Chapter - I
1. Introduction

1.1 Luminescence

Luminescence exists in nature as a cold glow from certain insects, fishes, plants, etc. ever since the evolution of life. When a substance absorbs energy in some form or other, a fraction of the absorbed energy may be re-emitted in the form of electromagnetic radiation in the visible or near visible region and this is defined as "Luminescence". Materials that are capable of emitting light, particularly in the visible range, are termed as "Luminescent phosphor" or simply a "phosphor" [1, 2].

Luminescence can be broadly classified as (i) Fluorescence and (ii) Phosphorescence [1, 2]. When luminescent materials are excited, emission occurs simultaneously with absorption of energy and if the emission stops as soon as the excitation ceases (i.e. within $10^{-8}$ seconds), it is known as Fluorescence. If the emission continues even after the excitation ceases with decreasing intensity, then the process is called as Phosphorescence [2]. Fluorescence is independent of temperature while phosphorescence is strongly dependent on temperature. Further classification of luminescence is based on the mode of the excitation source [1-3].
The process in which incident electromagnetic radiation in the visible or near visible region causes a phosphor to give out luminescence is known as 'photoluminescence'. In 'electroluminescence', emission of radiation occurs during the application of a strong electric field. In 'cathodoluminescence', the emission occurs due to an electron bombardment. 'Radioluminescence' is caused by ionizing radiations like X-rays and γ-rays. If the excitation energy is supplied by a mechanical energy then the luminescence is called 'Triboluminescence'. Light emitted during a chemical reaction is known as 'Chemiluminescence'.

Among the different kinds of luminescence processes, the luminescence observed due to a secondary stimulation subsequent to a primary excitation (usually by ionizing radiations such as X-rays and γ-rays) is called "Stimulated luminescence" [1]. When an ionic crystal such as an alkali halide is excited by exposing it to ionizing radiations, a part of the excitation energy is stored in the form of electron and holes trapped at defect sites (discussed in a later section). On warming the crystal subsequent to such a primary excitation, some of the trapped charges are released from their traps and they recombine with their counterparts emitting light. This is known as "Thermally stimulated luminescence" (TSL) or thermo luminescence (TL) [1]. If the luminescence is due to a secondary stimulation by photons after the primary excitation, then it is known as
"Photostimulated luminescence" (PSL) [1]. TSL and PSL of ionic materials have been studied extensively. These studies in undoped and impurities doped alkali halides have helped the scientists to understand the processes and defects involved in these materials.

1.2 Alkali halides

Alkali halides have large band gaps and so single crystals of alkali halides are transparent over a wide frequency range including visible, near infrared and near ultra violet. The crystals are essentially ionic in nature. Most of the alkali halides crystallize in the rock salt structure while some of them crystallize in the caesium chloride structure [4]. Preparation of single crystals of alkali halides is simple as the melting temperatures of alkali halides are relatively low in comparison with those of oxides and sulfides. It is well known that many of the useful properties of solids are controlled/ altered by the defects present in them and the study of defects is relatively easier in alkali halides [4, 5]. Thus, they constitute almost ideal hosts for the study of defects or impurity centres that perturb the optical properties of the perfect crystals.

1.3 Point Defects

Point defects play a major role in all luminescence processes of solids.
Understanding the science behind the interaction of defect centres or mechanism of defect formation in the crystal lattice is essential for the development of materials for practical applications [1, 2]. These point defects mainly involve vacancies and interstitials. In ionic crystals such as alkali halides, equal numbers of cation and anion vacancies are present under thermodynamic equilibrium conditions so that the system has a minimum free energy and the charge neutrality of the crystal is maintained [5]. An anion vacancy and a cation vacancy constitute the defect called 'Schottky pair'. If an ion occupies an interstitial position leaving its normal site vacant, it is known as a 'Frenkel defect'. The formation of a particular type of defect in a crystal is most favoured if it requires a smaller energy of formation. According to theoretical calculations, the energy of formation for Schottky defects is lower than that for Frenkel defects in alkali halides and hence Schottky defects are the most favored in alkali halides [6]. By doping the crystal with aliovalent impurity ions, excess of vacancies of one sign or the other can be created.

A cation vacancy bears an effective negative charge and an anion vacancy an effective positive charge. They may form an associated pair because of the electrostatic force between them. Such a pair is an electrically neutral entity. Similarly, a divalent cation impurity in the substitutional site will have an electrostatic attraction towards the cation vacancy which results in a neutral entity
and associated impurity-vacancy (I-V) complex [6]. The binding energy of such a complex is relatively small (a few tenths of an electron volt). A large number of these vacancies exist in this associated form at room temperature [5, 6].

1.4 Colour centres

Colour centres are also point defects. They involve vacancies and / or interstitials with trapped electrons or holes. Colour centres are produced by photolysis, radiolysis, additive colouration and electrolysis [7]. While the radiolysis and photolysis methods are known to produce both electron excess and electron deficient centres simultaneously, the other methods give rise to only one type of defect centres (either electron excess or electron deficient centres) [7]. Ionizing radiations produce free electrons and holes in ionic crystals during irradiation. Most of these electrons and holes recombine immediately resulting in the emission of light or lattice vibrations. The remaining free charges get trapped at the defect centres which may be present in the host material either inherently or by doping, thus forming Colour centres.

The colour centres and also several impurity centres produce optical absorption bands in the otherwise transparent crystals such as alkali halides, alkaline earth halides, etc. [7, 8]. Theoretical studies guided by detailed experimental works have yielded a deep understanding of colour centres.
Colour centre research on luminescent materials has led to many practical applications such as radiation dosimetry, high-density memory devices, tunable lasers, etc. [9 - 12]. Structure and properties of different kinds of colour centres are briefly discussed in the following section.

