CHAPTER VIII

DISCUSSION AND CONCLUSIONS
8.1 Introduction

The alkaline earth oxides are structurally among the simplest in the oxygen-dominated phosphors with the anion and cation being situated at the corners of two interpenetrating cubic sub lattices. Here an attempt has been made to study the effect of an absorber (CdO) on the luminescence characteristics of a wide band gap material (CaO), having the same space group $O_h^5$ and with band gaps 2.0 eV and 7.7 eV respectively.

The absorption spectra, emission under X-rays, thermoluminescence, temperature dependence of emission under X-rays and UV (2537 Å), electroluminescence and cathodoluminescence of CaO and mixed oxides of CaO and CdO in particular ratios activated by europium and zinc are discussed in the present chapter.

8.2 Absorption Spectra and X-ray diffraction

The brown colour of CdO indicates its absorption capacity in the visible range. CdO has no defined absorption edge due to a small, unavoidable excess of Cd of about 0.1 to 0.4%. When CdO is incorporated into the lattice of CaO which has a well-defined absorption edge in the UV region (Fig. 3.1), the brown colour no longer appears; with increasing CdO
concentration the absorption edge shifts continuously from the ultraviolet to the red (Figs. 3.1 - 3.4). Continuous solubility is here associated with a continuous shift of the absorption edge as reported by Lange.  

The lattice constants of CaO and CdO differ very little and hence during the formation of various solid solutions the change in lattice parameter is small. However, the absorption edge shifts from 2750 Å for CaO to 4510 Å for CaO : CdO (3 : 7) showing that there is a marked change in the band gap of CaO on addition of CdO.

From X-ray diffraction patterns, it is seen that there is complete solid solubility between CaO and CdO through the entire concentration range. X-ray diffraction patterns show sharp lines indicating good crystallisation.

8.3 Emission

The electronic structure of rare earths can be written as [Xe] 4f^n 5d^0 6s^2. The inner 4f shell, which may hold a total of 14 electrons, is well-shielded from the perturbing influence of the crystal field by the outer electron shells. As a result the energy states of the partly filled 4f shell are only slightly affected by the surrounding environment and electronic transitions
between them can be observed as narrow line-like bands in both emission and absorption. 

Exciting the ions by directly irradiating the 4f bands with monochromatic radiation of energy matching that of the transitions involved, although possible, is not an efficient method of producing useful fluorescence. Among the other methods of exciting the ions, there is the first possibility of exciting the $4f^n \rightarrow 4f^{n-1} 5d$ transition where the excited electron in the d-shell is well exposed to the crystal field so that its energy states are broadened and further the transition can be totally allowed. Because the 5d orbit lies at the surface of the ion the lattice also affects the excitation spectrum. 

It is well known that many Eu$^{3+}$ activated phosphors are efficiently excited by 254 nm radiation, which is true for our samples too, but as the $4f^n \rightarrow 4f^{n-1} 5d$ transition in Eu$^{3+}$ is expected at wavelengths below 200 nm this excitation must be due to another transition and is instead assigned to a charge-transfer absorption. This is a second possible mechanism where one of the electrons of the surrounding anions of the lattice jumps across to the 4f orbit of the central rare earth ions.

Since completely or half-filled shells are very stable, in the case of Tb$^{3+}$ (4f$^8$, half-filled plus one) the 4f shell readily releases one electron, and the transition $4f^8 \rightarrow 4f^7 5d$ takes place at relatively low energy, while in the case of Eu$^{3+}$
(4f$^6$, half-filled less one) the 4f shell readily accepts an electron and thus the charge-transfer state has a low energy.

Optical transitions between 4f levels

Electric-dipole transitions between the 4f levels of rare earth ions are in principle strictly forbidden. This is because the parity of the wave function of the electrons does not change (Laporte's selection rule). Because the 7F and 5D states both originate from the 4f$^6$ configuration they have the same parity. This implies that only weak magnetic-dipole transitions ($\Delta J = 0, \pm 1$ with $J = 0 \leftrightarrow 0$ forbidden) are allowed.\textsuperscript{6-8}

Because of spin-orbit coupling it is necessary to consider the 7F states as being composed of a pure 7F state with a slight 'admixture' of the pure 5D state. Consequently this spin prohibition no longer applies so strictly. The parity prohibition can be lifted by mixing the 4f$^6$ configuration with a state possessing a different parity. The interaction responsible for this is formed by the odd-crystal field terms,\textsuperscript{9} that is to say those terms that change sign on inversion with respect to the rare earth ion. If the rare earth is located at a site that is a centre of symmetry in the relevant crystal lattice, then the odd crystal field terms are absent and the
parity prohibition cannot be lifted.

If the Eu$^{3+}$ ion is situated at a centre of symmetry and is brought into the $^5D_0$ state, the only possible transition accompanied by the emission of radiation is $^5D_0 \rightarrow ^7F_1$ (magnetic-dipole emission, initial level $J = 0$, final level $J = 1$, $\Delta J = +1$). In the case of BaGdNbO$_6$, which has ordered perovskite structure $^{10}$ the rare earth ion occupies regular octahedron of oxygens. The spectral emission consists of a sharp line at 5950 Å and some weak lines in the region 6100-6300 Å. The sharp line at 5950 Å corresponds to $^5D_0 \rightarrow ^7F_1$ and is due to magnetic-dipole transition and as such is allowed.

