CHAPTER VI

DISCUSSION
The ability of a given material to luminesce is very frequently related to an activator impurity. The activator may occupy normal lattice sites or may enter the interstices of the host lattice. Also solid solution formation may take place between the host crystal material, activator and flux present. Lattice defects e.g. vacant lattice sites also play an important role in the luminescent processes. A brief discussion of various types of solid solution will not be out of place.

Any solid solution may be classified as one of the following types solely on the basis of crystallography:

(i) Interstitial,
(ii) Substitutional,
   a - Random  b - ordered  c - defect.

(1) The interstitial solid solution:

An interstitial solid solution of B in A takes place when B atom is very small compared to A atoms, so that it can enter the interstices of lattice A without causing much distortion. The ionic radii of atoms entering in interstitial position is less than 1 Å (1,2). The only important solid solutions known in metallurgy are those formed between elements like Carbon, Boron, Nitrogen, Hydrogen all of which have atomic diameters less than 2 Å. The interstitial solid solution is always accompanied by increase in solvent lattice. The lattice parameters of solvent lattice having cubic symmetry increases, while there may be decrease in one of the lattice parameters accompanied by increase in other parameter in
solvents having other crystal structure.

The density of interstitial solid solution is given by the basic density equation

\[ P = \frac{1.6620 \ \Sigma A}{V} \quad \ldots \ldots \ 6.1 \]

where \( \Sigma A = n_s \ A_s + n_i \ A_i \ \ldots \ldots \ 6.2 \)

\( n_s \) and \( n_i \) being the numbers of solvent and interstitial atoms respectively per unit cell, \( A_s \) and \( A_i \) the atomic weights of solvent and interstitial atoms respectively. The value of \( n_s \) is constant and independent of the concentration of interstitial atoms.

(ii) **Substitutional Solid Solution**:

a - Random

The random solid solution of B in A may be accompanied by an increase or decrease in volume of solvent depending upon whether B atom is larger or smaller than A. In continuous solid solution of ionic salts, the lattice parameter is directly proportional to solute present. The relation is known as Vegard's law. The density of random substitutional solid solution is given by (6.1) with \( \Sigma A \) factor being replaced by

\[ \Sigma A = n_{\text{solvent}} \ A_{\text{solvent}} + n_{\text{solute}} \ A_{\text{solute}} \]

where \( n \) refers to the number of atoms per unit cell and \( A \) refers to the atomic weight.
b - Ordered

In most substitutional solid solutions the two atoms A and B occupy lattice sites quite randomly. The effect of temperature change in such cases is only to increase or decrease the thermal vibration of atoms. In certain cases, however, the random structure is stable only at elevated temperature. When the temperature is reduced below a critical value the solvents and the solute atoms arrange themselves in an orderly manner. Such a structure is known as an ordered structure.

c - Defect solid solution

The defect substitutional solid solution is one in which lattice sites at certain compositions are simply vacant at other composition. The first evidence of such a defect structure was demonstrated by Bradley and Taylor (3).

Position of Foreign atoms

The position occupied by foreign atoms in a compound of type MX depends upon the energy balance. Factors such as chemical bonding, van der Waal's forces and Born's repulsion will play a role (4). As far as lattice positions are concerned it can be said that foreign atoms tend to occupy the position of the atom to which they are closest on the electronegativity scale, if there is a marked difference between the electronegativities of M and X. Thus metal atoms occupy M position and metalloids X position. The influence of size may dominate if electronegativity is intermediate between M and X. Thus Pb atoms may occupy Indium sites in InSb but Antimony sites in AlSb (4).
For foreign atoms to occupy substitutional lattice sites, the ionic radii of the host lattice and the foreign atoms should be within 15% (1,5,6). If the difference is more, it usually goes in the interstitial position.

The different environment of the two types of activators leads to marked differences in the properties of the phosphor. Substitutional phosphors decay exponentially while interstitial phosphors have hyperbolic decay characteristics. This is because S-activated centres are well buffered by close coupling to the host crystal. On the other hand i-activated centres occupy positions foreign to the ideal pattern of the host crystal. So in general S-activated centres should be more difficult to ionize since crystal forces as well as local forces must be overcome to free an electron. This is the probable reason of the two types of decay in the above phosphors.

