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Synthesis and dosimetry characteristics of a new high sensitivity TLD phosphor $NaLi_2PO_4:Eu^{3+}$

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HIGHLIGHTS

- Synthesis and characterization of a new $NaLi_2PO_4:Eu^{3+}$ TLD phosphor.
- TL dosimetry studies such as dose response, fading and reusability have been done.
- Simple glow curve, high sensitivity, low fading, wider dose range for γ radiation.
- Comparison with commercially available phosphors.
- Comparative studies show that it is very much suitable TLD phosphor for dosimetry.

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ABSTRACT

A new highly sensitive, low-Z ($Z_{eff} \approx 10.8$) TLD phosphor, Eu^{3+} doped $NaLi_2PO_4$, was successfully synthesized via solid state diffusion method. The formation of the single phase compound was confirmed by Powder X-Ray diffraction (PXRD) analysis. Variation of the doping level has shown that the impurity (Eu^{3+}) concentration for maximum TL sensitivity is 0.5 mol%. Heat treatments given to achieve the high TL sensitivity of this phosphor also showed that it needs to be annealed at 973 K for 1 h. Incorporation of the impurity in the Eu^{+3} states was confirmed by the PL emission peaks. The TL glow curve consists of a prominent dosimetry peak at around 458 K besides small shoulders on both sides at around 400 and 500 K. The dose response of the phosphor was found to be sub-linear up to 10 Gy of the dose and later it becomes linear till it start saturating beyond 1 kGy. The TL sensitivity of the newly developed $NaLi_2PO_4:Eu^{3+}$ phosphor to γ radiation from ^{137}Cs (in the linear dose range) was compared to some standard commercially available phosphors, such as, TLD-100, TLD-400, TLD-700H and TLD-900. It was found to be much more sensitive than these phosphors except TLD-700H, which is ~2 times more sensitive. Easy method of synthesis, simple glow curve structure, high sensitivity, low fading, wide range of doses and very good reusability make the phosphor a suitable candidate for the TL dosimetry.

1. Introduction

Thermoluminescence (TL) is a simple and reliable technique for dosimetry of high-energy radiation. The numbers of electron/hole traps generated during the irradiation by high-energy radiation depend on the number of such high-energy particles passing through the material. The traps are generally stable at room temperature and need to be stimulated for their release and recombination. In TL, they are stimulated by thermal energy and the energy of recombination (TL emission, generally in the visible range) is recorded as a function of temperature. The intensity of light emitted by phosphor is proportional to the radiation doses given to it and by establishing calibration with known doses of high-energy radiation, unknown doses could be estimated. A number of good reviews and references on the subject could be found in the literature (Aitken, 1985; McKeever, 1985; Chen and Kirsh, 1981; Attix, 1986; Khalil and Olga, 2006; Furetta, 2010; Azorín et al., 1993). There are several commercially available TLD phosphors such as LiF:Mg,Ti (TLD-100), LiF:Mg,Cu,P (TLD-700), CaF_2:Dy (TLD-200), CaF_2:Tm (TLD-300), CaF_2:Mn (TLD-400), Al_2O_3:C (TLD-500) and $CaSO_4$:Dy (TLD-900) available. However, every phosphor has one or the other drawback(s) (Azorín et al., 1993). For example, $CaSO_4$:Dy is highly sensitive to radiation but not tissue equivalent. CaF_2:Mn is

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also very sensitive but is not tissue equivalent and its instability and high fading introduces errors in estimation of doses. There are not many tissue equivalent (low-Z) phosphors and those available are also not really ideal ones. LiF:Mg,Ti, BeO:A (A = Li, Na, K) and LiF:Mg,Cu,P are a few to name. They are also not ideal as the first one is not very sensitive, second one highly sensitive but loses reusability if proper care is not taken while readouts, and the third is toxic and need special facilities for synthesis and its use. Therefore, efforts are being made either to develop new ones or to improve the existing ones (Azorín et al., 1993; Sahare and Moharil, 1990; Ginther and Kirk, 1957; Madhusoodanan et al., 1999; Lakshmanan et al., 2002; Shinde et al., 2001; Salah et al., 2007; Sahare et al., 2007; Lochab et al., 2007).

In the present paper, we have studied TL dosimetry properties of a new highly sensitive, low-Z ($Z_{eff} \approx 10.8$) TLD phosphor $NaLi_2PO_4:Eu^{3+}$. To the best of our knowledge, this material has not been explored for its application as TLD phosphor, though it has been studied as a red phosphor for lighting purpose (Shinde and Dhoble, 2013). Good TL characteristics, such as, simple method of preparation (solid state diffusion 1073 K), simple glow curve structure (apparently a single peak around 458 K), wider and linear dose response 0.1 Gy to 1.0 kGy, low fading (around 15% in 90 days) and excellent reusability (no change in glow curve structure on repeated usage) make it a suitable candidate for radiation monitoring using thermoluminescence technique.

