4.1 **INTRODUCTION** :- A study of the temperature dependence of basic phosphor properties provides valuable information on luminescence and the processes accompanying it\(^1\). Thus for example, data concerning the effect of temperature on the position and width of absorption and emission bands of the phosphor make it possible to draw certain conclusions concerning the nature of centres which absorb to emit luminous energy and their interaction with lattice vibrations\(^2,3\). The nature of the nonradiative processes in the phosphor may be determined from the temperature variation of luminescence yield\(^4\). The variation in temperature of a phosphor may influence the intensity and the colour of luminescence and may broaden the emission band\(^5\). The location of the levels involved in the emission transition may be obtained from the measurements of the emission intensity as a function of temperature\(^6\).

Another reason for studying the temperature dependence of fluorescence is the practical value of such data for designing new phosphors or improving existing ones. Phosphors with good temperature dependence find applications, for instance, in high pressure mercury lamps\(^7\), in high loaded fluorescent lamps, in colour television screens\(^8\) etc.. For example, europium activated pyrophosphates have been found very suitable for application in low as well as high pressure mercury lamps\(^9\).

HAAKE\(^10\) has considered some of the physical aspects of temperature dependence and pointed out that there are two important factors to be considered: (i) an increasing absorption with temperature leading to higher intensity of
emission and [ii] a decrease in the efficiency of fluorescence with temperature due to competing phonon processes. Because the effects work against each other the brightness versus temperature curves often show a maximum, the position of which will depend on the relative importance of the two factors. Increasing the temperature of a phosphor results in a high 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 ion with the surrounding host ions\(^1\). This interaction is small when the transition occurs in an inner shell as in the case of rare earth activated phosphors possessing in general a high quenching temperature\(^2\).

4.2 QUANTITIES RELATED WITH TEMPERATURE DEPENDENCE OF LUMINESCEENCE : The graphical representation of fluorescence intensity versus temperature in fig. (4.1) exhibits a general form of the temperature dependence curve. It illustrates that the intensity of fluorescence first rises to maximum and then rapidly falls with to a further rise of temperature. Normally, the shape of the curve depends on the wavelength of the exciting radiation.

[a] QUENCHING RANGE \(\Delta T\) :- The quenching range may be defined as the temperature range within which the luminescence intensity decreases with temperature after non-radiative transitions begin to dominate\(^3\) and is given by: \(T_2 - T_1 = \Delta T\)
FIG. 4.1 TEMPERATURE DEPENDENCE OF FLUORESCENCE
\[
\Delta T = \frac{5}{3k} \left\{ (\log S - \log 4)^{-1} - (\log S + \log 4)^{-1} \right\} \quad \ldots \ [1]
\]

where \( T_1 \) and \( T_2 \) are taken as the temperature corresponding to points of intersection of the line drawn through the points at which the intensities have fallen to 80% and 20% of the maximum value, with horizontal line drawn at the 100% and 0% levels.

[b] QUENCHING_TEMPERATURE \( T_q \): It is defined as the point of intersection of the abcissa and a straight line drawn through the points at which intensity has fallen to 80% and 20% of the maximum value. In fig.(4.1) \( T_2 \) is termed as the quenching temperature, since \( T_q \) and \( T_2 \) lie fairly close to each other.

\[
T_q = \frac{5}{3k} \left\{ 4 (\log S - \log 4)^{-1} - (\log S + \log 4)^{-1} \right\} \quad \ldots \ [2]
\]

[c] BREAK_POINT_TEMPERATURE \( T_B \): It is the temperature at which non-radiative transitions set in. It is the temperature point corresponding to maximum luminescence intensity and is approximately given by

\[
T_B = \frac{\frac{\log S}{k}}{\log S + 0.9} \quad \ldots \ldots \ [3]
\]

[d] HALF_VALUE_TEMPERATURE \( T_H \): It is the temperature at which the intensity decreased to half its maximum value within the quenching range \( \Delta T \). It is given by the expression

\[
T_H = \frac{\frac{\log S}{k}}{\log S} \quad \ldots \ldots \ [4]
\]