A further measure of the different perturbabilities is the difference in the optimum activator concentration. This is about hundred times greater for substitutionally activated phosphors. Also i- activator centres are generally perturbed by the presence of impurities or other identical centres which are on an average five times as remote in the case of S-activated centres (5).

In the case of S-activated phosphors there is a jumpwise shift of emission spectra i.e. the intensity of one emission band increases at the cost of other when activator concentration
is changed. In the case of i-activated phosphors there is a gradual shift of emission spectra towards higher wavelength with changing activator concentration (5).

In the present investigation CaS is the host crystal, Zirconium is the activator, Sodium fluoride, sodium sulphate and sodium thiosulphate in optimum proportions were used as flux. To decide whether Zirconium is going into substitutional or interstitial positions, the factors discussed earlier will have to be considered.

There is a difference of nineteen percent in the atomic radii of Calcium and Zirconium. Atomic radii of calcium and Zirconium are given in table 6.1

<table>
<thead>
<tr>
<th>Element</th>
<th>Charge</th>
<th>Radius in Angstroms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>0</td>
<td>1.97</td>
</tr>
<tr>
<td></td>
<td>+ 2</td>
<td>0.99*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.06</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>+ 4</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.80*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.89</td>
</tr>
</tbody>
</table>

* Values have been computed on the basis of wave mechanics.
Considering the above values of atomic radii of calcium and Zirconium, it may be said that conditions are not favourable for Zirconium to substitute calcium in CaS host crystal.

If we consider the electronegativity of calcium, sulphur, and Zirconium we find that too is not favourable for Zirconium to replace calcium. The values of electro-negativities are given in table 6.2.

**Table 6.2**

*Table of Electronegativity*

Quoted from Chemistry by N.S. Seinko and R.A. Plane. p. 87

McGraw Hill Book Company (U.S.A) 1961

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>1.0</td>
</tr>
<tr>
<td>Zirconium</td>
<td>1.40</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Thus we find that there is 40% difference in the electro-negativities of calcium and Zirconium and hence we may say that Zirconium is probably going in an interstitial position.

This is further supported by the fact that the optimum activator concentration is low. It is of the order of 0.08%. The percentage of activator required for emission to be fully quenched is 0.6% which is fairly low. If Zirconium was substituting for calcium, a higher percentage of activator might have been required for quenching of emission.
Decay characteristics of CaS:Zr have been studied by Agnihotri (7) in our laboratories. The phosphors were found to have a power law decay and not an exponential decay as for S-type phosphor systems.

Spectroscopic studies carried out here by Rawat (8) reveal that there are two fluorescence bands, one in the red region and the other in the blue region. In phosphorescence the red band is predominant. However, in a few samples of lower concentration the green band is also present. The fluorescence bands shift by 200 Å as activator concentration is increased. This also supports the possibility of an interstitial position for Zirconium.

From X-ray powder photographs values of lattice constant of CaS:Zr were determined. To determine accurately the values of lattice constant, values (of lattice constant) computed from back reflection lines were plotted against \( \frac{1}{\sin \theta} (\cos^2 \theta + \cos^2 \theta) \) and the graph was extrapolated to \( \theta = 90^\circ \). The value of lattice constant as given in N.B.S. data (9) for pure CaS is 5.694 Å. The value obtained by extrapolation graphs for CaS:Zr phosphor is 5.699 Å. No significant change in the value of lattice constant was noticed as percentage of activator increased from zero to maximum. Hence, Zirconium seems to be occupying an interstitial position. Fonda (10) had arrived at a similar conclusion by X-ray diffraction studies of CaO: Pb where also no variation of lattice constant was found as lead content increased.
Neutral Zr atom going in interstitial position in CaS phosphor will produce energy levels below the conduction band, just like any other foreign atoms going in interstitial position in compounds of the type MX as suggested by Kröger and Vink (11). Ionized Zirconium will give levels further below and the levels will then act as traps for electrons. The group of traps involved in the present studies appear to be independent of activator concentration as shown by Agnihotri (7). Similar behaviour of traps is also reported by Lenard for CaS : Bi (12). He deduced the principal trap groups from phosphorescent light sums at room temperature as having depths of 1.0, 0.9, and 0.8 ev. These were found to be independent of activator concentration. The trap group of depth 1.2 ev in the phosphor appears to be associated with CaS lattice itself (13). Zirconium might be introducing traps which are deeper and were not revealed in the investigation carried out by Agnihotri (7). Therefore, the other possibility that the Zirconium is associated with the luminescent centre can not be ruled out. In this case Zirconium will probably create levels close to the conduction band and it should be thought to be an excited state of Zirconium which is produced due to the perturbation of Zirconium atoms by host lattice atoms. In addition there could be levels belonging to host which lattice atoms are/under the perturbing influence of activator. Rawat (8) has tried to explain the two emission bands due to transitions from excited state of activator atoms and the host lattice atoms to their respective ground states.
Action of Flux:

