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Study of electron-vibrational interaction and concentration quenching effect of Cu^+ ions in lithium based sulphate phosphors

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ABSTRACT

The objective of this work is to study electron-vibrational interaction (EVI) and concentration quenching and their manifestation in experimental photoluminescence spectra of Cu^+ ion in various lithium based phosphors namely, Li_2SO_4, $LiNaSO_4$ and $LiKSO_4$. The main parameters of EVI, such as the Stokes shift, Huang-Rhys factor and zero-phonon line positions, were estimated. The studied systems shows strong electron lattice coupling. The validity of results was established by modeling the shape of the emission spectra, which was found to be in good agreement with experimental photoluminescence spectra. The concentration quenching study is also carried out for these compounds. The studied systems correspond to the nearest neighbor energy transfer mechanism.

1. Introduction

The optical transitions of transition metals manifest themselves either as sharp or broad emission bands depending on the strength of crystal field produced by impurity ion's environment and a character of a particular transition (whether it is spin-forbidden or spin-allowed, respectively). The symmetry properties of the electronic states involved in these transitions also affect the optical characteristics. Among transition metal activators monovalent copper ion (Cu^+) has been studied in relatively limited number of hosts as compared to rare-earths and other transition metals. The reason for such a lack of studies is that incorporation of monovalent copper into a crystal lattice is considered to be difficult and methods for incorporating Cu^+ ion have not been systematically worked out [1]. Luminescence of the Cu^+ ion activated phosphors ranges from ultraviolet (UV) to visible (VIS), which finds applications in thermoluminescence dosimetry [2–4], lasers [5,6], X-ray imaging [7–9] 0 and as blue component of full color electroluminescent display devices [10,11]. More common valency of copper is 2+, which is attributed to transition between conduction band and t^2 energy level of excited Cu^{2+} ion (d^9 configuration) in the host bandgap [12–14]. Cu^{2+} ion acts as a luminescence activator and as a compensator of n-type material for II–VI semiconductors [15–17].

The photoluminescence of Cu^+ ion is attributed to the $3d^{10} \leftrightarrow 3d^9 4s^1$ transitions, which are strictly forbidden in case of free ions, but become partially allowed in crystals or glasses due to mixing of states with odd parity, resulting in broad excitation and emission spectra. Such mixing is induced by absence of center of symmetry of ligand field or by destruction of center of symmetry by lattice vibration. Also, the energies of excited states and Stokes shift are greatly affected by the size and the symmetry of the Cu^+ ion site, which leads to strong modulations of spectral distribution [18]. When the Cu^+ ions are coordinated with other ions in the host, the energy levels of these d electrons are split by the electric field of the coordinating ions, instead of being degenerate as in case of free ions. Under the effect of crystal field of host lattice, the energy levels of the $3d^9 4s^1$ and $3d^9 4p^1$ configurations split several sublevels [19]. The energy level scheme of these two configurations with indication of the allowed transitions is shown in Fig. 1. The lowest excited states are populated due to the $3d^{10} \rightarrow 3d^9 4s$ and $3d^{10} \rightarrow 3d^9 4p$ transitions covering the energy range from 460 nm to 376 nm and from 150 nm to 135 nm, respectively [20]. The 4s electron has a strong antibonding towards the ligands and the 4p electron is partly bonding; therefore, upon incorporation into the crystal the $3d^9 4s$ levels are raised and the $3d^9 4p$ levels are lowered