**Emission of Eu**

All the phosphors activated by Eu under X-rays show line emission at 5950 Å. The spectra recorded with a large slit width are shown in Figs. 4.3 - 4.5 (b). The emission is asymmetric, with an extension on the larger wavelength side. This is probably due to weak emission between 6100 - 6200 Å as reported for CaO : Eu$^+$ by Lehmann $^5$ and also by Raman. $^{11}$ The Eu$^+$ ion occupies a substitutional site in the CaO lattice as Eu$^{3+}$. The main emission is due to the transition $^5D_0 \rightarrow ^7F_1$ (Fig. 8.1) and is magnetic-dipole in character. The emission is prominent whenever the Eu$^{3+}$ ion occupies a site with inversion symmetry.
Fig. 8.1 - Energy levels of Eu$^{3+}$
while the $^{5D_0} \rightarrow ^{7F_2}$ electric-dipole transition is forbidden due to the selection rules. The weak and broad bands corresponding to $^{5D_0} \rightarrow ^{7F_2}$ emission may be caused by a coupling with lattice vibrations which can give rise to temporary deviations from pure cubic symmetry. A foreign atom such as fluorine in an interstitial position cause such a deviation.

There is no shift in the peak position of the Eu activated CaO phosphor by the addition of CdO. It is well known that the emission is due to the presence of deep-lying 4f shells in the Eu ions. The electrons of this shell are screened by the outer electron shells, and as a result they give rise to a number of discrete energy levels which are unaffected by the crystal lattice.

It is found that the intensity of emission shows an increase on addition of CdO to CaO up to a ratio of 3:7, before decreasing. During excitation, a large number of electrons are released by ionisation and the mechanism of luminescence is similar to that of cathodoluminescence. The efficiency of luminescence among other things, would depend upon the efficient transfer of energy through the lattice. The addition of CdO to CaO results in a progressive decrease in band gap. A decrease in band gap would lead to greater mobility and hence a better
transfer of energy by electrons. Further in roentgeno-luminescent phosphors it is considered an advantage to introduce heavy elements since they increase the absorptivity of the materials for high energy photons. Since Cd has a higher atomic number than Ca, the absorptivity for X-rays would be increased because of its incorporation. In the case of X-ray excitation, the high energy primary photons may excite more than one luminescence photon through the intermediate action of high energy photoelectrons produced within the phosphor which in turn produce further electrons by a cascade process. Shockley has estimated that if the band gap is $E_g$ then the mean energy required for the production of a free electron and free hole pair is, for equal effective masses of the carriers, $1.5 E_g$. This factor also be importance when the band gap decreases progressively. The addition of CdO on the other hand may also lead to some lattice distortion or defects which may result in a decrease of luminescence since a high degree of crystallinity is necessary for efficient energy transfer between the random points of primary absorption and the luminescence centres. CdO itself strongly absorbs red. Besides, the defects introduced by CdO in the lattice may form colour centres during X-ray irradiation, and this could also result in a decrease in luminescence. Thus it appears that the luminescence of CaO-CdO :Eu phosphors is a resultant of two competing processes, one tending
to increase emission by efficient transfer of energy and the other quenching or absorbing the emission.

The colour co-ordinates of all samples activated by Eu are calculated. It is seen that in all these phosphors the prominent emission lies nearby 5800 Å as is to be expected.

Emission of Zn

The emission of Zn activated samples under X-rays are shown in Figs. 4.6(a) - 4.6(d). Here the peak emission of all the samples is around 3400 Å. Visual observation under X-ray excitation showed an increase in brightness of the phosphors on initial addition of CdO. This has been confirmed by the observation that in the recorded spectra, emission in the visible region gets enhanced with addition of CdO and extends beyond 4900 Å.

Jones and Mee 14 have reported that CaO shows self-emission at 3500 Å which they attribute to oxygen vacancies produced by thermionic activation. Fonda and Froelich 15 have also reported a band at 3450 Å in pure CaO. According to Lehmann, 5 the emission of CaO containing about 0.1% ZnO consists of a broad band in the ultraviolet (326 - 340 nm). His results show that whereas pure CaO does not luminesce, CaO : Zn and CaO : F show ultra-violet emissions which closely resemble each
other. Further, the emission of CaO:Zn could not be excited by 2537 Å radiation while the efficiency was relatively high under electron beam excitation. Substitution of Ca\(^{2+}\) by Zn\(^{2+}\) has been tentatively suggested as the defect responsible for the emission. Both Lange and Lehmann have observed that CdO in CaO produces luminescence in the ultra-violet (3050 and 3100 Å respectively). However, the observations relate to low concentration of CdO of the order of 1.0% or less. Both CaO:Zn and CaO:Cd show an exponential decay after electron pulse excitation and their emissions have obvious similarities.