1.4.1 Electron excess centres

1.4.1.1 F-centre

F-centre is the prototype to all electron excess centres. The name F-centre comes from the German word for colour, Farbe, as crystals containing these point defects appear to be coloured. These defects have been investigated by various spectroscopic techniques [13 - 15]. The optical absorption due to F-centres in alkali halides generally falls in the visible region of the electromagnetic spectrum. It is due to the 1s - 2p transition of the F-centre electron. The F-centre absorption is bell shaped and Gaussian. It is broad due to the strong interaction between the electron and the surrounding lattice. The peak position ($\lambda_m$) of the F-band absorption is related to the lattice constant 'd' of the host lattice by the Mollwo-Ivey relation [16],

$$\lambda_m \text{ (in Å)} = 703d^{1.84}$$

With increasing temperatures, the F-band peak position shifts to low energies and also the half-width of the F-band increases with temperature. F-absorption band is
independent of added impurity and is the characteristic of the host crystal. The unpaired electron of the F-centre gives rise to a characteristic ESR spectrum [17].

1.4.1.2 F' centres

The colour centre with two electrons trapped at a single anion vacancy is the generally accepted model of F' centres (Fig. 1.1). F' centres are generally formed by F-light bleaching (illumination at F-band) of an alkali halide crystal containing F-centres. They are stable only at low temperatures [13]. In comparison with the F-band, these centres produce a broader absorption band on the low energy side of the F-band. This centre is thermally and optically unstable and is in equilibrium with the F-centres by a reaction: \(2F \leftrightarrow F' + \text{anion vacancy}\) [18]. The efficiency of conversion between F and F' centres is temperature dependent. F'-centres are suggested to be formed temporarily during the photochemical production of perturbed F-centres and F-aggregate centres [18].

1.4.1.3 F-aggregate centres

F-aggregate centres are formed when the crystal containing F-centres is subjected to suitable thermal and/or optical treatments near room temperature. Generally, due to F-aggregate centres new absorption bands appear on the long wavelength side of the F-band absorption. The existence of several bands
indicates a reduction in the symmetry of these F- aggregate centres. The sequence of F- aggregate centre formation is M, R and N respectively [8, 19]. The M centre is an associated pair of F-centres formed along <110> direction (Fig. 1.1) [19, 20]. M centres can be produced by F-light bleaching the crystals containing a higher concentration of F-centres. These M centres were found to show dichroic absorption on irradiation with the linearly polarized light so that the equal distribution of M-centres along equivalent orientations is changed in favour of one orientation. The other aggregate centres, viz, R and N centres can be produced by extended photo bleaching of F-centres [14]. R and N centres are considered as three F-centres bound together in (111) plane and an aggregate of four F-centres with at least two different atomic arrangements respectively (Fig. 1.1). F-aggregate centres are more easily formed in additively coloured crystals than in crystals exposed to ionizing radiations.

1.4.1.4 Perturbed F -centre

The symmetry of F-centre is reduced when a new colour centre is produced due to perturbation effect of another point imperfection on the F-centre. Commonly formed two such perturbed F-centres are $F_A$ and $F_z$ centres [20]. These centres are believed to be formed via the formation of F'centres similar to the formation of F-aggregate centres. The $F_A$ centre is an F-centre with substitutional
monovalent cationic impurity of smaller size than the host cation in the first
neighbour position [21]. The symmetry of F-centre (O_h) is reduced to C_{4v} (in fcc
alkali halides) under which the excited 2p state of the F-centres splits into doublet
and singlet components. The transition from the ground state to the singlet state is
designated as F_{A1} and to doubly degenerate level as F_{A2}. These transitions give rise
to optical bands which show dichroism [7].

The perturbation on the F-centre caused by a substitutional divalent cationic
impurity and its associated cation vacancy (I-V) complex leads to the formation of
another type of perturbed F-centres called Z-centres [8] (Fig. 1.1). Different types
of Z centres (Z_i to Z_5) have been reported to be formed in coloured alkali halides
after suitable optical and / or thermal treatments [22]. Alkali halides doped with
divalent cationic impurities having a lower second ionization potential (eg. Ca^{2+},
Sr^{2+}, Ba^{2+}, Eu^{2+}, Yb^{2+}, etc.) give rise to Z centres [22, 23]. The well known Z_1
centre is formed in these crystals on bleaching them with F-light subsequent to
colouration [22]. In some cases, the Z_1 centres are reported to be formed along
with F-centres in the as-irradiated crystals [24 - 27].

The peak position of the absorption band due to Z_1 centres depends on the
lattice constant. The structure and characteristics of Z_1-centres are studied using
optical absorption, electron spin resonance, photoconductivity studies, Stark
Fig. 1.1 Colour centres in alkali halides [12]

effect, etc [20] Such studies revealed that $Z_1$ centre is a F-centre perturbed by an adjacent I-V complex [22] The divalent impurity does not play any direct role, although its presence (in the form of I-V complex) is essential for the formation of $Z_1$ centres
1.4.2 Electron deficient (hole) centres

Hole trapped centres are molecular ions embedded in lattice defects with weak lattice interaction. The properties like structure and energy levels of these electron deficient centres are governed by their molecular properties. Though additive colouration by halogen vapour under pressure and electrolytic colouration [28] can also produce hole centres, most of the investigations on these centres have been performed on crystals exposed to ionizing radiations. The type of hole-centres formed in the crystal depends on temperature of irradiation, temperature of measurement, nature of impurities present in the crystal and so on [8].

1.4.2.1 $V_K$-centres

$V_K$-centre is a halogen molecular ion, $X_2^-$ ($X$ = halogen), oriented along one of the $<110>$ axes of the crystal [29] (Fig. 1.1). It is formed by the loss of an electron from a halide ion, followed by the pulling together of the resulting atom with an adjacent normal halide ion. These centres are generally formed in an alkali halide crystal when it is irradiated by high energy radiations at liquid Nitrogen temperature [7, 8]. However $V_K$ centres are not stable above 200 K. As the $V_K$ centres are paramagnetic, they give rise to ESR [13]. ESR results have shown that the molecular ion constituting a $V_K$-centre is oriented along one of the six equivalent $<110>$ direction [13]. Luminescence of $V_K$ centre and ($V_K$ +electron)
recombination luminescence are of great significance in the understanding of processes of recombination of electron and holes in many alkali halide phosphors [30].

