MECHANISM OF THERMOLUMINESCENCE IN FLUORIDE BASED MATERIALS FOR IONIZING RADIATION DOSIMETRY

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ABSTRACT: Radiation dosimetry is the most extensive application of thermoluminescence. TLD is most versatile technique for the quantitative measurement of X, gamma and beta radiation. These materials have number of application. Numerous applied studies of luminescence material based on fluoride have been performed over the past several years. Optical absorption and thermoluminescence measurements are used to study the X-ray induced reduction of trivalent rare-earth ions to the divalent state in CaF2. A discussion of dosimetric properties of fluoride based materials is given in this paper for an academic interest.

Keywords: Thermoluminescence (TL), Fluoride based materials, ionizing radiation dosimetry.

INTRODUCTION:

TL or more specifically Thermally Stimulated Luminescence (TSL) is stimulated thermally after initial irradiation given to a phosphor by some other means (α-rays, γ-rays, β-rays, UV-rays and X-rays). Unlike other luminescence process such as Electroluminescence, Chemiluminescence, here heat is not an exciting agent, but it acts only as a stimulant. Hence, it is better known as thermally stimulated luminescence (TSL). Historically, thermo luminescence (TL), or more appropriately Thermally Stimulated Luminescence (TSL) may be said to have its beginning in 1663 with Robert Boyle who reported to the Royal Society of London (Boyle, 1664) his observation that, “I observed some kind of glimmering light by taking natural diamond into bed with me and holding it a good while upon a warm part of my naked body.” Farrington Daniels and his group first suggested the use of TSL as a technique in radiation dosimetry through studies on LiF as a TSL material. 

Lithium fluoride was used to measure radiation dose after a bomb test. Soon the idea of using TSL in dosimetry caught on and many groups started working in the field of thermoluminescent dosimetry (TLD).

TLDs have been widely used since the 1950 in a number of applications with different materials. These applications include personal dosimetry, environmental and retrospective dosimetry, geological and archaeological dating, and in a variety of medical applications such as radiation therapy, diagnostic radiology and radiotherapy mailed dosimetry. Thermoluminescent Dosimeters (TLDs) are increasingly accepted for radiation dosimetry for the following reasons:

A] The existence of nearly tissue equivalent thermoluminescent materials,
B] Sufficiently high sensitivity and accuracy for both personal and environmental monitoring,
C] Commercial availability as small sized solid detectors adaptable for both manual and automatic processing,
D] Suitability for skin and extremity dosimetry,
E] Availability of materials with excellent long-term stability under varying environmental conditions,
F] Ease of processing,
G] Reusability and
H] Linearity of response with dose and dose rate over a large range [1].

In last four decades, many new and dosimetrically useful TLD materials like Li,BV2O4:Mn; CaF2: Dy; CaSO4: Dy; CaSO4: Tm; BeO: Al2O3:Mg,Y; Al2O3:Si, Ti; CaF2: Tm; LiF:Mg, Cu, P; Li,B2O3:Cu; MgB2O4:Dy or Tm; Al2O3:C were reported. Discuss on thermoluminescence mechanism of various types of material is necessary to find new TLD material. In this paper a discussion on mechanism of thermoluminescence in some fluoride based materials is reported.

2. DISCUSSION OF THERMOLUMINESCENCE MECHANISM: Thermoluminescence dosimetry (TLD) is generally recognized as a most versatile technique for the quantitative measurement of X, gamma and beta radiations, especially in personnel monitoring. For the developments in this field of radiation protection dosimetry A.S. Pradhan in 1981 has discussed the characteristics of some commercially available TLD systems and their associated problems. The usefulness of CaSO4: Dy detectors for X-ray and gamma ray dose measurement is discussed [2]. Effects of β, X and VUV irradiation on the optical properties have been studied by N. Kristianpoller et.al. in 2007 in various simple and complex fluoride crystals by using optical absorption, X and UV excited luminescence (XL and PL), thermoluminescence (TL) and photo-transferred TL (PTTL) techniques. In most tested crystals, the main TL peaks with the same thermal activation energies appear after VUV as well as after X or β irradiation, thus indicating that the same traps are induced by the different types of radiation. The TL excitation spectra generally show absorption maxima on the long wavelengths tail of the fundamental absorption. Within this study, various dosimetric properties, as well as the possible application of the crystals as sensitive radiation detectors and dosimeters for the VUV have also been investigated. The TL sensitivities of the various studied materials have been compared to that of the classic dosimeter TLD-100 (LiF:Mg,Ti). The sensitivity of SrF2:Pr+ has been found to be the highest among the examined crystals and at a dose of 90 Gy its response is higher by a factor of 3 than that of TLD-100. The sensitivity of CsGdF3:Pr+ and KYF2:Pr2+ are slightly higher than that of TLD-100, where as that of nanostructured CaF2:ZnO crystals is about twice that of TLD-100, but the sensitivity of LiF:Eu is much lower. The SrF2:Pr+ crystals also showed some important dosimetric properties [3].