The ultra-violet emission observed at 3400 Å in the present instance is probably the same band observed by Jones and Mee and attributed to oxygen vacancies. The addition of Zn could result in oxygen vacancies just as anion vacancies are produced by heating an alkali halide in alkali vapour, since Zn\(^{2+}\) can occupy Ca\(^{2+}\) sites. This would also account for Lehmann's observations. However, the visible tail of the spectrum that extends to the blue region has to be distinguished from the ultra-violet band because its intensity increases on initial addition of CdO while that of the latter decreases. The possibility that this emission is due to a centre other than the one producing the 3400 Å band has been checked out by
investigating the thermoluminescence, temperature dependence and cathodoluminescence characteristics. The colour co-ordinate studies also indicate that the prominent emission in the visible region lies around 4900 Å and the intensity of this emission increases on addition of CdO.

8.4 Thermoluminescence

Thermoluminescence is an important solid state physical phenomenon which can be used for the elucidation of the nature of charge carrier, trap centres associated with the glow peaks, the mechanism of generation of traps and luminescence centres and the significance of trap depths in colour centres. Thermoluminescence has been found to be sensitive to small traces of impurities and thermal treatment. A number of formulae for analysing the thermoluminescence curve have been proposed by many workers and reviews of these methods have been given by Shalgaonkar et al., Chen and Nambi etc. It is seen that the mutual interference of one peak with another leads to widely divergent and inconsistent values whenever a formula depending on the shape factor is used. Without a clear knowledge of the recombination kinetics, no accurate information about trap depths, frequency parameters and other related parameters can be calculated.
Studying the colour of thermoluminescence emission enables one to infer whether the emission is due to only one trap with different recombination centres $^{28}$ or different traps with one recombination centre $^{29}$ when the number of peaks are more than one.

As is seen from Figs. 5.1(a) - 5.1(d), the addition of CdO to Eu activated phosphores causes an increase in the intensity of the thermoluminescence peak up to the ratio CaO : CdO (8 : 2) and then there is a decrease. There are two peaks in the case of CaO : Eu and CaO : CdO (9 : 1) : Eu. The first peak becomes sharper as the percentage of CdO increases. Further, the addition of CdO moves glow peak to lower temperatures. The asymmetry of the first peak in all these samples could be due to an interference from the second peak. The intensity of the second peak is less in the case of CaO : CdO (8 : 2) : Eu and CaO : CdO (7 : 3) : Eu so that it appears a part of first peak and is no longer resolved.

The thermoluminescence emission of the samples was found to be of the same colour as that of the fluorescence of the samples so that the centre responsible for both appears to be the same.

In the case of CaO : Zn also there are two peaks. Here the intensity of the first TL peak goes down with the addition of CdO. The second peak gets enhanced at CaO : CdO (9:1) but is
absent in the 6 : 2 and 7 : 3 samples. Here also the position of the peaks get shifted to the lower temperature side with the addition of CdO.

Since the emission of Zn activated samples, consists of two bands, the thermoluminescence study has been performed taking the two particular wavelengths viz., 4900 and 3400 Å. It is seen that both have the same shape but the second peak which was recorded while studying the total emission, is no longer apparent. It is seen that in thermoluminescence 4900 Å predominates while the intensity of 3400 Å emission is only about 30.0% of the total emission. This observation supports the possibility that two different centres are involved in the fluorescence of Zn activated phosphors. The fact that the 4900 Å band appears to be brighter in thermoluminescence while it is relatively weak in fluorescence indicates that either the probability of recombination is greater for this centre or that it has better temperature dependence characteristics. Since the glow curve recorded at 3400 Å and 4900 Å are entirely similar, it appears that the same traps are involved in both cases. Temperature dependence of both emissions were recorded separately and the results do not indicate better temperature characteristics for the 4900 Å. However, the curve shows a rise in the region corresponding to the thermoluminescence maximum. This indicates that electrons freed from traps recombine preferentially with the centres responsible for the blue band.
The trap depths of all these samples were calculated using different formulae. The values calculated using Randall and Wilkins' formula with $S = 10^9 \text{sec}^{-1}$ and Curie's formula, where the shape factor is not taken into account, are found to tally with each other. It was found that the use of formulae depending upon shape factors led to widely divergent and inconsistent values of trap depth. Even for small changes in the values of the geometrical factors $\alpha$, $\beta$, and $\gamma$, the variation in the E values was large. This may be on account of a mutual interference between the glow curves which were not sufficiently isolated in the present case. According to Garlick weak excitation is one of the requisite conditions for retrapping. Since in the present study the phosphors were irradiated with X-rays, thus ensuring saturation filling of traps, the application of Randall and Wilkins' theory which neglects retrapping, is considered justifiable.

Variation of trap depth with the addition of CdO to CaO lattice

It is seen that in Eu activated as well as Zn activated systems, the addition of CdO to CaO shifts the temperature corresponding the maximum of thermoluminescence intensity to the lower temperature side. Consequently the trap depth decreases in the mixed system. As CdO, having band width of $\sim 2.0$ eV, is added to CaO (7.7 eV) the band width decreases.
As a consequence, the trap depths in the mixed phosphor system would be expected to show a decreasing trend as the CaO content is increased.