When the value of frequency factor \( S \) is large, \( T_q \) and \( T_B \) change to \( T_H \) which can be calculated most conveniently.
4.3 FACTORS AFFECTING THE TEMPERATURE DEPENDENCE OF LUMINESCENCE:

Many factors such as activator and its concentration, host composition and crystal structure, thickness of the phosphor, change in pressure, method and mode of excitation etc. influence the slope of the initial rise of fluorescence, the temperature of maximum intensity of the phosphor, efficiency and quenching temperature.

[A] EFFECT OF HOST AND CRYSTAL STRUCTURE:— According to BLASSE and J.DEVRIES the vibrations in the host lattice play an important part in the quenching process and at high temperature the rate of multiphonon processes varies approximately as $T^n$ where $T$ is the absolute temperature and $n$ is the number of phonons involved, so that when high energy phonons are available $n$ will be small and the variation of the efficiency will be less prominent.

The wide variation in the behaviour between the same activator in different matrix and between different activators in the same matrices suggests that the temperature characteristics are determined by the nature of the matrix and activator combination. The crystal structure of the phosphor also has a strong influence on the temperature dependence characteristics. For e.g. both $\alpha$-Sr$_3$(PO$_4$)$_2$ : Ce$^{3+}$ and $\alpha$-Sr$_3$(PO$_4$)$_2$ : Eu$^{2+}$ measured with cathode ray excitation and $\alpha$-Sr$_3$(PO$_4$)$_2$ : Eu$^{2+}$ show high quenching temperature. The introduction of small amounts of Mg in Sr$_3$(PO$_4$)$_2$ causes transformation to the $\beta$ crystal structure and GORBACHEVA noticed a much lower quenching temperature. KROGER has also pointed out that phosphors which are badly crystallized have a low quenching point.
BLASSE et al.\textsuperscript{28-31} have also studied the temperature dependence of Eu\textsuperscript{2+} emission in alkaline earth pyrophosphate, silicates, aluminates and octaborates and found that quenching temperature of these compounds increases usually as metal ion is changed from calcium to strontium to barium within an isomorphous series.

The addition of comparatively minor constituents to the composition of a phosphor can improve the temperature characteristics of several phosphor systems. FROELICH and MARGOLIS\textsuperscript{32}, for example, have shown that certain alkali metals can improve the temperature characteristics of calcium phosphate activated with Ce and Mn, and have suggested that these additives may produce a lattice with fewer vacancies or defects. KLASENS\textsuperscript{33} has observed a similar improvement with magnesium arsenate activated by Mn containing Li. The effect of silica content in the triple silicates, represents a further example the importance of small change in phosphors composition on temperature characteristics.

\[B\] EFFECT OF ACTIVATOR AND ITS CONCENTRATION :-

In Calcium orthophosphate phosphors activated with Ce and Mn\textsuperscript{32}, comparatively large quantity of Ce of the order of 10\% by weight of the matrix, gives the brightest fluorescence at ambient temperature. Although the temperature characteristics of these phosphors are not critically dependent on the Ce content, increase in Ce lowers the temperature at which optimum brightness occurs while the rate of depreciation beyond this point is reduced.
Mn content influences the color and the intensity of fluorescence but, even in amounts which reduce the initial brightness do not alter markedly the shape of the temperature dependence curves, provided optimum silica ratio are maintained.

The temperature dependence of luminescence of ZnS : Mn phosphors with different activator concentrations has been studied by various workers. According to VLASENKO\(^1\) an increase in concentration causes a monotonic decrease in temperature at which quenching begins. According to LEVSHIN & TUNITSKAYA\(^2\) the absorption and hence emission in the region of fundamental band gradually decreases as the Mn concentration increases.