The important role of albedo dosimeters (LiF + LiF) pair and their limitations are analyzed by A. R. Lakshmanan in 1982. The advantages of 2-hit TL system such as the 250°C peak in LiF:Mg, Ti and 240°C peak in CaF2:Tm over the conventional 1-hit TL system for high-LET radiation dosimetry are stressed. The development of irradiation-cross-linked polyethylene
(IPE), a heat-resistant proton radiator, is outlined. A method is suggested to reduce the background TL from IPE [4]. A model allowing theoretical prediction of the maximum possible energy conversion efficiency of a thermoluminescence (TL) material has been described by A. J. J. Bos 2001. The model is based on an earlier work on the prediction of the efficiency of inorganic scintillators. The maximum possible efficiency of well-known TL materials does not vary much and is found to be approximately 13%. The important parameters in the model are highlighted on the basis of two recently developed hypersensitive TL materials CaF$_2$:Cu and KMgF$_2$:Ce$^{3+}$ which show efficiencies only a factor 3 below the theoretical limit. Among the distinct steps in the conversion process (trapping, transfer and recombination under the emission of light), the trapping appears to be the least efficient [5].

Concentration of manganese in CaF$_2$:Mn (TLD-400) is shown to exert the most essential influence on thermoluminescent (TL) properties. The TL curve demonstrates a single high-temperature peak only when CaF$_2$ is doped with a high manganese concentration, being close but still below the decomposition threshold of a solid solution. In case of lower manganese concentrations, the TL curve shows several peaks overlapping with each other. The optimum manganese concentration in thermoluminophor is found to be about 2.12.5 mol%. The influence of different factors on the actual Mn concentration in CaF$_2$:Mn is reported by Mikhail Danilkin et.al. in 2006 for the case where the material is prepared by the co-precipitation method. The CaF$_2$ crystal lattice stress due to the Mn incorporation is studied by means of the X-ray diffraction technique. The solid solution decomposition threshold is estimated. The EPR studies of both γ-irradiated and non-irradiated samples have demonstrated that the amount of Mn$^{2+}$ does not change as a result of the irradiation. The model of energy storage is suggested. It is based on a pair of $V_x$ and F centres, induced by radiation near Mn$^{2+}$, which immediately turns into an excitation like state with a partial relaxation of the lattice stress caused by the Mn impurity. Partial relaxation of the lattice stress increases the thermal stability of the stored excitation [6]. A Li,XAlF$_3$,Mn glass system doped with CaF$_2$ and Mn was synthesized by fusion and its physical properties were investigated using thermoluminescence (TL) and differential thermal analysis (DTA) techniques. The TL glow curve peaks, resulting from this analysis, are characteristic of metastable levels intrinsic to CaF$_2$ crystals that have undergone γ-ray irradiation from a cobalt-60 ($^{60}$Co) source. This provides evidence of CaF$_2$ crystal formation in the glass system. Furthermore, the TL glow peak at about 480 K was stable at room temperature, sensitive to $^{60}$Co γ-rays and showed good linearity with doses ranging from 3 Gy to approximately 100 Gy, and consequently could be used to quantify radiation doses. High quality synthesis of these crystals permits control of their thermoluminescent properties [7].