2. Experimental

2.1. Synthesis

$NaLi_2PO_4:Eu^{3+}$ phosphor was synthesized by solid state reaction taking LiOH and NaH_2PO_4 (procured from CDH, India) as starting materials. All the chemicals used were of analytical reagent (AR) grade. The samples were prepared taking into consideration the following chemical reaction:

$$LiOH + NaH_2PO_4 + EuCl_3(0.1 - 3.0\ \text{mol\%}) \xrightarrow{\text{heating at 1073 K for 12 h}} Li_2NaPO_4 + NaLi_2PO_4 : Eu^{3+} + H_2O$$

Firstly, LiOH and appropriate amount of the impurity salt ($EuCl_3.6H_2O$, also from CDH, India) was dissolved in triply distilled deionized water and the water was slowly evaporated. LiOH (impurity doped) and NaH_2PO_4 (in molar ratio 2:1) were mixed in an agate mortar for several hours in the presence of ethanol for better mixing. The mixed powder was firstly heated at 673 K for 12 h in a quartz crucible and cooled slowly to room temperature to remove the presence of ethanol and any moisture. It was crushed to fine particles again and heated at 873 K and 1073 K for the same period and slowly cooled to room temperature. The material thus synthesized was finally crushed and sieved to yield particles size in the range of 100–125 μm. All these powder samples were annealed later at various temperatures in air up to 1173 K for one hour and quenched to room temperature by putting the quartz crucible on a metal block for better sensitivity. Z_{eff} of the material was determined by the formula, $Z_{eff} = \sqrt[3]{\sum n_i X_i^4 / \sum n_i X_i}$, where n_i is the fractional part by weight of the whole compound occupied by the element the atomic number of which is Z_i (Glasser, 1947; Murty, 1965) and it was found to be ≈ 10.8.

2.2. Characterization

The Powder X-Ray Diffraction (PXRD) patterns were recorded using a high-resolution D8 Discover Bruker X-ray Diffractometer, equipped with a point detector (scintillation counter), employing monochromatized Cu $K_{\alpha 1}$ radiation obtained through a Göbel mirror with a scan rate of 1.0 s/step and step size of 0.02 at room temperature. For recording TL, the sample was irradiated to γ rays from the ^{137}Cs source (dose rate 0.6 Gy/min) for different doses in the range (0.1 Gy–100 kGy). TL was recorded on a Harshaw TLD Reader 3500HT immediately after the irradiation by taking ~5 mg of sample every time at the linear heating rate of 5 Ks^{-1}. The PL was taken on a Varian Eclipse Spectroflurometer having Xenon flash lamp as a source and a wide-band PMT as a detector.

3. Results and discussion

3.1. Powder X-ray diffraction (PXRD)

The formation of material was confirmed by powder X-ray diffraction (PXRD). The X-ray diffraction pattern of the $NaLi_2PO_4$ powder material is as shows in Fig. 1. The peaks present in the diffraction pattern of synthesized material were indexed and matched with data available in the literature (i.e., JCPDS file # 80-2110) and it was confirmed that the material has a single phase (Nalipoite) having the orthorhombic structure and space group Pmnb (Ercit, 1991). The stick pattern (plotted using the data in the JCPDS file # 80-2110) has also been given here for comparison.

3.2. Thermoluminescence (TL)

3.2.1. Optimization of the impurities (Eu^{3+}) concentration and effects of annealing

TL glow curve structure and the sensitivity of a TLD phosphor material depend on the impurity concentrations as well as its ionic state in the host matrix. In the present case, the material was doped for different impurity concentrations in the range of 0.1–3.0 mol%, annealed at 973 K, irradiated for different doses in the range 0.1 Gy–100 kGy from the ^{137}Cs source and the TL was taken. The TL sensitivity of the material to γ rays increased with the increase in the impurity concentration up to 0.5 mol% and then started decreasing (Fig. 2). The TL glow curve consisted of three peaks, the main prominent peak at around 458 K along with two shoulders (satellite peaks of low intensity) at around 400 K and 500 K on either side of the main peak. The TL glow curve structure is found to change a bit with the impurity concentration as the intensity of the satellite peaks change. Apparently, for lower concentrations (<0.5 mol%) three peaks (as mentioned earlier), for 0.5 mol% a single peak (the main peak at around 458 K) and at higher concentrations (>0.5 mol%), two peaks (the main as prominent peak at around 458 K along with the 500 K shoulder) were found to appear prominently. But, the computerized glow curve deconvolution (CGCD) and thermal cleaning (T_m–T_{stop}) method revealed that all the three peaks exist in all the glow curves. However, small changes in the glow curve structures may be due to the reorganization of the trap levels on incorporation of the impurity ions at different sites and the stress/strain generated due to differences in ionic sizes of the constituent atoms (Danilkin et al., 2006). The TL intensity has also been found to decrease due to non-radiative crossover transitions between Eu^{3+} ions on increasing the impurity concentration (concentration quenching) as they come closer than the critical separations (Blasse, 1989).

The material was also annealed at different temperatures to study the effect of annealing. The variation of TL sensitivity with annealing temperatures is as shown in the Fig. 3. It was observed that samples annealed at 973 K for 1 h show the highest TL sensitivity. There was not much change in the TL glow curve structure observed on annealing except a little change in the peak temperatures. Initially, the TL intensity goes on increasing with the corresponding annealing temperature till 973 K (at which the