Introduction of heavy metals like Ag and co-activator like Ni in ZnS phosphors, showed a significant decrease in quenching temperature, with an increase in Ni concentration\(^3\).\(^4\)

The temperature dependent emission was measured by ROBBIN et al.\(^3\) in the case of Y\(_{3}\)Al\(_{5}\)O\(_{12}\) crystals containing a series of concentrations of each of the ions Ce\(^{3+}\), Eu\(^{3+}\), Tb\(^{3+}\), and Gd\(^{3+}\) and they concluded that Ce\(^{3+}\) (and to some extent Tb\(^{3+}\)) shows an approximately linear dependence of intensity on concentration at the lowest temperature whereas intensity of Eu\(^{2+}\) luminescence is only dependent on concentration. WANMAKER et al.\(^9\) have reported that the quenching temperatures of Eu\(^{3+}\) activated alkaline earth pyrophosphates are much lower than those for Eu\(^{3+}\) activated phosphors where in contrast to the Eu\(^{2+}\) phosphors, no excitation of 4f electrons to outer shells takes place.
Excitation to outer shells renders the phosphors more susceptible to the influence of the surroundings of the activator ions.

The effect of concentration of activator is different in different hosts. In EuAl$_3$B$_4$O$_{12}$ there is no change due to Eu$^{3+}$ activator concentration, while in LaAlO$_3$ at higher Eu$^{3+}$ concentrations the number of radiationless transitions are increased by the concentration quenching of the Eu$^{3+}$ fluorescence.$^{10}$ The effect of activator concentration on the quenching temperature is found to be small in both Ca$_2$P$_2$O$_7$ : Eu and Sr$_2$P$_2$O$_7$ : Eu phosphors.$^9$

BOEHM and et. al.$^{35}$ have reported that the phenomenon in doubly activated phosphors is also temperature dependent. It is observed that energy transfer from Ce to Tm in phosphate glasses is independent of temperature while enhancement of intensity results in a pair of Ce$^{3+}$, Tb$^{3+}$ with increase in temperature.

[C] EFFECT OF PREPARATORY CONDITIONS AND THICKNESS OF THE PHOSPHOR :-

The temperature dependence of ZnS : Cu phosphors prepared in the temperature range 500°C to 1200°C has been studied by GARLICK$^{36}$. He observed a marked effect of preparation temperature on the temperature dependent luminescence characteristics of a phosphor. A marked improvement in temperature dependence with increase in firing time has been observed.$^{25}$ As reported by HALPERIN et.al.$^{37}$ for wavelengths within the lattice absorption the luminescence is independent of the thickness of the specimen.
It would rise, however, with the thickness of the specimen on excitation at longer wavelengths. This part of excitation spectrum would therefore become less pronounced on reducing the thickness of the specimen. According to HAAKE\textsuperscript{34} thick phosphor layers peak at lower temperature as compared to thin layers and slope of the initial fluorescence rise decreases with increasing thickness. In the case of powder phosphors the average particle size also influences the slope and the position of maximum to some extent.

[D] **EFFECT OF MODE OF EXCITATION** :- Many workers \textsuperscript{1,24,37,38} have reported that temperature dependence of luminescence is strictly related to the nature and wavelength of the exciting radiation. GARLICK\textsuperscript{36} and others have observed that in ZnS phosphor and Mn activated cadmium iodide phosphor the fluorescence efficiency shows a slow increase with temperature for wavelengths longer than the absorption edge (3340) but a slow decrease with temperature for shorter wavelengths. HALPERIN et.al\textsuperscript{37} investigated the case of ZnS:Cu:Cl crystal and found that luminescence completely disappears below 150 K. on excitation with light of 3330 Å, while the temperature quenching occurs at about 250 K. on exciting at 3400 Å.

WILLIAMS and EYRING\textsuperscript{39} tried to explain the slow variation on the assumption that changing excitation energy results in a varying absorption transitions within the emission centre. GARLICK and GIBSON \textsuperscript{38} and KROGER\textsuperscript{40} have given a better explanation on measuring the excitation spectra of various zinc sulphide phosphors over a wide range
of temperatures. The whole excitation spectrum is shifted to longer wavelength with rise of temperature. This shift in excitation spectrum causes a fall in luminescence efficiency for short wavelength excitation while at longer wavelengths an increase in efficiency is obtained.