1.4.2.2 H-centres

A major product of radiation damage at liquid helium temperature is H-centre. H centre is a halogen molecular ion \((X_2^-)\) situated at a single halide ion site along with two weakly bound halide ions adjacent to this site, one on the either end, in the \(<110>\) direction [31] (Fig. 1.1). The optical absorption of H-centres is similar to the \(V_k\) absorption. Detailed information on the H-centres was deduced from ESR investigations [32].

1.4.2.3 V-centres

When the temperature of the alkali halide crystal containing H and / or \(V_k\) centres is increased, these defect centres reorient, disintegrate and / or aggregate to form new types of hole centres called V centres [33]. Different types of V centres are formed at different temperatures of irradiation. Most of these centres involve \(X_3^-\) molecular ions \((X = \text{halogen})\) and a cation vacancy along \(<100>\) direction. Of these \(V_4\), \(V_2\) and \(V_3\) centres are formed in pure alkali halides on irradiation at 100 K, 200K and 300 K respectively [33]. The \(V_3\) centre is a \(X_3^-\) molecular ion at a
cation vacancy with no specific orientation, while \( V_2 \) and \( V_4 \) centres are reported to have \(<100>\) symmetry [34]. \( V \) centres perturbed by divalent cationic Impurity-Vacancy (I-V) complex, called \( V_2^M \) centres, were reported to be formed in alkaline earth ions doped KCl, RbCl, RbBr, etc. crystals upon irradiation at room temperature [35 - 38].

### 1.5 Impurities in alkali halides

Defects can also be produced by incorporation extrinsic impurities. The colouration phenomenon in alkali halides are influenced by these types of impurities to a large extent. Of many impurities, the simplest system is by substitution of alkali or halide ions that are foreign to the host crystal [8]. Solubility of the alkali halide crystals is the major property which determines the formation of mixed crystal. Among the various mixed alkali halides, mixed crystals such as KCl-KBr and RbCl-RbBr show complete miscibility while binary alkali halide systems such as KCl-KI, KBr-KI show only limited solid solubility [39- 41]. A systematic study of effect of these impurities on the spectral position, intensity and half width of the F- absorption band in the mixed crystals exposed to ionizing radiations and the influence of radiation dose on colouration have been made by several authors [41- 43]. Smakula et. al. in their study of optical properties of electron irradiated undoped mixed alkali halides (KCl-KBr, KCl-
RbCl, etc.) observed a shift in the spectral position of F-band with change in anion/cation composition in the mixed alkali halides [43]. In recent years, luminescence studies of impurities doped mixed alkali halides have gained importance as they are reported to show promising features of phosphors used in X-ray imaging plates, UV radiation dosimeters, etc. [44-47]. The difference in ionic sizes between the impurity and host crystal ions leads to a change in the lattice parameters and a strain in the local crystal environment. Also, it leads to a shift in the spectral peak position and broadening of the F-absorption bands in the host crystal [43, 47]. Generally, F-band peak positions in mixed alkali halides do not obey the Mollwo-Ivey relation (section 1.4.1.1) [43]. Borboa et. al. have investigated the characteristics of F-band absorption in KClₓBr₁₋ₓ:Eu²⁺ crystals [47]. They found that the F-band spectral position is more sensitive to lattice parameter in these Eu²⁺ doped mixed crystals than in pure FCC alkali halides. This was attributed to the distortion of the crystalline electric field caused locally at the F-centre by the mixed halide surroundings. Difference in ionic charge between the impurity and the host ions causes an imbalance in the concentration of positive and negative ion vacancies and in the colourability of the mixed alkali halide crystal [47].

The substitutional impurities doped in low concentrations play an important role in determining the optical properties of ionic crystals [48]. Some of these
impurities introduce localized energy levels which give rise to characteristic absorption bands of the impurity ions modified by the host lattice. Ionic crystals doped with suitable activators such as rare earth ions, \( \text{Tl}^+ \) like ions (ions with \( \text{ns}^2 \) electronic configuration in the ground state) etc. have been studied extensively and some of them find their applications in many technological areas such as X-ray imaging plates, scintillators and UV- radiation dosimeters [44, 49]. In ionic solids without high-frequency vibrations the rare earth ions offer good possibilities to obtain nearly 100\% luminescence quantum efficiency if the energy gap is reasonably large [1]. The presence of a deep-lying 4f level of rare earth (RE) ions, which is not entirely filled, leads to a unique property of RE ions. The electrons in the 4f shell of the rare earth ion are effectively screened by the outer electronic shells. So when a rare earth ion is introduced into an ionic crystal, the 4f electrons are weakly perturbed by the charges of surrounding ligands [50]. In the following section, a brief review of luminescent characteristics of \( \text{Eu}^{2+} \) and \( \text{Tl}^+ \) ions in alkali halides is discussed.

1.5.1 \( \text{Eu}^{2+} \) ions in alkali halides - General features of absorption and emission spectra

When \( \text{Eu}^{2+} \) ions are introduced as a substitutional impurity in an alkali halide crystal, it usually replaces with the host cation whose crystal field
symmetry depends on the crystal lattice. The electronic configuration of Eu$^{2+}$ ion in the ground state is $4f^7 5s^2 5p^6$. The electrons in the incompletely filled $4f$ shell (valence shell) are shielded from external field by the outer, completely filled $5s^2$ and $5p^6$ electronic shells [50]. In the ground state of Eu$^{2+}$ ion, there are seven $4f$ electrons. The lowest lying excited states are formed by the states within the $4f^6 5d$ configuration. The crystal field acting at the Eu$^{2+}$ site splits the fivefold orbital degeneracy of the d-energy level into a doubly degenerate ($E_g$) and a threefold degenerate ($T_{2g}$) energy levels. The relative positions of these two levels depend on the co-ordination of the ligands [50-52]. For the crystals with rock salt structure, the crystal field acting at the Eu$^{2+}$ site possesses cubic symmetry with

![Schematic energy level diagram of Eu$^{2+}$ in an alkali halide [50].](image)

Fig. 1.2 Schematic energy level diagram of Eu$^{2+}$ in an alkali halide [50].
sixfold coordination. The $T_{2g}$ level is situated at a lower energy compared with the $E_g$ energy level [51]. The absorption spectrum of the divalent europium ions in ionic crystals such as alkali halides consists of two structured broad bands related to a transition from the ground state $4f^7$ to the excited state $(4f^65d)$. In general, these excitation bands of Eu$^{2+}$ ions in ionic crystals are situated in the ultraviolet region of the electromagnetic spectrum [52]. Since these transitions are dipole allowed, their intensity is quite large [51]. Due to the thermal vibrations of the neighbouring ions of the host, the changing crystal field at the impurity rare earth ion produces a broadening effect on the spectral lines. As the temperature is lowered, the width of the $4f^7 \rightarrow 4f^65d$ absorption bands is reduced [52]. The width and structure of the broad bands observed in the optical absorption spectrum of Eu$^{2+}$ ions have been investigated extensively in the literature [51 - 53].