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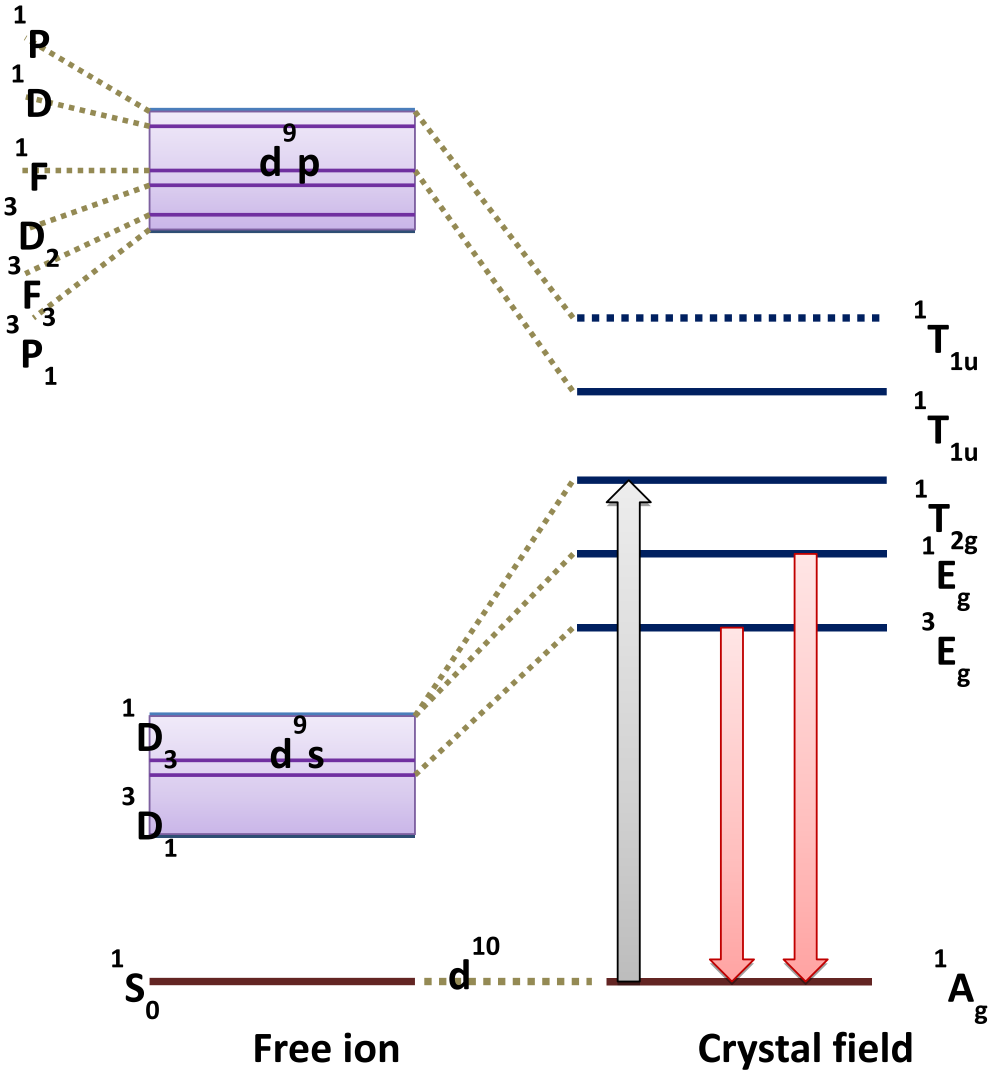

Fig. 1. Energy level of Cu^+ ion in presence of crystal field. The main energy levels are shown only; the excitation/emission transitions are indicated by the up-/downward arrows.

in energy by the same amount [21]. But such an evolution is not systematic. Cu^+ ion preferentially adopts a linear coordination which stabilizes the copper–ligand bond through the $3dz^2$–4s hybridization. In contrast, this hybridization will reduce the gap between fundamental and excited states. These two antagonistic effects, as well as the variations of the Stokes shift, which depends upon the host matrix, explains large range of emission spectra (UV to green) existing for Cu^+ ion [18]. Thus, the spectroscopic characteristics are largely influenced by surrounding environment of the host, hence the study of electron-vibration interaction (EVI) parameters become important.

Spectral properties of rare earth and transition metal doped phosphors can be used to investigate the electron–lattice interaction for different regimes of coupling strength. Interaction between electronic states of an impurity ion and vibrations of ligands is described by the EVI parameters such as the Stokes shift, Huang–Rhys factor, effective phonon energy and zero phonon line. Using the experimental data of photoluminescence spectra we have estimated the EVI parameters for Li_2SO_4, $LiNaSO_4$ and $LiKSO_4$ phosphors. Concentration quenching studies are also carried out for these phosphors. The emission spectra change with change in concentration of impurity ion, provided that increasing substitution does not apparently change effective crystal field experienced by activator. At higher concentration of activators, local environments as well as optical property of hosts are influenced due to agglomeration of activator ions. Agglomeration may lead to interaction between activator ions, which leads to quenching of luminescence intensity (concentration quenching) [22]. Cu^+ ion doped Li_2SO_4, $LiNaSO_4$ and $LiKSO_4$ phosphors show change in luminescence intensity with increasing concentration of Cu^+ ion; however, shape of luminescence spectra remains largely the same. The luminescence intensity first increases with increasing concentration of dopant but beyond critical concentration luminescence intensity starts decreasing. Concentration quenching study is important tool to study various interactions occurring between activators and the other defects (that may be present in the solid) which may lead to energy transfer to killer sites which drastically quenches the luminescence. Hence, critical level of energy migration can be studied for a system.

1.1. *Theoretical outline*

The electron-vibrational coupling can be best visualized with the configurational coordinate model. Under adiabatic approximation the electronics states can be represented by parabolas and vibrational levels of nuclei are represented by horizontal lines