**EFFECT OF PRESSURE** :- Under different pressure conditions CaAl$_2$O$_4$ phosphor activated by Europium is observed for temperature dependence of fluorescence intensity and lifetime by TYNER and DRICKAMER$^{19}$. They reported that temperature quenching increases with increasing pressure. They postulated the presence of a third state between the ground and excited states of the configuration coordinate model which explains the thermal quenching.

4.4 **THEORETICAL ASPECTS OF THERMAL QUENCHING OF LUMINESCENCE** :-

Luminescence efficiency of a phosphor is a function of temperature and is defined by WACHTEL$^{41}$ as the ratio of number of photons emitted from a phosphor layer to the number of photons absorbed by the same layer. The nature of efficiency has been investigated by a number of workers$^{40-44}$.

If $N_o$ be the number of luminescent centres in an excited state that make a transition to a ground state by emitting luminescent radiation, the number $N$ in the excited state at any time t may be given by

$$N = N_o \exp \left( -\frac{t}{\tau_L} \right) \quad \ldots \ldots [1]$$

If $P_r$ is the probability of luminescence emission, then,

$$P_r = 1/\tau_L \quad \ldots \ldots [2]$$

There may be a thermal process leading to radiationless
transition between the excited state and the ground state, along with the luminescent transition. The probability of non-radiative transition $P_{nr}$ may be given by

$$P_{nr} = S \exp \left( -\frac{W}{kT} \right) \quad \text{[3]}$$

Where $W$ is the activation energy and is equivalent to the energy of the intersection point above the minimum of the excited state on a configurational coordinate plot.

The efficiency of luminescence is the combined effect of $P_r$ and $P_{nr}$ and can be written as

$$\eta = \frac{P_r}{P_r + P_{nr}} \quad \text{[4]}$$

Using equation [3] this may be written as

$$\eta = \frac{1}{1 + \frac{A \exp \left( -\frac{W}{kT} \right)}{P_r}} \quad \text{[5]}$$

Where $I$ and $I_o$ are the emission intensities at temperature $T$ and temperature corresponding to maximum intensity $T(B)$ respectively and $A \& S$ are related quantities.

Equation [6] indicates that fluorescence intensity is directly proportional to excitation intensity. GISOLOF and KROGER\(^{45}\) observed a deviation from this linear relation in the case of ZnS : Mn phosphor. Their results follow a relation of the form:

$$I = \text{Constant} \cdot J^n \quad \text{[7]}$$

Where $J$ is the excitation intensity; $n$ is a constant. KLASSENS\(^{34}\) worked out a satisfactory explanation of the non-linear increase of fluorescence with excitation intensity and gave an expression of the form:
\[ \eta = 1 / \eta_0 = 1 / \left[ 1 + C (\alpha J)^{1/2} \right] \] \[ \ldots \ldots \ldots \ldots \text{[8]} \]

\[ C = \gamma \exp \left( -W / kT \right) \]

and \( \alpha \) is a constant.

GARLICK replaced equation [7] & [8] by the following empirical formula;

\[ \eta = l/l_0 = \left[ 1 + b \exp \left( -W / kT \right) / J^{n-1} \right] \] \[ \ldots \ldots \ldots \ldots \text{[9]} \]

Where \( b \) is a constant and value of index \( n \) varies between 1 and 2. He found a better agreement of this relation with his experimental results.

4.5 EVALUATION OF ACTIVATION ENERGY :- Activation energy is defined as equivalent to the energy of intersection point above the minimum of the excited state on the configuration coordinate plot.