Table 1.1 lists peak positions of the high and low energy absorption bands of Eu$^{2+}$ ions in alkali halides at RT [52]. These results indicate that the centre of gravity of the high energy band is shifted towards lower energy side as one moves from NaCl to RbCl, while that of the low energy band is shifted to high energy side. The similar behaviour is observed in the alkali bromide and iodide series as well. The separation between $E_g$ and $T_{2g}$ energy levels is the well known 10Dq splitting (Fig. 1.2) [52]. According to an electrostatic model for the cubic crystalline field, the 10Dq splitting is proportional to $R^{-5}$ where $R$ is the distance
between the impurity ion and the surrounding ligands. The values measured for the 10Dq splitting follow the spectrochemical series in which the ligands are ordered for inorganic complexes, in the following sequence [53]:

Free ion \( (Dq = 0) < I^- < Br^- < Cl^- < S^{2-} < F^- < O^{2-} \)

The emission from the \( \text{Eu}^{2+} \) ion can be excited by light lying in either of the two broad absorption bands. The emission spectra of many of the europium doped alkali halides consist of only one broad emission band due to the transition from

<table>
<thead>
<tr>
<th>Host</th>
<th>Centre of gravity of high energy band (nm)</th>
<th>Centre of gravity of high energy band (nm)</th>
<th>Peak position of the emission band (nm)</th>
<th>10 Dq splitting (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>204 49,020</td>
<td>326 30,675</td>
<td>422 23,697</td>
<td>18,345</td>
</tr>
<tr>
<td>KF</td>
<td>214 46,729</td>
<td>332 30,120</td>
<td>427 23,419</td>
<td>16,609</td>
</tr>
<tr>
<td>NaCl</td>
<td>240 41,667</td>
<td>347 28,818</td>
<td>427 23,419</td>
<td>12,849</td>
</tr>
<tr>
<td>KCl</td>
<td>243 41,152</td>
<td>343 29,155</td>
<td>419 23,866</td>
<td>11,997</td>
</tr>
<tr>
<td>RbCl</td>
<td>244 40,984</td>
<td>341 29,326</td>
<td>417 23,981</td>
<td>11,658</td>
</tr>
<tr>
<td>NaBr</td>
<td>249 40,161</td>
<td>352 28,409</td>
<td>428 23,364</td>
<td>11,752</td>
</tr>
<tr>
<td>KBr</td>
<td>250 40,000</td>
<td>344 29,070</td>
<td>418 23,923</td>
<td>10,930</td>
</tr>
<tr>
<td>RbBr</td>
<td>252 39,683</td>
<td>340 29,412</td>
<td>416 24,038</td>
<td>10,271</td>
</tr>
<tr>
<td>NaI</td>
<td>261 38,314</td>
<td>361 27,701</td>
<td>439 22,779</td>
<td>10,613</td>
</tr>
<tr>
<td>KI</td>
<td>262 38,168</td>
<td>349 28,653</td>
<td>427 23,419</td>
<td>9,515</td>
</tr>
<tr>
<td>RbI</td>
<td>264 37,879</td>
<td>347 28,818</td>
<td>426 23,474</td>
<td>9,061</td>
</tr>
</tbody>
</table>
the $E_g$ and $T_{2g}$ components of the $4f^65d$ configuration to the ground state $4f^7$ \cite{50-53}. A single emission band from two excited states of Eu$^{2+}$ ions in alkali halides doped with Eu$^{2+}$ ions is observed due to a non-radiative decay from the $E_g$ excited level to $T_{2g}$ excited level followed by a radiative relaxation from $T_{2g}$ level to the ground state. However it is observed that in all alkali halides doped with Eu$^{2+}$ ions, excitation with light lying in the high energy absorption band of Eu$^{2+}$ ions leads to a relatively less intense radiative emission than the excitation in the low energy band \cite{54}. The peak position of the emission band moves to shorter wavelengths as the lattice parameter of the alkali halide host increases \cite{55, 56}.

1.5.1.1 Aggregation of Eu$^{2+}$ impurities in alkali halides

The divalent Eu$^{2+}$ ions, usually, replace substitutionally the host monovalent cations of the alkali halides. They form impurity vacancy (I-V) dipoles by associating themselves with their charge compensating cation vacancies. These I-V dipoles can easily migrate through the alkali halide lattice to form small clusters such as dimers, trimers, metastable and stable second phase precipitates depending upon impurity concentration, annealing temperature, etc. \cite{57}. Several authors have reported that both absorption and emission spectra are sensitive to the precipitation state of the Eu$^{2+}$ ions in the alkali halide matrix \cite{57 -
Different types of europium aggregates (such as first phase of aggregates, Suzuki type, metastable EuCl₂ type precipitates, etc.) result in some additional absorption and emission bands as well as shifting of characteristic bands of Eu²⁺ monomer ions to the long wavelength side in alkali halides [60, 61]. Optical and luminescence characteristics of Eu²⁺ aggregates in different alkali halides have been studied by several authors [57 - 62] and have been reviewed by Rubio et al [63].

