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Luminescence properties on Tm^{3+} doped KBr single crystals

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Abstract:- *Single crystal of Tm^{3+} doped KBr were grown by Bridgemann stockbarger technique. The grown crystal characterized by photoluminescence (PL) and Thermoluminescence (TL). The photoluminescence spectrum excited at 250nm shows the broad emission band centered at 463nm, which is attributed to blue emission of Tm^{3+} ions in the transition of ${}^1G_4$-${}^3H_6$. The grown crystal were annealed at 400°C and then irradiated at γ-ray dose of 5Gy before taking the TL. The TL was observed up to 600K at a heating rate of 120°C/min. TL glow peak were deconvoluted by means of using "origin5.0" software. The glow peak reveals two peaks around 440K and 475K. The calculated parameters show that peak correspond to 440K follow the first and to 475K follow second order kinetics. The calculated parameters for 440K and 475K glow peaks are 0.42 and 0.52 respectively. The various parameters of grown crystals such as activation energy, frequency factor and trap depth were calculated using Chen's method and results are discussed in details.*

Keywords: *KBr,Tm^{3+}, PL, TL*

1. Introduction

Over the past few years the crystal growth and characterizations of the rare earth materials have attracted to a great extent attention due to their interesting applications in display devices and light technology[1].Alkali halides due to their simple structure have made the comprehension of many properties of insulators possible, especially with regard to calculation of defect parameters, ionic conduction, considering the interaction etc. The lattice parameters of the alkali halides is in a wide range, from 7.34Å for RbI to 4.03Å for LiF. The ionic radius of K^+ is 1.33Å. This large ionic radius of potassium makes attainable to incorporate impurity ions of different sizes in their lattice[2-5].Alkali halides provides them intrinsically transparent in the UV, Visible and near IR making them convenient for creating defect states in the gap that could be studied optically for their radiative and non radiative recombination process. The generation of visible light from rare earth(RE) doped alkali halide materials are still very interesting work among researchers from the last few decades. This is due to their wide applications viz. display devices, temperature sensor etc. In this respect,Tm^{3+} ion has been considered the most suitable candidate to generate a blue emission, because it is an ideal visible luminescent center which has a broadest wavelength range from 400-700nm among all the rare earth ions. The luminescence from Tm^{3+} doped phosphors was of great interest due to their strong blue emission corresponding to the G-H transition. Here, Tm^{3+}doped KBr single crystals has been successfully grown by Bridgeman Stockbarger technique. The grown crystal were characterized by Photoluminescence(PL) and Thermoluminesence(TL).

2. Experimental details

Single crystals of thulium doped KBr (99.99% purity) were grown using the Bridgman Stockbarger technique. Thulium was added in the form of thulium fluoride (Aldrich 99.99% purity). The crystals were grown in three different concentrations of the impurity 1%, 3% and 5% by weight. Samples of size approximately $5\times 5 \times 1mm^3$ were used for all except the PL studies. The results of the three concentrations were similar and hence only the results pertaining to a thulium concentration of 3% by weight are presented and discussed. PL spectra were recorded at room temperature using Perkin Elmer LS 55 Luminescence spectrometer in the region 200–900 nm with a spectral width of 5 nm. TL glows were recorded using a PC-based TL analyzer (Hitachi) at a heating rate of 120˚C/min. They were irradiated with a ^{60}Co *γ-ray* source with a dosage rate of 10.6 Gy per minute. Before every experiment the crystals were annealed at 400˚C for half an hour and then quenched to room temperature to ensure homogeneous distribution of impurity and to remove any storage effect.

3. Photoluminescence

Fig. 1 and **2** shows typical excitation and emission spectra. It can be seen from the **Fig.1** that there are single broad excitation band at 250nm, which correspond to internal Tm^{3+} transitions. The intense broad peak of emission centered at 463nm were observed in **Fig.2** are due to the $^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions. From this, it is concluded that the Tm^{3+} ion is one of the blue phosphor material. The emission spectra show the strongest blue emission line at 463nm. This emission bands were observed in CaF_2:Tm phosphor when it is excited with 250nm light[6]. PL emission bands are assigned to inner ionic transition of isolated Tm^{3+} ions occupying potassium cation site. The blue emission was very useful in the field of displays, LEDs.