**Nature of Traps**

Taylor and Hect have reported three glow peaks above room temperature in the case of X-ray irradiated unactivated CaO. However, in our present study these peaks could not be observed, possibly because they were too weak for detection. Since the thermoluminescence of unactivated CaO has been observed by Khare and Raman also, it appears that the number of host defects responsible for these peaks may vary between large limits depending upon the method of preparation.

The first glow peak observed in the case of Eu and Zn activated CaO phosphors occurs at the same temperature and this peak also has been reported by Raman in the case of CaO : Tb. It is therefore possible that this glow peak is caused by a host lattice defect produced on account of the introduction of an activator. However, the second glow peak in the case of CaO : Eu and CaO : Zn occur at widely different temperatures and hence may be specific for the kind of impurity introduced.

**Thermoluminescence Model**

The glow curve recorded at 5950 A in the case of CaO : Eu
has the same features as that of the total thermoluminescence. Similarly the glow curves recorded at 3400 Å and 4900 Å in the case of CaO : Zn are similar to the total glow except for the obliteration of the second glow peak which may be due to the low intensity involved.

Bhasin and Sasidharan\textsuperscript{34} have proposed a model in which the defects acting as traps and recombination centres are not distributed independently and randomly but are organised in some ordered configurations which contribute thermoluminescence units. The charge carriers released from traps have a high probability of being captured by one of the recombination centres surrounding the trap. According to this model, the glow peak generated is characteristic of the configuration of the thermoluminescence unit except when the charge carriers escape and recombine elsewhere in the crystal. Bhasin et al. have however considered that the distribution of the potential thermoluminescence units is entirely random within a phosphor.

In the present investigation it is found that one of the glow peaks is the same for both Eu and Zn activated phosphors. However, in each case the colour of thermoluminescence is characteristic of the particular activator. This would seem to indicate that rather than being randomly distributed, the potential TL units are preferentially surrounded by the respective
activator centres and there is an energy transfer between these units and the luminescence centres. This is further supported by the fact that in the case of CaO : Zn phosphors there is apparently a better transfer between these Ti units and the centres responsible for the blue emission. Such a selective transfer has also been observed in the case of calcite activated by Mn. Medlin has explained the wide variation in thermoluminescence efficiencies of X-ray irradiated calcite crystals on the basis of a non-radiative energy transfer between recombination centres and Mn$^{2+}$ ions.

8.5 Temperature dependence of emission

Investigations on temperature dependence of the fluorescence intensity of phosphors are of great interest as, in combination with other pertinent data, they yield qualitative and sometimes also quantitative insight into the mechanism of luminescence. Increasing the temperature of a phosphor results in a higher probability of radiationless transitions within the activator ions. Consequently for all phosphors temperature quenching occurs. The temperature at which the quenching occurs provides information about the interaction of the activator ions with the surrounding host lattice ions. This interaction is small when the transitions occur in an inner shell as in the case of rare earth activated phosphors which consequently possess a
high quenching temperature.\textsuperscript{37} For example, the quenching
temperatures of $\text{Eu}^{2+}$ activated alkaline earth pyrophosphates
are much lower than those found for most $\text{Eu}^{3+}$ activated
phosphors.\textsuperscript{38} The difference is reasonable, as in $\text{Eu}^{3+}$
activated phosphors, in contrast to the $\text{Eu}^{2+}$ phosphors, no
excitation of $4f$ electrons to outer shells takes place.

Haake\textsuperscript{39} has pointed out that there are two important
factors to be considered in temperature dependence of emission,
an increasing absorption with temperature leading to a higher
emission, and a decrease in efficiency of the fluorescence due
to competing phonon processes. Because the effects work against
each other, the brightness–temperature curve sometimes shows a
maximum, the position of which will depend on the relative
importance of the two factors.

Blasse and Bril\textsuperscript{40–44} suggested that $\Delta r$, the
equilibrium distance between the ground and excited states as
also the radius and charge of the cations surrounding the
relevant luminescent centre determine the quenching temperature
of fluorescence to a great extent. By making reasonable
assumptions concerning the parameters involved Blasse\textsuperscript{42,43} has
shown that a necessary but not a sufficient condition for
efficient fluorescence is that $\Delta r$ should be about 0.3 Å. For
small values of $\Delta r$, $\Delta E$ is large, and efficient fluorescence
occurs even at higher temperatures. It is possible to obtain a rough measure of $\Delta r$ from the set of radii corresponding to the principal maximum in the radial wavefunctions for atoms and ions given by Weber and Cromer. In the case of Eu$^{3+}$ phosphors, when the ground and excited states both belong to the 4f configuration the excitation transition is $2p^2 \rightarrow 4f$ and the outer orbital (5p) radius is 0.74 A for both states, and hence $\Delta r$ is zero. In this case the quenching temperature is high.