1.5.2 Tl⁺ ions - Optical Properties of Tl⁺ ions in alkali halides

Alkali halide crystals doped with ions having ns² electronic configuration in their ground state (such as Ga⁺, In⁺, Tl⁺, Sn²⁺, Pb²⁺, etc.) have been studied extensively [64 - 67]. Generally, absorption spectra of ns² (Tl⁺ - type) impurity ions introduced substitutionally into alkali halide hosts, exhibit bands that have been labeled A, B, C and D bands in order of increasing energy [68]. The A, B and C bands are due to electronic excitation from the ns² ground state to nsnp excited states while the D- bands lying near the absorption edge are due to charge transfer transition from the halide ion to the ns² ion [68].

Earlier, Seitz proposed a simple atomic model assuming that a Tl⁺ ion occupies substitutionally an alkali cation site in an alkali halide crystal and it is placed in an octahedral (O₆) crystal field [69]. A free Tl⁺ ion with the ground state
configuration $6s^2$ has the electronic ground state $^1S_0$. The first excited state $6s6p$ consists of a triplet $^3P_j$ and a singlet $^1P_1$ in Russell-Saunders (R-S) Coupling [69]. In the order of increasing energy, these states are $^3P_0$, $^3P_1$, $^3P_2$ and $^1P_1$. The energy levels of the Ti$^+$ ions are labeled by the irreducible representation of the $O_h$ point group as follows:

(Ground state)  
$^1S_0 \rightarrow ^1A_{1g}$

(Excited states)  
$^3P_0 \rightarrow ^3A_{1u}$  
$^3P_1 \rightarrow ^3T_{1u}^*$  
$^3P_2 \rightarrow ^3E_u + ^3T_{2u}$ and  
$^1P_1 \rightarrow ^1T_{1u}^*$

The * denotes that $^3P_1$ and $^1P_1$ are not pure RS states but mixed by the off-diagonal matrix elements of the electron- interaction and Spin-orbit coupling matrix [70].

The $^1A_{1g} \rightarrow ^1T_{1u}$ transition ($^1S_0 \rightarrow ^1P_0$) is a dipole allowed transition while the $^1A_{1g} \rightarrow ^3A_{1u}$ ($^1S_0 \rightarrow ^3P_0$) transition is strictly forbidden [69, 70]. The $^1A_{1g} \rightarrow ^3A_{1u}$ ($^1S_0 \rightarrow ^3P_1$) transition is spin-orbit allowed (i.e. partially allowed by the mixing of singlet $^1T_{1u}$ with the triplet $^3T_{1u}$ by the spin- orbit interactions) and the $^1A_{1g} \rightarrow ^3E_u$ and $^3T_{2u}$ ($^1S_0 \rightarrow ^3P_2$) transition allowed due to vibronic mixing of $^3E_u$.
and $^3T_{2u}$ [68]. Thus, the observed absorption bands are assigned as follows:

<table>
<thead>
<tr>
<th>Band</th>
<th>Transition</th>
<th>Allowed</th>
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<tbody>
<tr>
<td>A</td>
<td>$^1S_o \rightarrow ^3P_1$</td>
<td>Spin orbit allowed</td>
</tr>
<tr>
<td>B</td>
<td>$^1S_o \rightarrow ^3P_2$</td>
<td>Allowed due to vibronic mixing</td>
</tr>
<tr>
<td>C</td>
<td>$^1S_o \rightarrow ^1P_1$</td>
<td>Dipole and spin allowed</td>
</tr>
</tbody>
</table>

The high energy D-band absorption was attributed to a transition from $^1A_{1g}$ ground state to the lowest perturbed exciton state [67]. A number of articles on the experimental and theoretical studies have been published investigating the structures of the A, B and C bands of Ti$^+$ like ions in alkali halides due to Jahn-Teller effect on the degenerate electronic states of the nsnp configuration and temperature dependence of these absorption bands [64, 65, 67]. The schematic energy level diagram of Ti$^+$ ions in alkali halide crystals is shown in Fig. 1.3.

Ti$^+$ - impurity ion introduced substitutionally into alkali halide host lattices exhibit two emission bands on excitation in the A-absorption band. The two emission bands are usually designated as $A_X$ and $A_T$ emission in order of increasing energy [64]. If the excitation occurs in the B, C and D-bands, the luminescence spectrum is given by the same emission observed under optical excitation at A-absorption band accompanied by one or more additional emission...
bands at higher energy. The relative intensities of these additional emission bands change greatly with host crystal, the excitation wavelength and the temperature. A-band luminescence has been studied extensively (both theoretical and experimental). Generally, the change in emission process of Tl⁺-type impurities doped alkali halide phosphors with temperature are classified into three

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Fig. 1.3 Schematic energy level diagram of Tl⁺ ions in alkali halide Crystals

\[ H_0 -\text{ due to electron nuclear interaction} \]

\[ H_{SL} -\text{ Russell-Saunders coupling which give rise to } ^1P_1, ^3P_2, ^3P_1, ^3P_0 \text{ states} \]

\[ H_{el.} -\text{ Vibronic energy level coupling give rise to absorption bands (A, B and C)} \]

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groups [64]. In the first group, the emission is mainly composed of $A_X$ band at RT. In the second group the $A_T$ and $A_X$ bands coexist with almost the same order of intensity at RT. In the third group only the $A_T$ band is observed over a wide temperature range. KCl and RbCl crystals doped with Tl$^+$ ions fall in the third group while the Tl$^+$ ions doped KBr and RbBr crystals fall in the second group with two emission bands at all temperatures [68]. The mechanism of the emission band is ascribed to the spin orbit interaction between the $A$ band emitting state (the triplet $^3T_{1u}$ state) and the upper singlet $^1T_{1u}$ state. If the spin orbit interaction is strong enough, the $^3T_{1u}$ state and $^1T_{1u}$ states repel each other, so that the lower triplet state is deformed into relaxed excited state with two minima. Thus, the two emission bands are produced from the two minima T and X [70]. The relative intensity of the Tl$^+$ emission bands in alkali halides depends upon temperature and the emission bands are well resolved at low temperatures [71].