Equation [6] can be expressed as;

\[ \left[ I_0 / I - 1 \right] = A \exp \left( -W / kT \right) \]

\[ \log \left( I_0 / I - 1 \right) = \log A - W / kT \] \[ \ldots \ldots \ldots \ldots \text{[10]} \]

If the slope is large i.e. \( A \exp(-W/kT) \gg 1 \), then equation [6] reduces to;

\[ I_0 / I = A \exp \left( -W / kT \right) \] \[ \ldots \ldots \ldots \ldots \text{[11]} \]

or \( \log \left[ I_0 / I \right] = \log A - W / kT \) \[ \ldots \ldots \ldots \ldots \text{[12]} \]

Hence a plot of \( \log \left[ I_0 / I - 1 \right] \) or \( \log \left( I_0 / I \right) \), as the case may be, \( V \text{s} \) \( 1/T \) will yield a straight line and its slope will give the value of \( W/k \) from which \( W \) can be calculated.
4.6 THEORETICAL MODEL: BLASSE and BRIL\textsuperscript{28,46,47} propounded a model which serves to explain the quenching temperature of characteristic luminescence of activators in solids. Referring to the configuration coordinate model given by MOTT – SEITZ, DEXTER – KLICK – RUSSELL and SEITZ model, they suggested that $\Delta r$, the equilibrium distance between the ground state and the excited state, the radius and the charge of cations surrounding the relevant luminescence centre determine the quenching temperature of fluorescence to a great extent. The larger the value of $\Delta r$ lower will be the quenching temperature of luminescence.

The centres were divided into two groups:

[a] Those with $\Delta r > 0$ [charge transfer transitions] and 
[b] Those with $\Delta r < 0$ [Rydberg transitions].

If a high $T_q$ is desired, centres with $\Delta r > 0$ should be substituted for smaller ions e.g. Eu\textsuperscript{3+} [0.98 Å] for Lu\textsuperscript{3+} [0.85 Å] and centre with $\Delta r < 0$ for larger ions e.g., Eu\textsuperscript{2+} for Ba\textsuperscript{2+}.

The sign of $\Delta r$ depends on the nature of the luminescence centre. If a cation is excited, the electronic charge distribution extends farther away from the nucleus rendering it effectively positive. In KCl : Tl\textsuperscript{+} system, upon excitation, the luminescent centre shrinks\textsuperscript{48}. In the case of anion excitation $\Delta r$ is positive as is seen on excitation into charge-transfer absorption bands [tungstate, Eu\textsuperscript{3+} activated].

The value of $\Delta r$ is affected by:

[1] The size of the host lattice cation for which the activator is substituted.
The size and charge of the cations in the neighbourhood of the activator.

If the activator ion is larger than the host lattice ion, the surroundings of the activator will be forced to expand. If upon excitation $\Delta r$ is positive this means a further expansion which will be opposed by the lattice, so that $\Delta r$ will be relatively small and the quenching temperature $T_q$ high. If however $\Delta r$ is negative, excitation brings about a shrinkage. Since the lattice was expanded in the ground state, it will shrink easily, so that $\Delta r$ is relatively large and $T_q$ low. The reverse is true if the activator is smaller than the host lattice ions. It is obvious that $\Delta r$ will be relatively small if the centre is surrounded by a rigid lattice, i.e., a lattice containing small cations with a high charge. In such lattices we may therefore expect a high $T_q$.