Temperature dependence of fluorescence of Eu activated phosphors

The fluorescence of CaO : Eu goes on increasing under X-ray excitation up to $220 \pm 10^0C$ from where it decreases with further increase of temperature. An increase in fluorescence with temperature can be due to several possibilities:

(a) an increase in the absorption of the incident radiation due to a change in the absorption spectrum of the host with temperature; 

(b) a temperature dependant transfer of energy between the activator and the host;

(c) a change in the spectral distribution to a region of higher sensitivity of the detector.
(d) an emptying of traps and a consequent radiative recombination of electrons and activator centres.

The emission spectrum was recorded at 35, 100 and 150°C. There was only an increase in intensity but no shift in emission could be observed. Since the excitation was by X-rays, the first possibility, which applies to excitation by monochromatic radiation, is ruled out. The temperature dependence was studied under UV (2537 Å) excitation and the intensity showed a steady decrease from room temperature (≈ 30°C) onwards.

If there is a temperature dependant energy transfer to any other emission centre, a rise in fluorescence intensity with temperature could take place. In the present system for example, the Eu emission would go down fast while a second emission band would rise rapidly so that the resultant intensity could show an upward trend. Such a phenomenon has been observed in the case of CaWO₄ : Sm and CaMoO₄ : Sm⁴⁷ where the Sm emission rises rapidly more than off setting the quenching of WO₄ or MoO₄ emissions. The temperature dependence of Eu emission was examined through a spectrograph and the result was identical to that of the total emission. This rules out the possibility of a temperature dependant energy transfer being responsible for the observed rise in fluorescence.

To confirm that the rise in fluorescence was caused by a
release of electrons from traps, the phosphors were pre-excited by X-rays for five minutes before studying their temperature dependence under UV excitation. The results show convincingly that release of electrons from traps is responsible for the observed increase in emission with temperature. Ultra-violet excitation is obviously incapable of filling the electron traps. This was also confirmed by the poor thermoluminescence following excitation by 2537 Å radiation. A comparison of the glow curve with temperature dependence curve also confirmed the above conclusion.

In the case of CaO : CdO (9:1), the temperature dependence curve shows a pronounced first peak while the second peak is not only reduced in intensity but also occurs at a lower temperature. According to the conclusion reached earlier this would indicate that the number of shallower traps is increased and the trap depth of the deeper traps is decreased. In thermoluminescence also the second glow maximum shifts from 210°C to about 165°C while the first glow peak rises in intensity sharply. On further addition of CdO, the second maximum disappears, the temperature dependence curves show only one maximum. This feature was found also in thermoluminescence.

In the temperature dependence of CaO : CdO (9:1): Eu the first peak is more prominent than the second one when total emission is examined. However, when examined through a
spectrograph at 5950 Å, the intensities of the two peaks are comparable. The difference in the two cases is the tail part of the emission curve (emission > 6000 Å). It is possible that this feature is due to the different dependence on temperature of the electric-dipole transitions. It was not possible to verify this because of the low intensity of emission in this region.

The activation energies calculated for the Eu phosphors show an increase up to CaO : CdO (8:2) and then there is a decrease. In the case of CaO : Eu and CaO : CdO (9:1), Eu, there is a hump in the temperature dependence curve at high temperatures. This is caused by the release of electrons from deeper traps. This disturbance, which is absent in the higher members of this series, may be responsible for the low values of activation energy and these values may not be reliable.

Temperature dependence of fluorescence of Zn activated phosphors

The temperature dependence curve of CaO:Zn (0.1%) shows an initial rise with temperature before falling off at high temperatures. The maximum occurs at about 75 °C which is also the temperature at which the glow maximum was observed in thermoluminescence. Addition of CdO shifts this maximum to a lower temperature in the case of CaO : CdO (9:1). A similar
shift was also observed in the thermoluminescence peak of this phosphor. As the CdO concentration is increased the position of the peak apparently shifts to low temperatures so that even with the help of a freezing mixture it could not be located.

A comparison of the temperature dependence of the total emission and that of the 3400 and 4900 Å emissions shows that the ultra-violet band does not show a maximum but falls continuously with temperature. The visible band, however, shows a maximum at 75°C and hence the total emission is obviously a composite of the two separate temperature dependence curves. Since the maximum in the curve has been attributed to the freeing of electrons from traps (increased phosphorescence) it appears that there is a better transfer of energy between the thermoluminescence units and the centres responsible for the blue emission. This conclusion has also borne out by the thermoluminescence studies of the two emissions.

Addition of CdO shifts the quenching to lower temperatures and the activation energy goes on decreasing. The addition of CdO decreases the band gap of the phosphor and the absorption moves to longer wavelengths. Wachtel has observed that when the equilibrium distance between the ground and excited states remains fixed and the absorption moves to
shorter wavelengths, the activation energy for non-radiative transitions is increased.\textsuperscript{48} Since in the present instance, the shift of the absorption is in the opposite direction, a decrease in activation energy should be expected. Such a decrease in activation energy with a shift of absorption to longer wavelengths has been observed in the case of octahedral niobate centre by Machtel. This relation has also been found to hold for the $\text{Eu}^{3+}$ centre in oxides\textsuperscript{49,50} and the $\text{UO}_6$ centre in the rock-salt lattice.\textsuperscript{51}

A shift in the temperature-quenching curve could also be due to the formation of 'killer' centres,\textsuperscript{52} i.e., centres in which excitation energy is dissipated without the production of radiation. Such killer centres could well be formed by the addition of CdO.