4. Thermoluminescence glow curve

The deconvoluted TL glowcurve of KBr:Tm^{3+} crystals is shown in **Fig.3.** The grown crystal were annealed at 400°C and then irradiated at a γ-ray dose of 5GY before taking the TL. TL was taken out soon after the irradiation to eliminate the possibility of error. The TL was observed up to 600K at a heating rate of 120°C/min. the glow curve reveals two clear and well distinguished peaks at 440K and 475K the TL intensity of this sample is low compared with the standard thermoluniscence dosimetry(TLD) material and therefore does not have any direct application in dosimetry. The TL glow curve are very useful to analyze the nature of traps present in the material and also gives us information about the energy absorbed by the material during irradiation. The kinetic parameters such as activation energy(E) and frequency factor(s) gives information about defect centers cause TL in the material[7,8]. So, we calculated these parameters of the prepared sample. The dosimetry properties of the TL materials mainly depend on the kinetic parameters of the glow peak. Considering this aspect, the parameters were calculated using Chen's peak shape method. This method is one of the widely used technique to determine the kinetic parameters of the glow peak of TL materials.

For the calculation of these parameters the following shape parameters were to be evaluated $\omega = T_2 - T_1$(total half intensity width): $\delta = T_2 - T_m$(high temperature half width): and $\tau = T_m - T_1$(low temperature half width). The order of kinetics can be evaluated from the geometric factor (μ_g) of the glow peak ($\mu = \delta/\omega$) and depends on the glow peak. The value of μ_g for first and second order kinetics is 0.42 and 0.52 respectively. For both glow peaks, the geometric factor is around 0.5 and indicates that the crystal obeys second-order kinetics. The activation energy(E) and frequency factor(s) can be calculated from equations reported in earlier work[9,10]. The trap depth for 440K glow peak is 0.275ev and for 475K glow peak is 0.88ev. frequency factor for the 440K and 475K glow peak were found to be $2.63 \times 10^2\ s^{-1}$ and $1.32 \times 10^9\ s^{-1}$respectively. From the data, it is clear that the glow peak is follow second order kinetics and there is more chance of retrapping. The activation energy and frequency factor values are different for both peaks. This confirms the various escaping and retrapping probabilities of both peaks. The peak at high temperature (i.e) 475K is due to high energy traps. The calculated parameters were matched well with the previous reported work[11]. The charge carrier concentration (n_0) for both peaks were calculated by using the equation reported in earlier work[12]. The more charge carriers were trapped at high temperature peak (475K). so this peak has more charge carrier concentration compared to the peak at 440K. From this, we conclude that high temperature peak are related with deep traps. The kinetic parameters values are tabulated in **table.I.**

Conclusions

In conclusion, Photoluminescence (PL) and Thermoluminescence (TL) properties of KBr:Tm^{3+} single crystals in the visible ranges were studied. To have a better understanding of the electron transition of Tm ion photoluminescence studies were carried out on un irradiated crystals of Tm^{3+} doped KBr. From the emission band in the luminescence spectra it is observed that Tm participates in the luminescence process. In their work on intense visible fluorescence studies on rare earth doped KBr crystals have reported Tm^{3+} emission at 463nm. The present Thermoluminescence results about gamma ray irradiated source of Tm doped KBr crystals shows fair TL characteristic with deconvoluted glow peaks calculated of kinetic parameters for using Chen's peak shape method shows that is follows both second order kinetics. Hence there is chance of retrapping in the second order glow peak. Thulium enters the KBr lattice in its trivalent state. The TL process has been recognized to be due to thermal mobilization of electrons.