By making a number of reasonable assumptions concerning the parameters involved BLASSE$^{49,50}$ has shown that a necessary, but not a sufficient condition for efficient fluorescence is that $\Delta r$ should be $0.3 \text{ Å}$ or less. For small values of $\Delta r$, $\Delta E$ is large, and efficient fluorescence occurs even at higher temperatures. An empirical estimate of $\Delta r$ can be obtained from the WABER & CROMER radii of the elements which give the maxima of the charge distribution of the outer electron orbitals of the elements. It is thus possible to extract the difference in radii between two electron shells from these figures, and the difference can be taken as a measure of $\Delta r$. In the case of Eu$^{3+}$ phosphor, when the ground
and excited states both belong to the 4f configuration, so that $\Delta r$ is zero, the quenching temperature is high\textsuperscript{49}. Many phosphors with $\text{Sn}^{2+}$, $\text{Ce}^{3+}$ and $\text{Pb}^{2+}$ show high efficiencies at very high temperatures as $\Delta r = 0.2 \text{Å}$ only\textsuperscript{49}. The phosphor $\text{Ca}_3(\text{VO}_4)_2 : \text{Eu}^{3+}$ shows a very high quenching temperature when the vanadate group is excited by UV excitation\textsuperscript{50}. This process is followed by energy transfer from the vanadate group to the $\text{Eu}^{3+}$ ion which is not excited in its charge-transfer state \{where radiationless losses may occur\}, but in one of the levels of the $4f^6$ configuration \{where radiationless decay is rather improbable\}\textsuperscript{28}.

When the equilibrium distance between the ground and excited states remains fixed, the activation energy for non-radiative transitions goes on increasing as the absorption band moves to shorter wavelengths. It has been found that in the case of octahedral niobate centre the position of the first absorption band moves to longer wave lengths and quenching temperature of the fluorescence consequently decreases\textsuperscript{41}.

4.7 EXPERIMENTAL ARRANGEMENT: - The experimental set up used by BOTDEN\textsuperscript{52}, KREHER\textsuperscript{53}, Yu and PARK\textsuperscript{54} is utilized to make the present study of temperature dependence. The system consists of sample holder, source of X-ray excitation, programmer to provide a constant heating rate, detecting unit in the form of a photomultiplier and D.C. microvolt meter.

4.8 PRESENT METHOD: - The experimental alignment of the setup is the same as that followed for TL studies. Investigations of
FIG. 4-2 TEMPERATURE DEPENDENCE OF FLUORESCENCE
FIG 4.3 TEMPERATURE DEPENDENCE OF FLUORESCENCE
FIG. 4.4 TEMPERATURE DEPENDENCE OF FLUORESCENCE

The graph shows the temperature dependence of fluorescence intensity for various ions at different temperatures. The intensity is measured in arb units and the temperature is in Kelvin (K). The legend indicates the following:

- $\text{Tb}^{3+} (10^{-2})$
- $\text{Gd}^{3+} (10^{-1})$
- $\text{Gd}^{3+} (10)$
- $\text{Gd}^{3+} (10^-4)$
- $\text{Gd}^{3+} (10^-5)$
- $\text{Gd}^{3+} (10^-6)$
FIG. 4.5 TEMPERATURE DEPENDENCE OF FLUORESCENCE
FIG. 4.6 TEMPERATURE DEPENDENCE OF FLUORESCENCE
FIG. 4.7 TEMPERATURE DEPENDENCE OF FLUORESCENCE
temperature on the luminescence of calcium meta silicate phosphor activated by Terbium and Gadolinium have been made in the temperature range of 302 to 515K. The sample is pressed in the cavity of the sample holder. The sample is exposed to the source of X-rays till saturation. The saturation duration is determined experimentally by a series of runs and found to be 10 minutes. The warming of the sample is achieved by a kanthal strip heater, which is attached just behind the sample holder cavity. The total fluorescence intensity is recorded on the micro volt meter.

For finding the temperature of the phosphor at any time during heating, the heating element was calibrated. For this purpose the temperature versus time graph was obtained by using a Cr/Al thermocouple in conjunction with a Unitech Digital Temperature Indicator Controller Model No. UT 29T.

The intensity is noted after every 5 sec. and then a graph is plotted between intensity and temperature, with the help of the calibration curve.

4.9 RESULTS:

The temperature dependence curves were obtained for all the series and are shown in Figs. 4.2 to 4.7. The curves do not conform to the standard curve shown in Fig. 4.1. The intensity starts increasing from its room temperature value as temperature is raised and in most cases exhibits three maxima and in a few cases four. The intensity does not fall to low values even at 515 K and is in fact only slightly less than the initial value.

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