In heavily Tl$^+$ doped alkali halides, new absorption bands attributed to the double thallium ion centres i.e. Tl$^+$ dimers have been reported [72-75]. Two types of Tl$^+$ dimers with different symmetries (such as $D_{2h}$, $D_{4h}$) are known to be formed in alkali halides heavily doped with Tl$^+$ ions. Two Tl$^+$ ions occupying nearest neighbour cation sites along $<110>$ direction form $D_{2h}$ dimers while two Tl$^+$ ions at the second nearest cation sites along a $<100>$ direction between them is known
as $D_{4h}$ dimers. Some weak emission bands were also observed in the heavily Tl$^+$ doped alkali halides due to Tl$^+$ dimers [74]. Optical and luminescence properties of dimer centres have been reviewed by Tsuboi and Jacobs [75].

### 1.6 Thermostimulated luminescence (TSL)

Thermostimulated luminescence (TSL), which is also known as Thermoluminescence (TL) plays an important role in the fields of radiation dosimetry and archaeological dating [76]. TSL is the thermally stimulated release of energy stored in a material from previous excitation. The excitation of the crystal can be achieved by the well known methods like ionizing radiation, UV rays, etc. TSL in alkali halide crystals is related to thermal annihilation of colour centres produced upon irradiation. The phenomenon of TSL is explained using a band picture of solids with respect to its electronic energy levels. It is known that a crystal contains certain number of lattice defects such as vacancies, interstitials and dislocations inherently present in it as well as some additional defects created by doping them with chemical impurities [76]. These defects introduce localized energy levels (i.e donor and acceptor levels) in the forbidden energy gap [77]. These levels either belong to the impurities / lattice defects present in the crystal or the host lattice under the influence of them.

Free electrons and holes are generated in a crystal, upon exposure to
ionizing radiation and most of them recombine immediately resulting in the emission of light or in lattice vibrations. However, some of the electrons and holes are trapped at the donor and acceptor levels respectively resulting in the formation of colour centres. Most of them are trapped charges at vacancies (like F-centres, F-aggregates, etc.) or at interstitials (like V centres). According to Pooley, this process of colour centre production by radiolysis is known to proceed through an excitonic mechanism [78]. On warming the crystal after irradiation, electrons (or holes) are released from their traps, become mobilized and wander through the crystal. When they meet their counterparts, recombination between electrons and holes occurs with a part of the recombination energy released in the form of light and this is termed as TSL [76, 77].

Usually in TSL studies, the irradiated sample is heated at uniform heating rates. The plot of total light intensity emitted with temperature of the sample is called as glow curve while the spectral distribution of the luminescence at a particular temperature is called as TSL emission spectrum [76, 77]. The energy required to release the electrons (or holes) from the trap is called thermal activation energy ‘E’ and the area under the glow peak is related to the concentration of filled traps [79]. Normally, a number of trapping sites may exist with different activation energies. On heating the material with uniform heating rate, charge carriers are released from these traps at different temperatures. This
results in the appearance of a number of glow peaks in a glow curve with their maxima at different temperatures, each glow peak representing the thermal annihilation of particular type of defect / colour centre in the crystal [79]. The basic mathematical model of TSL was first provided by Randall and Wilkins [80] in 1945 and all the later theoretical models have been reviewed by Chen and McKeever [81].

1.7 Photostimulated Luminescence (PSL)

Naturally or artificially irradiated minerals may emit light with decreasing intensity upon illumination with light. This effect is clearly different from fluorescence excited by short wavelength electromagnetic radiations or phosphorescence which decays slowly after the cessation of illumination. Earlier, Prizbram [82] observed that the colouration of kunzite (rose fluorspar) crystals induced by ionizing radiations was bleached not only by heating, but also by exposure to light, and that in some cases phosphorescence was detectable. The emission of light from irradiated substances upon illumination with light of appropriate wavelength was described first as radio-photoluminescence [82]. Now this phenomenon is called as Photostimulated luminescence (PSL).

The mechanism of PSL emission may be suggested from a trap model. The schematic diagram of the band model is shown in Fig. 1.4. The PSL phenomenon
is based on the presence of electron and/or hole traps. As discussed earlier, irradiation of a crystal such as an alkali halide leads to the formation of electron trapped centres such as F-centres and some hole trapped centres. Detrapping of the trapped charge carriers from their respective traps requires energy. When the energy is provided by stimulating the irradiated phosphor material by light of wavelength within the F-band absorption, the trapped electrons in some of the F-centres get liberated into conduction band. A part of the free electrons radiatively recombine with trapped holes under the emission of light. This emission of light is termed as Photostimulated luminescence [83].
1.8 Applications of PSL phosphors

Photostimulated luminescence phenomenon play a major role in the field of medical diagnosis. Computed radiography using X-ray imaging plates (IP) based on PSL phenomenon offers an alternative to conventional X-ray radiography which consists of a photographic film and an intensifying screen [84]. Commercial IP’s are also used in various applications such as X-ray diffraction analysis, protein crystallography, transmission electron microscopy, computerized tomography, etc. [83 - 85]. The imaging plates have a number of advantages such as linear dose response, high detection sensitivity, reduced dosage of exposure of X-rays to patients in medical diagnosis, reusability, etc. [83, 85]. PSL process is also used in the field of archaeological and geological dating [86]. In the field of Non destructive testing, IPs are used as radiation detectors in autoradiography, neutron radiography, etc. Some PSL phosphors are also used for data storage in optical memory devices [83 - 85].

1.9 X-ray imaging plates

Computed radiography (CR) is a practical, efficient method of capturing and converting radiographic images into digital form [83, 85]. The commercial imaging plate (IP) screen is approximately 0.5 mm thick and is composed of a 250μm thick flexible plastic support plate coated with fine photostimulable
powder phosphors combined with an organic binder and a 10 μm thick transparent film on top (Fig. 1.5 (a)). This screen is mounted on a black aluminium plate to provide a flat stable surface suitable for normal handling and repeated use [84]. BaFBr:Eu$^{2+}$ is the first commercialized photostimulable phosphor employed in IPs [83]. Recently, some new transparent or translucent phosphors based on alkali halides which provide a better image resolution have been developed as an alternative to BaFBr:Eu$^{2+}$ phosphors (discussed in section 1.9) [87, 88].