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FIGURE No.1

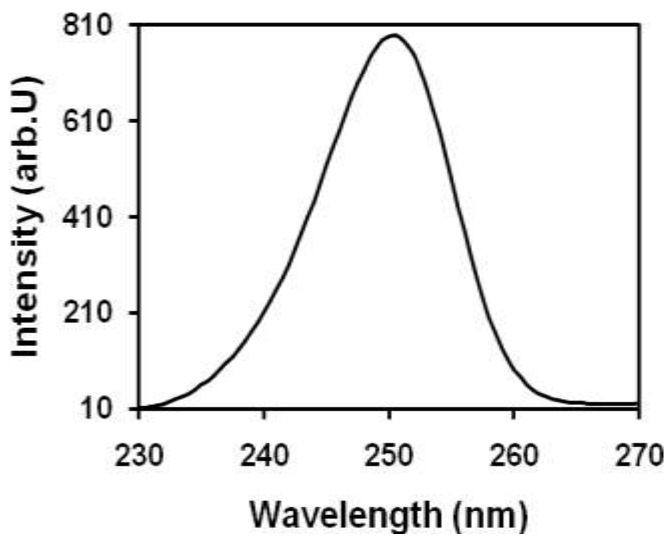

Fig.1. PL Excitation spectrum of KBr:Tm^{3+} for Emission at 460nm

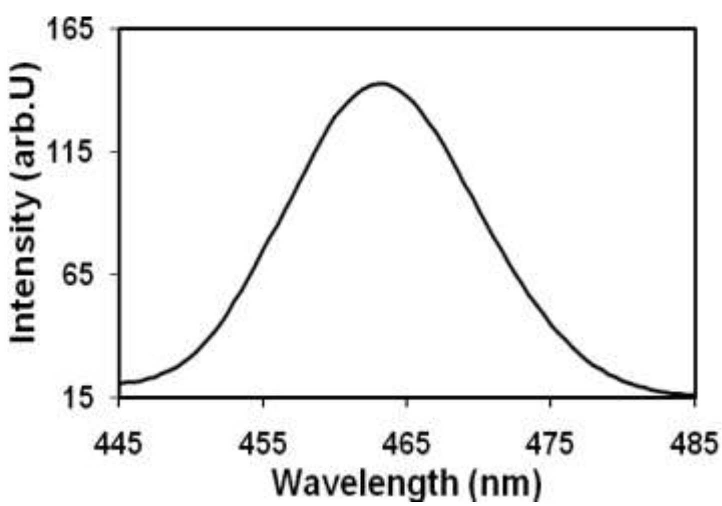

Fig.2. PL Emission Spectrum of KBr:$Tm^{3+}$for excitation at 250nm

FIGURE No.3

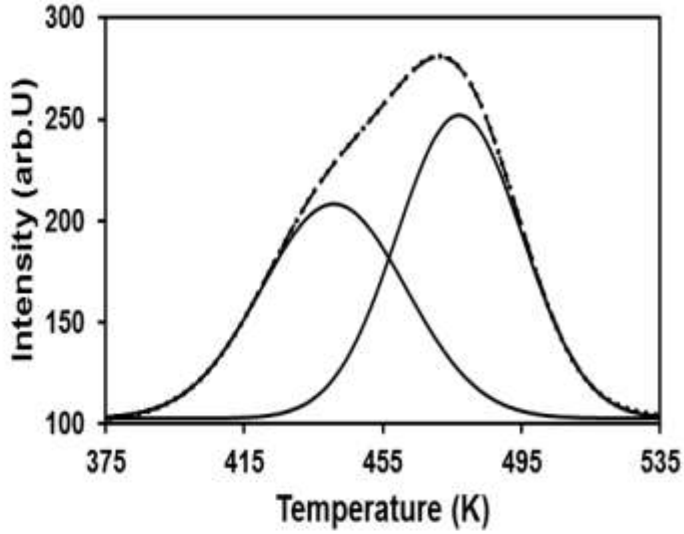

Fig.3 Thermoluminescence Spectrum of KBr:Tm^{3+} Crystals after γ– ray irradiation for 1-hour

TABLE No.I

Table.I Calculated Kinetic Parameters of TL glow curve of KBr : Sm^{3+} Tb^{3+} crystals

Glow Peak Temperature Tg (K)	Intensity (arb.U)	Geometric factor $\mu_g = \delta/\omega$	Activation Energy E (eV)	Frequency factor s (s^{-1})	Concentration of charge carriers n_o $(Cm^3)^{-1}$	Order of kinetics
440	208	0.50	0.275	2.63×10^2	19.17	II
475	252	0.51	0.883	1.32×10^9	13.36	II