A lower degree of perfection could also be responsible for the shift in the quenching curve.\textsuperscript{53} Since the CaO : Zn phosphor could not be excited by ultra-violet radiation up to 2537 Å it was not possible to confirm if the lattice imperfections or killer centres were responsible for the quenching. The shift would be expected to be greater for longer wavelength excitation in such a case.

The activation energy decreases with increasing zinc content in the phosphor. An explanation for this could be that
a zinc ion with another at a nearby cation site might form 'zinc-pairs' which can act as quenching centres. Such a feature has been observed in Zn₂SiO₄ : Mn. 54,55 Absorption in these groups or near these groups would not lead to fluorescence and the efficiency will decrease.

9.6 Electroluminescence

There are a number of small regions in the crystal where the strength of the alternating field exceeds the average field strength in the crystal by orders of magnitude. If conduction electrons are present in these field regions they become accelerated to such an extent that they are able to ionize activator centres by inelastic collisions. 56 There are several sources for the initial electrons in the high field regions. 57

1. There are always some electrons in the conduction band;
2. Electrons are injected from the second phase into the barrier region;
3. Filled traps lying only a few tenths of an eV below the bottom of the conduction band can release electrons due to thermal activation.

Piper and Williams 58 assumed that on the surface of a ZnS crystal, potential barriers of the Mott–Schottky type exist.
At the metal semiconductor contact of the ZnS : Mn, Cl films a similar barrier probably exists and EL occurs only when the metal electrode is negative. Zalm has indicated how a Mott-Schottky layer might still be effective in a powder cell. Though the nature of the barrier remains uncertain, its presence is necessary for the collision-excitation mechanism and consequent emission within the phosphors.

The concentration of activator determines to a great extent the efficiency of an electroluminescent phosphor. The optimum concentrations for electroluminescent specimens are higher than for photoluminescence. This expected in view of the low probability of impact ionization.

Good crystallization is necessary for good electroluminescence. The crystals must have donors for the generation of accelerated electrons but few traps. Phosphors showing good EL generally have little phosphorescence.

The EL of CaO phosphors has been studied in our laboratories recently with different activators. In the present investigation, the frequency and voltage dependence of CaO - CdO (Eu, Zn) phosphors were studied. The EL of CaO : Eu (0.1%) was too weak to record but that of CaO : Eu (0.5%) was fairly good. The optimum concentration of Eu was
0.1% in photoluminescence whereas in EL the optimum is 
found to shift to higher concentrations. The fluorescence 
and phosphorescence of Eu activated samples were very much 
brighter compared to those of Zn activated samples. The 
op optimum concentration of Zn required for EL was greater 
(1.0%) as compared to that for photoluminescence (0.5%).
The CaO : Zn phosphors show better electroluminescence than 
the Eu activated phosphors.

Voltage Dependence

The voltage dependence of EL, keeping other parameters 
constant, is of considerable interest since it may provide some 
information regarding the processes involved.

It is found in CaO and CaO : CdO (Zn 1.0%) phosphors 
that light output is an increasing function of the exciting 
voltage. This can be understood on the basis that initially 
the number of particles in which the electroluminescence takes 
place is small, but on increasing the voltage more and more 
active regions are exposed to voltage gradients above the 
threshold level.

A number of empirical relations based on experimental 
and theoretical grounds have been suggested for the voltage 
dependence of brightness. Lehmann suggested a basic equation
for the emission of a single particle as:

\[ L = L_0 \exp \left( -\frac{b}{V} \right) \]

where \( L \) is the brightness in arbitrary units and \( V \) the voltage in volts. Alfrey and Taylor \(^{62}\) and Zalm \(^{63}\) have taken into account the statistical effect in powder phosphores due to large numbers of particles with different sizes and have modified the expression to:

\[ L = L_0 \exp \left( -\frac{b}{\sqrt{V}} \right) \]

where \( L_0 \) and \( b \) are constants depending on the frequency, temperature and construction of the test cell. Harmann and Raybold \(^{64}\) suggested the power law relation:

\[ L = L_0 V^n \]

Since no fixed relationship between brightness and the voltage has been established and a number of empirical relations, besides those given above, have been suggested, different plots of \( \log L \) vs. \( 1/V \), \( \log L \) vs. \( 1/\sqrt{V} \), \( \log L \) vs. \( \log V \), \( \log L/V \) vs. \( 1/\sqrt{V} \) and \( L \) vs. \( V \) have been tried. Out of these, \( \log L \) vs. \( 1/\sqrt{V} \) shows a linear relationship for different frequencies for these samples. All the samples show the same nature with changes in the emission intensity which is maximum for CaO : CdO (7 : 3). The close agreement of the
experimental curves with the above formula suggests the validity of the Mott–Schottky exhaustion barrier where the field is proportional to \( \sqrt{V} \) and the emission results as a consequence of collision–excitation mechanism. As the CdO content is increased the band gap reduces and this leads to greater mobilities of the electrons. 65 Further, the addition of CdO is found to decrease the number of deep traps significantly. This would also tend to increase the mean free path of the electrons. 66 The two effects may probably be responsible for the increased electroluminescence observed since the latter is produced on account of collision–excitation. This increase in intensity can occur up to an optimum concentration of the two constituents CaO and CdO after which the presence of imperfections in the system brings down the intensity.