Fig. 1.5 (a) Composite structure of imaging plate
(b) Process of image formation [84]

1.9.1 Imaging process in IP

The process of imaging with image plates consists of: (i) the X-ray exposure,
(ii) the information readout and (iii) the optical erasure of the residual information. During the X-ray exposure, the object exposed to ionizing radiation, generates a latent image consisting of trapped electron-hole pairs in the phosphor grains in the image plate [84, 85]. The readout is performed by means of an optical source (such as He-Ne laser) for scanning the image plate pixel by pixel (Fig. 1.5. (b)). The trapped electrons in some of F-centres are liberated by photostimulation and they recombine with trapped holes under the luminescence emission. The emitted photons are collected in a photomultiplier tube which converts the detected light signal into an electric signal. The observed signals are digitized by means of an A/D converter and sent to a computer for the reconstruction of the image. The remaining information in the image plate will then be completely erased by intense radiation from a halogen lamp so that the image plate can be reused [84 - 87]. The major requirements of an X-ray storage phosphor are as follows:

1. It must have high X-ray absorption co-efficient so that the absorbed energy is high even at low X-ray exposures
2. For high signal to noise ratio (S/N), the stimulating light and the stimulated emission should be well separated
3. An optical stimulation spectrum in the range of commercially available laser such as He-Ne and a blue emission spectrum matching with peak sensitivity of the commercially available photomultipliers is desirable
4 The PSL phosphor must have a storage capacity for electrons and holes so that the post-irradiation stability at room temperature is high.

5 Good dose linearity.

1.10 Mechanism of storage of information in X-ray storage phosphors

The luminescence and storage mechanism of the X-ray storage phosphors has been a subject of discussion for the past few years. But the exact mechanism of the PSL process is still not clear. At least three different models describing the PSL process have been proposed in the commercial BaFBr:Eu$^{2+}$ phosphors [89 - 91]. All models envisage F-centres as electron trapped centres involved in the PSL process. However, the models differ in the way in which F-centres are formed, the process in which the electron from the F-centre is transferred to the trapped hole and identification of hole traps.

Recombination model proposed by Takahashi et. al. for BaFBr:Eu$^{2+}$ phosphors suggested that upon exposure to ionizing radiation, electron and hole pairs proportional to the absorbed radiation energy are produced [89]. Some of the free electrons released into the conduction band are trapped at anion vacancies forming F-centres while Eu$^{2+}$ ions trap holes and become Eu$^{3+}$ ions. On photostimulation in the F- band absorption, the trapped electrons in F-centres are
released into the conduction band, and then they recombine with Eu$^{3+}$ ions converting them into Eu$^{2+}$ ions in the excited state leading to PSL emission [89]. In the model suggested by Von Seggern et. al. [90] photostimulable luminescence complex consisting of an F-centre and a Eu$^{3+}$ ion in close proximity are formed in the irradiated phosphors and the electron – hole recombination upon photostimulation at F-band occurs through tunneling. The other models included the role of oxygen or hydrogen ions substituting the halide ions in the BaFBr:Eu$^{2+}$ PSL phosphors [91, 92].

1.11 A brief review on PhotoStimulated Luminescence (PSL) studies on Alkali halides

X-ray imaging plates based on BaFBr:Eu$^{2+}$ phosphors utilizing PSL phenomenon was introduced in 1983 as new X-ray detector system. [83]. Inferior spatial resolution of commercially available X-ray imaging plates [IP] using BaFBr:Eu$^{2+}$ due to birefringence has led to the search for a possible alternative material. Alkali halides due to their transparency have been proposed as an alternative storage phosphor for these IPs [88, 90]. Amitani et. al. [93] reported a transparent Tl$^{+}$-doped RbBr phosphor as one of the most promising candidate for X-ray imaging sensors. Von Seggern et. al.[90] carried out PSL experiments on RbBr:Tl$^{+}$ and compared their effectiveness with commercial BaFBr :Eu$^{2+}$ X-ray storage phosphors. From the experimental results on the PSL lifetime of RbBr:Tl$^{+}$
phosphors investigated between 5K -300 K, they proposed a physical mechanism involving tunneling phenomenon for PSL emission. Semiconductor laser-stimulable RbBr:Ti$^+$ film type imaging plate has been commercialized by Konica [88].

PSL studies of alkali halides doped with europium have been carried out by Nanto et. al.[94]. The PSL phenomenon induced in KCl:Eu$^{2+}$ single crystals by excitation with ionizing radiation such as X-rays, UV -rays have been studied [94]. X-ray irradiated KCl:Eu$^{2+}$ phosphors have been reported to exhibit better fading characteristics [94]. The Eu$^{2+}$ emission has been observed around 420 nm in these phosphors. X-irradiated NaCl:Cu single crystals exhibited an intense PSL emission around 353 nm when stimulated at F-band light (470 nm) [95]. The intensity of PSL emission and PSL stimulation bands have been found to show a linear dose response. PSL studies of KCl:Eu$^{2+}$ phosphors synthesized using a melt quenching technique has been studied by Jaganathan et. al [96]. PL and PSL properties of the films prepared are found to be comparable to single-crystals system. The optical stimulation maximum for the UV / X-ray irradiated melt quenched sample exhibited a red shift.

Plavina et. al. reported that X-ray storage efficiency in KBr:In phosphors is comparable to BaFBr:Eu$^{2+}$ phosphors [97]. Their optical absorption and PSL studies suggested that X-ray energy storage in KBr:In crystals was due to the
formation of close F centre-In$^{2+}$ pairs.

Thoms et. al. studied PSL emission and stimulation experiments as well as life time studies of Rbl crystals doped with Tl$^+$, In$^{2+}$, Eu$^{2+}$ and Pb$^{2+}$ impurities [98]. Dependence of different hole storage centres on the irradiation temperature has been reported. A PSL life time of about 0.41 μs was observed in Rbl:Tl$^+$ crystals. However, the stored image faded away within minutes at RT. Therefore, it has been suggested that unless a very fast read out process was initiated immediately after taking the image, the PSL phosphors based on Rbl system were less adequate for practical use [98].