Development, preparation and characterization of several new single-crystal scintillators based on binary and complex oxide or fluoride host crystals is reviewed by Martin Nikl et.al in 2006 for the case where the material is prepared by the co-precipitation method. The CaF$_2$ crystal lattice stress due to the Mn incorporation is studied by means of the X-ray diffraction technique. The solid solution decomposition threshold is estimated. The EPR studies of both γ-irradiated and non-irradiated samples have demonstrated that the amount of Mn$^{2+}$ does not change as a result of the irradiation. The model of energy storage is suggested. It is based on a pair of $V_x$ and F centres, induced by radiation near Mn$^{2+}$, which immediately turns into an excitation like state with a partial relaxation of the lattice stress caused by the Mn impurity. Partial relaxation of the lattice stress increases the thermal stability of the stored excitation [6]. A Li,XAlF$_3$,Mn glass system doped with CaF$_2$ and Mn was synthesized by fusion and its physical properties were investigated using thermoluminescence (TL) and differential thermal analysis (DTA) techniques. The TL glow curve peaks, resulting from this analysis, are characteristic of metastable levels intrinsic to CaF$_2$ crystals that have undergone γ-ray irradiation from a cobalt-60 ($^{60}$Co) source. This provides evidence of CaF$_2$ crystal formation in the glass system. Furthermore, the TL glow peak at about 480 K was stable at room temperature, sensitive to $^{60}$Co γ-rays and showed good linearity with doses ranging from 3 Gy to approximately 100 Gy, and consequently could be used to quantify radiation doses. High quality synthesis of these crystals permits control of their thermoluminescent properties [7].

Development, preparation and characterization of several new single-crystal scintillators based on binary and complex oxide or fluoride host crystals is reviewed by Martin Nikl et.al in 2006. The micropulling-down technique was used to efficiently screen and optimize the material composition. Thermoluminescent (TL) properties of two concentration series lithium potassium yttrium fluoride doped with praseodymium (LiKYF$_3$:Pr$^{3+}$) and potassium yttrium fluoride doped with thulium (KYF$_3$:Tm$^{3+}$) have been investigated after gamma and neutron irradiation. The main purpose of this research is to see whether these materials are suitable for gamma and/or neutron dosimetry purposes. It has been found that the compounds of both series are sensitive to $^{60}$Co gamma radiation. A maximal TL sensitivity is found for LiKY$_{0.999}$Pr$_{0.001}$F$_3$ and KY$_{0.99}$Tm$_{0.01}$F$_3$. However, for this doping level the intensity of the TL glow peak is about 7% less than that for LiF:Mg,Ti (TLD-700). The TL sensitivity to thermal neutron is relatively higher than that to $^{60}$Co photons. No TL sensitivity to fast neutrons was observed [8]. The thermoluminescence (TL) properties of yttrium fluorides K$_2$YF$_3$, K$_2$YF$_5$ and KY$_3$, singly doped with Ce$^{3+}$, Tb$^{3+}$, Dy$^{3+}$ or Tm$^{3+}$ have been studied by H.W. Kui in 2006, in the range from 30 °C to 500 °C after α or β irradiation. It has been found that K$_2$YF$_3$ doped with 5.0 at% Ce$^{3+}$, K$_2$YF$_5$ doped with 1.0 at% Tb$^{3+}$ and KYF$_3$ doped with 5.0 at% Tb$^{3+}$ show TL sensitivity of the same order as that of the well known TLD-100 (LiF:Mg,Ti) phosphor. Strongly different TL response to α or β irradiation has been found for Tb$^{3+}$ doped KYF$_3$ crystals. The TL mechanism in these phosphors is discussed by taking into account the TL emission spectra from irradiated samples, which are identical to the emission spectra of the appropriate doping rare earth ions, and the kinetics parameters obtained with the method of various heating rates [9]. The fluoride single-crystal material for use in a thermoluminescence dosimeter contains a compound represented by LiXAlF$_3$, wherein X is selected from the group consisting of Ca, Sr, Mg, and Ba, and, as serving as a dopant, at least one species selected from among Ce, Na, Eu, Nd, Pr, Tm, Tb, and Er[10].

### CONCLUSION:

From the above discussion it is concluded that most of the fluoride based TLD materials are useful for ionizing radiation dosimetry and personal dosimetry as well based on their known thermoluminescence properties. Results of pioneering materials are briefly presented in this paper as an academic interest.

### REFERENCES:


