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Photoluminescence and thermal stability of 5.5 eV and Ti centres in gamma irradiated LiF : Mg,Ti crystals

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Abstract

Photoluminescence (PL) and thermoluminescence (TL) measurements of LiF : Mg,Ti (DTG-4) single crystals, previously gamma irradiated with 500 Gy and thermally treated, were performed. The behaviour of the Mg centres, related to the known 5.5 eV optical absorption band, PL emission after repeated heating cycles with a heating rate of 1 K/s up to 373–653 K indicate that these centres are created simultaneously with the destruction of TL peaks. The decay of the PL emission after repeated heating cycles followed by 10 min annealing at 643 K coincides with the decreasing of the TL sensitisation factors of peaks 2, 3 and 5. Both these facts support the point of view that the precursors of the 5.5 eV centres act as competitive traps during TL readout. The behaviour of the Ti-related PL emission was found to be unexpectedly complex. Noticeable change of the Ti band shape and ambiguous behaviour of the Ti emission during subsequent heating indicate the possible presence of an additional Ti band.

Keywords: LiF : Mg, Ti; Photoluminescence; Sensitization

1. Introduction

It is well-known that irradiation of dosimetric LiF : Mg,Ti with high dose followed by high temperature annealing lead to an increase (sensitization) or a decrease (damage) of the sensitivity of thermoluminescence (TL) peaks. The competition-during-heating model is usually suggested as a mechanism for description of TL supralinearity and sensitization phenomena (see McKeever, 1990 and references from therein). The Mg optical absorption (OA) band at 5.5 eV increases and decreases together with the creation and destruction of TL sensitization and the precursors of the 5.5 eV centres are the main candidates for competitors in the TL process. Below we will name a centre responsible for the 5.5 eV OA band as the Mg^0 centre (Mg atom on anion site with cation vacancy) (Radzhabov and Nepomnyachikh, 1981). Usually the Mg^0 centres are measured by OA. Due to the strong overlap of the 5.5 eV band by tails of the F-band (5.0 eV) and the Ti-band (6.2 eV) a correct determination of dependencies of the 5.5 eV band on thermal and optical treatment is not an easy task. As a result, the direct evidence that the Mg^0 centres are connected with TL sensitization is absent. Absorption of light at 5.5 eV band yields a well-pronounced photoluminescence (PL) peak at 2 eV (Mort and Zimmerman, 1966), providing an additional possibility to investigate the behaviour of the band and Mg^0 centres (Rogalev and Chernov, 1995).

The aim of this work is to obtain further insight into the possible connection between TL sensitization and the Mg^0 centres using PL to detect the Mg^0 centres instead of OA.

2. Materials and methods

LiF : