Photoluminescence of F -aggregate centres in thermal neutron irradiated LiF TLD-100 single crystals

A R LAKSHMANAN*, U MADHUSOODANAN,
A NATARAJAN and B S PANIGRAHI

Safety Research and Health Physics Group, *Materials Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

Abstract. In LiF, the photoluminescence emission of F_2 and F_3^+ centres are produced on irradiation peaks in the red (660 nm) and green (520 nm) region respectively. In this work, their relative sensitivities for thermal neutrons and gamma rays are compared.

Keywords. Photoluminescence; F -aggregate centres; LiF; thermal neutrons; radiation dosimetry.

1. Introduction

Excitation at room temperature (RT) into the F_2 centre optical absorption (OA) band of pure and doped LiF after X-irradiation produces intense photoluminescence (PL). In irradiated LiF TLD-100 (LiF: Mg, Ti), the absorption in the 441 nm region is a composite band of the F_2 and F_3^+ centres. However, their emission spectra are well separated, having red (670 nm) and green (520 nm) emissions, respectively (Nahum and Wiegand 1967; Regulla 1972; Farge *et al* 1967). In LiF, during X-irradiation, the formation of ionized centres (F_2^+ and F_3^+) precedes the formation of neutral centres (F_2 and F_3). F_2^+ and F_3^+ centre formation occur through diffusion of α and F_2^+ centres respectively, towards F centres ($\alpha + F \rightarrow F_2^+$ and $F_2^+ + F \rightarrow F_3^+$). When electrons are available, the F_2^+ and F_3^+ centres capture electrons and transform to F_2 and F_3 centres respectively. Unlike the case with γ -rays, the OA band around 445 nm in LiF TLD-100 can be observed even at relatively low thermal neutron fluences (Lakshmanan 1994). This has prompted us to conduct a fluorimetric study of the F -aggregate centres in thermal neutron and γ -ray irradiated LiF TLD-100 and undoped LiF crystals. Multi-vacancy centres such as F_2 or F_3^+ are likely to be produced with a greater efficiency on irradiation with radiations (α -particles, etc) having high specific ionization density ($SID > 50 \text{ keV } \mu\text{m}^{-1}$) compared to radiations (X, γ -rays, etc) having low SID ($\sim 1 \text{ keV } \mu\text{m}^{-1}$). With densely ionizing radiations such as the α and triton tracks produced during the capture of thermal neutrons by the ^6Li in LiF (abundance of ^6Li in natural LiF is about 7%), the anion vacancies will be created in close proximities and hence the F -centre aggregation process can be expected to take place more efficiently during irradiation and storage after irradiation. To confirm this view, a comparison of the PL from LiF after thermal neutron and γ -irradiations was made for the first time.

2. Experimental

Harshaw made LiF:Mg,Ti (commonly known as TLD-100) and undoped LiF single crystals ($6 \times 6 \times 2 \text{ mm}^3$) were used in this study after a pre-irradiation annealing

*Author for correspondence

treatment at 400°C for 20 min. They were irradiated with thermal neutrons at the thermal column of the CIRUS reactor. γ irradiations were performed in a ^{60}Co γ cell. The PL measurements were carried out after a minimum post-irradiation interval of three days at RT with a Shimadzu RF 5000 spectrofluorimeter having R-452-01 and Hamamatsu R-928-08 photomultipliers for photometry with a measuring wavelength range 200–700 and 200–900 nm respectively. In both cases, the PL spectra were not corrected for the instrumental response. The excitation source for PL was a 150 W CW xenon lamp and the band width for the excitation and emission monochromators were set at 1.5 nm.

3. Results and discussion

With R-452-01 photomultiplier, the PL excitation and emission spectra were found to peak at 445 nm and 515 nm respectively for thermal neutron irradiance levels up to 10^{12} n/cm² and gamma dose levels up to 3×10^4 Gy. At higher irradiance levels i.e. 10^{13} n/cm² of thermal neutrons and 10^5 Gy of gamma rays, the excitation spectra shows two maxima (figure 1). Figure 2 shows the integrated intensity of PL (460 to 600 nm) as a function of thermal neutron fluence at the excitation wavelength of 445 nm. The PL intensity of gamma irradiated LiF TLD-100 also shows a similar increase with gamma ray dose.

When red sensitive Hamamatsu R-928-08 photomultiplier was used the PL emission spectra at three thermal neutron irradiance levels with 445 nm excitation shows clearly

Figure 1. PL excitation spectra measured at $\lambda_{\text{emi}} = 515$ nm; (— 10^5 Gy, --- 10^{13} n cm⁻²) and PL emission spectra measured using $\lambda_{\text{exc}} = 445$ nm: (····· 10 Gy, — · — 10^{13} n cm⁻²).

Figure 2. PL (460–600 nm) as a function of neutron fluence and γ ray dose.

Figure 3. PL emission spectra of TLD-100 ($\lambda_{\text{exc}} = 445$ nm) for three thermal neutron irradiance levels: — 10^{11} , 10^{12} and - - - - 10^{13} n cm $^{-2}$.

the presence of an intense red emission peaking at 656 nm and a shoulder peak at about 614 nm accompanying the green emission at about 521 nm. However, the PL intensity of 521 nm emission is more than the 656 and 615 nm emissions at all neutron fluence levels studied. Figures 3 and 4 show respectively the emission spectra of LiF TLD-100

Figure 4. PL emission spectra of TLD-100 for $\lambda_{\text{exc}} = 445$ nm after gamma irradiation: ----- 5×10^3 , 10^4 , — 3×10^4 , and — — 10^5 Gy.

after neutron and γ irradiations at different dose levels. The intensity ratio of 521 nm to 656 nm PL emission for thermal neutrons at low neutron fluence levels is nearly 3 times higher than that for γ rays. This difference comes down gradually at higher neutron fluence. For γ rays, the 521 nm to 656 nm emission ratio is nearly 1 up to 3×10^4 Gy. At higher γ dose levels this ratio becomes < 1 . The dependence of 521 nm to 656 nm PL emission ratio on the neutron fluence appears to be related to the higher growth of the F_2 centres. In general, ionization density dependent effects are dominant at low exposure levels (Zimmerman 1972). With increasing dose the secondary electron tracks converge resulting in track interaction which reduce the above ionization density effects. Even for α -particles, the presence of such track interaction effects, though to a lesser extent, has been proposed (Horowitz 1990).

Figure 2 shows that the neutron induced PL (green emission) is nearly 1350 times more intense than that induced by γ rays on a dose equivalent (DE) basis. Since the two PL response curves are similar, the thermal neutron DE (NDE) can be calculated using the simple linear relation $\text{NDE} = 1350 \text{ EGDE}$, where EGDE is the equivalent γ DE. The advantage of this relation is that it will be valid in any fluorimeter irrespective of its instrumental response, since for all emission measurements, the same spectral region is to be used in the PL measurements. Hence the instrumental response correction will be unnecessary. Based on earlier studies (Ayyangar *et al* 1974), the PL from F_3^+ centres in TLD-100 can be shown to be nearly 45 times more efficient than that of TL of the 200°C peak from the point of view of discriminative measurement of radiations of high SID in mixed fields. On the contrary, for the 656 nm PL from F_2 centres, this discrimination factor will be lower since the 656 nm to 521 nm PL intensity ratio is

lower for thermal neutrons. Obviously for fast neutron dosimetry, the LiF sample should be intimately mixed with a proton irradiator. If the sensitivity to thermal neutrons is to be avoided, then it is better to use ^7LiF rather than natural LiF. A positive outcome of this study with LiF TLD-100 is the comparison of its PL and TL sensitivities to thermal neutrons and γ rays. It is worth noting that F -aggregate centres in LiF TLD-100 do not give rise to any TL peak above RT. Thus their properties can be studied only with PL or OA.

Even the F_2 centres are expected to be produced with a greater efficiency (than say, F centres) by thermal neutrons relative to γ rays, since they are di-vacancy centres. Indeed, the 656 nm PL from F_2 centres is about a factor of 15 times more sensitive to thermal neutrons than the TL sensitivity of 200°C dosimetric peak in LiF TLD-100. But the mechanism of production of F -aggregate centres is quite complex. The F -aggregate centres formed due to the migration and aggregation of defects created by inter-tracks could mask the F -aggregate centres created by intra-tracks. Thus the actual number of F -aggregate centres at different SID will be difficult to predict on the basis of simple defect centre models.

In LiF, F_2 and F_3^+ colour centres are known to be laser active. In the CW mode on Argon ion (457 nm) laser excitation, the F_2 emission shows no quenching whereas a pumping power dependent quenching of F_3^+ laser emission intensity has been reported which limits its use as a colour centre laser to pulsed mode operation (Paciornik *et al* 1991). X- or γ -irradiation produces a concentration of F_2 centres higher than F_3^+ centres and to increase the lasing efficiency in the green region. The F_2 centres were eliminated at RT with the 308 nm light from an excimer laser. Present studies show that thermal neutron irradiation provide a relatively higher concentration of F_3^+ centres as compared to γ rays.

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