonite
Fig. 8.3(b) Emission spectrum of thomsonite
Fig. 8.4 Thermogravimetric analysis curves of
1. stilbite
2. heulandite
3. scolecite
4. VSZ