Luminescence of RbBr:Ga$^+$ and CsBr:Ga$^+$ crystals were investigated by Rogulis et.al.[99] . Formation of gallium centres is found to be complex in these phosphors. Their figure of merit is found to be comparable to the commercial X-ray storage phosphor BaFBr:Eu$^{2+}$ phosphors [99].

CsBr doped with Eu$^{2+}$ ions has a figure of merit as high as that of BaFBr:Eu$^{2+}$ phosphors [100]. A significant PSL emission after irradiation at RT was observed irrespective of the absence of PL emission [100]. Agglomeration of Eu$^{2+}$ dipoles were found to be easily formed in CsBr:Eu$^{2+}$ phosphors [101]. PL studies have indicated the presence of isolated Eu$^{2+}$ -V$_{c}$ (I-V)dipoles as well as
different Eu$^{2+}$ aggregates in RbBr:Eu$^{2+}$ phosphors [100].

In recent years, luminescence studies on impurities doped mixed alkali halides have gained momentum [102-108]. Nanto et. al. have reported that in X-irradiated KCl$_{1-x}$Br$_x$:Eu$^{2+}$ mixed crystals the spectral peak position of the PSL stimulation band shifts towards long wavelength side with increasing KBr content [102]. The PSL intensity was also found to increase with increasing radiation dose. Fading characteristics of PSL of KBr:Eu$^{2+}$ phosphors was found to be much better than that of other KCl$_{1-x}$Br$_x$:Eu$^{2+}$ mixed crystals [103, 104].

Similar to Eu$^{2+}$ doped KCl-KBr mixed crystals, effect of gamma colouration in KCl$_{1-x}$Br$_x$:Pb$^{2+}$ as a function of dose rate and impurity concentration has been investigated by Cruz et.al. [105]. Photoluminescence studies on Eu$^{2+}$ doped KCl:KBr:RbCl:RbBr quaternary crystals have also been reported [106]. PSL studies of such quaternary mixed crystals in the future may yield interesting results.

Luminescence studies of CsCl$_{1-x}$Br$_x$:Eu$^{2+}$ mixed crystals was carried out by Ganapathy et.al [107,108]. PSL efficiency was found to increase with decrease in bromine content in CsCl$_{1-x}$Br$_x$:Eu$^{2+}$ mixed crystals. The PSL emission lifetime of CsCl$_{1-x}$Br$_x$:Eu$^{2+}$ mixed crystals was found to be less than that of the BaFBr:Eu$^{2+}$

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commercial screen phosphors [107]. Short PSL decay time is advantageous for IPs since long read out times lead to ghost images [108].

Recently, Agfa has introduced new IP based on CsBr:Eu$^{2+}$ needle crystals [109]. CsBr:Eu$^{2+}$ needle image plates (NIP) have been reported to show a higher resolution than powder imaging screens [110]. However, radiation damage studies of these NIPs showed a significant deterioration of PSL due to agglomeration of Eu$^{2+}$ ions in these CsBr:Eu$^{2+}$ phosphors [111]. Recently, dose response and optimum sintering conditions of CsBr :Eu$^{2+}$ powder phosphors have been studied by Nanto et al. [112].

1.11 Scope of the present work

Alkali halides doped with activators such as europium and Ti$^+$ - like ions are known to exhibit excellent luminescent properties and they have been studied extensively [50 - 56, 64 - 71]. In recent years, several alkali halide phosphors like KCl:Eu$^{2+}$, KBr:Eu$^{2+}$ and KBr:In$^+$ and mixed alkali halide phosphors such as KCl$_{1-x}$Br$_x$:Eu$^{2+}$ and KCl$_{1-x}$Br$_x$:Pb$^{2+}$ crystals have been reported to show the required characteristics of X-ray storage phosphors [94 - 96, 102-107]. In general, Eu$^{2+}$ doped phosphors are synthesized in inert/ reducing atmosphere so as to avoid the undesirable oxidation of Eu$^{2+}$ into Eu$^{3+}$ states during sintering. However, Eu$^{2+}$ doped potassium halide phosphors have been synthesized in pelletized form by
sintering in air [113]. In the present study, KCl$_{1-x}$Br$_x$:Eu$^{2+}$ powder phosphors have been prepared under different conditions by solid state reaction method and their PL and PSL characteristics have been investigated.

Goaded by the interesting results reported on the PSL studies on Eu$^{2+}$ doped mixed alkali halides such as KCl$_{1-x}$Br$_x$:Eu$^{2+}$ [102 - 104] and CsCl$_{1-x}$Br$_x$:Eu$^{2+}$ crystals [107, 108], optical absorption and luminescence studies of mixed crystals based on RbCl$_{1-x}$Br$_x$:Eu$^{2+}$ have been studied. An understanding of the phenomenon involved in the process of luminescence for any new system is best obtained in the study of single crystals. To the best knowledge of the author, luminescence of RbCl$_{1-x}$Br$_x$:Eu$^{2+}$ mixed crystals has been studied for the first time and reported in the present work.

Alkali halides doped with Tl$^+$ like ions with ns$^2$ electronic configuration in the ground state are known to exhibit absorption bands designated as A, B, C and D bands due to the transition from ns$^2$ ground state to nsnp excited state and their luminescence properties have been extensively studied [64 - 71]. From earlier reports, it is understood that the spectral regions of the A-band emission and excitation bands of Tl$^+$ ions in any of the above crystals (KCl, KBr or RbCl) overlap partially with the spectral regions of the excitation bands of Eu$^{2+}$ ions in the same host. This suggests a possibility of an energy transfer from Tl$^+$ to Eu$^{2+}$.
ions in these crystals when they are doubly doped with both Tl$^+$ and Eu$^{2+}$ ions.

With this view in mind, the influence of Tl$^+$ ions on the luminescence characteristics of (i) KCl:Eu$^{2+}$, (ii) KCl$_{0.5}$KBr$_{0.5}$:Eu$^{2+}$, (iii) KBr:Eu$^{2+}$ powder phosphors and (iv) RbCl:Eu$^{2+}$ single crystals have been studied and reported in the thesis.
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