According to Primak et al. (14) complicated interaction usually occurs between the base material and flux. According to them some of the phenomena found to occur are:

1. Reciprocal salt systems are formed,
2. Reactions may occur between flux and the base material,
3. Cationic and anionic exchange between flux and base material may occur.

Nature of flux anions itself is reported to have considerable influence on luminescence emission. According to Asano (15), fluoride when added as flux in CaS : Cu phosphor increases the intensity of the band at 4950 Å. According to Agnihotri (7) in the present phosphor system fluoride in association with sulphur vacancy forms a trapping state, a scheme somewhat identical to ZnS : Cu with Cl as co-activator (16).

In the presence of NaF which was one of the fluxes used, zirconium also forms complexes of the type M₂ZrF₆ and M₃ZrF₇ where M is an alkali element. Zirconium also combines with fluorine to give a compound of the type ZrF₄ (17). The above complexes and compounds are fairly stable and the possibility of their formation can not be ruled out. However, no diffraction lines corresponding to these are recorded, probably because of the small amount of Zirconium in the phosphor sample.

CaF₂ seems to be forming in small proportion. In the powder diffraction photographs, as mentioned in the previous
chapter diffraction lines corresponding to 3.12 Å, 1.9030 Å, 1.1090 Å, and 1.0510 Å 'd' spacing have been ascribed to 111, 220, 422 and 511 of CaF₂. Presence of CaF₂ in the phosphor samples may be due to cationic exchange as suggested by Primak (14).

There is a chance that Na₂SO₄ used as one of the fluxes may be reduced to Na₂S during the firing process. However, since Na₂S is amorphous and is likely to be in small quantities no indications of its presence were found in the diffraction patterns.

Presence of CaO:

Presence of CaO in CaS phosphor prepared with and without flux was investigated by Tunitskaya (18). It was found that CaO was present in phosphor prepared without flux (X-ray powder photograph of phosphor prepared without flux clearly showed the presence of CaO). However, in phosphor which were prepared with Na₂SO₄ flux, CaO was formed in extremely small quantities and luminescence spectra due to CaO was not recorded. According to Curie (19) CaO is usually present in CaS phosphors. Presence of SrO in SrS : Bi (Borax) phosphor was suspected by Gautam (20). However, he preferred to ascribe the diffraction maxima's due to a new phase instead of SrO.

In the present investigation of phosphor samples diffraction lines corresponding to 2.4088 Å and 1.7055 Å have been indexed as 200 and 220 of CaO phase. These diffraction maxima's are present in almost all the samples. However, the amount of
CaO formed seems to be small and it is very doubtful if its luminescence spectra could be recorded. According to Sancier et al (21) a temperature of $1500^\circ K$ is necessary for appreciable defects to be formed by thermal decomposition under vacuum heating. As the firing temperature in the present investigation was only $900^\circ C$ the possibility of CaO : Zr forming an efficient luminescent system seems to be remote as calcium oxide exhibits very low response to photo conduction.

In the end the following conclusions may be drawn:

(i) Zirconium is probably going in an interstitial position,

(ii) Reactions may occur between flux and base material,

(iii) Slight amount of Calcium oxide seems to be forming in phosphor samples.
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