Frequency Dependence

A number of workers including Thornton 67 and Curie 68 have derived expressions for the frequency dependence of EL. The samples studied show a linear nature of plots between \( \log L \) Vs. \( \log f \). The result is obvious because the emptying and refilling of luminescent centres take place more rapidly with increase in frequency. 69 However, when the time period of the applied AC becomes comparable with the life time of
excited electrons in traps, the increasing frequency cannot impart a proportional increase in average intensity as the electrons do not have enough time to emerge out from the traps and hence a decrease in emission can be expected in the high frequency range giving rise to a maximum in the frequency brightness curve. However, in the present investigation such a maximum has not been obtained even at a frequency of 5 KHz.

8.7 Cathodoluminescence

The samples activated by Eu show peak emission at 5950 Å as in photoluminescence; which corresponds to the $^5D_0 \rightarrow ^7F_1$ transition. The weak emission observed under X-ray excitation between 6100 - 6200 Å corresponding to $^5D_0 \rightarrow ^7F_2$ transition is also clear in all these phosphors. CaO : Zn shows two emission peaks, one at 3400 Å and second at 4400 Å. The latter appears as a shoulder to the main UV emission. In the case of CaO : CdO (9:1): Zn, the ultra-violet band shifts to 4050 Å while the second band shifts to 4800 Å. The second peak appears reasonably resolved in this phosphor. Further addition of CdO causes only a decrease in intensity of the ultra-violet band while the second band is no longer clearly resolved. The optimum concentration of Zn for CaO phosphor is 1.0% while for X-ray excitation the optimum was 0.5%. From the colour co-ordinate measurement, the dominant
wavelength comes out to be around 4950 Å. Under cathode ray excitation the phosphors glow with great intensity initially but after sometime the intensity falls to a lower but reasonably steady value. The phosphor surface examined after the experiment invariably showed a slightly blackening. This is probably on account of 'ion burn' caused by bombardment of the screen by negative ions (e.g. $O^{2-}$). The heavy ions cause atomic dislocations and tend to remain on the surface layer as inert absorbing material which absorbs both electron energy as well as luminescence from phosphors. Because the deterioration depends particle size, packing of the material etc., it is not safe to make comparisons of the intensities of the various phosphors. The initial intensities were however, in the same order as under X-ray excitation.

Probably because of the much greater intensities of the phosphors involved and unequal deterioration of the component bands, the blue band could be observed more clearly in these experiments while they were not clearly brought out under X-ray excitation. According to Garlick the radiative intensities of different emission bands in the same phosphor may be different in photoluminescence and cathodoluminescence because of different excitation density conditions. A similar argument may hold good for X-ray excited luminescence and cathodoluminescence.

Since there is a systematic decrease of band gap with the
addition of CdO, a gradual shift of the emission bands towards longer wavelengths would be normally expected in such circumstances as in the case of ZnS : CdS; ZnS : ZnSe etc. Lehmann has studied the ZnO : CdO system up to the limit of solubility of the latter and found that both the edge emission as well as green emission show a shift to longer wavelengths with the decrease in band gap. However, under X-ray excitation no shift was observed while under cathode ray excitation there was a shift of the ultra-violet and visible bands only for CaO : CdO (911) : Zn, the peak positions remaining unaffected with further addition of CdO. The absence of shift in the peak positions in the case of X-ray excitation could be ascribed to a non-involvement of levels close to the conduction band in the emission process. However, the constant shift observed for the CaO : CdO phosphors under cathode ray excitation is difficult to explain. Since the excitation was not by sufficiently high energy electrons, ionic displacements or vacancy production could be ruled out particularly in CaO. The electron beam could at most produce colour centres involving defects already present in the material and this could be expected to produce new emission bands. However, the total suppression of the bands at 3400 and 4400 Å observed in CaO : Zn and the production of two similar bands in shifted positions would be too coincidental. One possibility however, is that because of the larger electron densities in this excitation, the valence
states of the centres responsible for the earlier emissions may be altered thereby causing a shift in both the bands and the stabilisation of the electron at the defect may be occasioned by the presence of cadmium. Only detailed studies such as magnetic susceptibility, electron paramagnetic resonance, colour centre formation, reversibility of the phenomenon etc. can serve to solve the problem fully.

8.8 Colour Co-ordinates

Under X-ray excitation the dominant wavelength of Eu activated phosphors lies around 5740 Å and the colours are saturated (near 100% purity). In cathodoluminescence also the purity is close to 100%. The result is significant since in applications of phosphors the aim is always to obtain phosphors whose colour co-ordinates lie close to the response curve of the average eye so that there is little loss of information.

The Zn activated phosphors have a dominant wavelength around 4900 Å and the purity is fairly high under X-ray excitation. In cathodoluminescence however the purity is less and this is probably due to a slight shift of the emission to longer wavelengths as is evidenced by a slight shift in the dominant wavelength to about 4950 Å.
As has already been pointed out, the ultra-violet band at 3400 Å observed in CaO:Zn phosphors is the host emission caused by oxygen vacancies. The visible band in the blue region is one that has not been reported by earlier workers such as Lehmann. Because of the change in its relative intensity with respect to the 3400 Å band on addition of CaO and also cathodoluminescence, it can be treated as a separate emission and attributed to a different centre. Further the emission predominates in thermoluminescence and has a different temperature dependence from the UV band.

Chen et al. have observed a band at 4750 Å in deformed CaO crystals which they attribute to vacancy clusters. As has been mentioned earlier, the addition of Zn may produce anion vacancies in addition to those already present in the material. The blue emission can therefore be on account of a Zn ion adjacent to an oxygen vacancy (similar to FA centre) or due to high-order vacancy complexes. The latter alternative seems to be a little more plausible since the trapped electron in thermoluminescence is apparently more readily captured at these sites leading to a predominant blue emission in thermoluminescence.
8.10 Conclusions

(1) X-ray diffraction patterns show sharp lines indicating good crystallisation.

(2) The absorption edge shifts from 2750 Å for CaO to 4510 Å for CaO : CdO (3 : 7) showing that there is a marked change in the band gap of CaO on addition of CdO.

(3) Eu$^{3+}$ occupies a site with inversion symmetry.

(4) CaO : Eu$^{3+}$ and (CaO - CdO) : Eu$^{3+}$ show prominent line emission at 3950 Å and the transitions assigned are:

\[ 5D_0 \rightarrow 7F_1 \]

which is magnetic-dipole in character.

(5) The emission is asymmetric, with an extension on the longer wavelength side due to weak emission between 6100 and 6200 Å which corresponds to the transition:

\[ 5D_0 \rightarrow 7F_2 \]

which is electric-dipole in character. This may be caused by a coupling with lattice vibrations reducing the site symmetry.

(6) The absence of shift in the emission spectra is due to 4f - transitions which are well-shielded by the outer electron shells.
(7) There is an increase in the intensity of emission with addition of CdO to CaO : Eu up to a ratio 3:7 which can be due to the combination of,

the progressive decrease in band gap leading to a greater mobility and hence a better transfer of energy by electrons and

the increase in absorptivity for X-rays due to the higher atomic number of Cd.

The lattice distortions or defects however decrease the emission for large CdO contents.

(8) The peak emission of CaO : Zn and (CaO - CdO) : Zn is around 3400 Å which can be attributed to oxygen vacancies.

(9) The addition of CdO enhances the visible portion of the spectra up to the ratio CaO : CdO (8:2).

(10) The first thermoluminescence peaks in CaO : Eu and CaO : Zn lie around the same temperature (75°C) and the trap depths obtained lie between 0.72 and 0.70 eV indicating the same group of traps which may be due to host lattice defects.

(11) The second peaks in CaO : Eu and CaO : Zn occur at widely different temperatures with trap depths 1.00 and 0.79 eV. The traps may be specific to the kind of impurity involved.

(12) The addition of CdO to CaO shifts the trap depth to low energy values which can be due to the decrease in band width.
(13) The colours of thermoluminescence and fluorescence are identical in CaO: Eu indicating a transfer of energy between a potential thermoluminescent unit and the activator.

(14) The TL of CaO: Zn consists of two colours with wavelengths 3400 Å and 4900 Å with a better transfer between TL units and the blue centres.

(15) The steady rise in fluorescence of CaO: Eu up to 220 ± 10°C is due to the release of electrons from traps.

(16) Temperature dependence of 3400 and 4900 Å emissions in CaO: Zn shows that the blue band shows a maximum at 75°C whereas the other does not. This shows a better transfer of energy between TL units and the centres responsible for blue emission.

(17) The relation between the brightness (L) and voltage (V) is found to follow the relation $L = L_0 \exp \left(- \frac{b}{\sqrt{V}} \right)$ suggesting the possibility of a Mott-Schottky barrier in Zn activated phosphores.

(18) A plot of log L Vs. log f is found to be linear up to 5 KHz.

(19) The concentration of activator required is more in electroluminescence than in photoluminescence.
(20) CaO : Zn under cathode rays shows peak emissions at 3400 and 4400 Å the second being weak. In CaO:CeO (9:1): Zn the ultra-violet band shifts to 4050 Å while the second band shifts to 4800 Å which is well-resolved.

(21) The Eu emission is close to 100% purity.

(22) The blue emission in Zn activated phosphors may be on account of high-vacancy complexes.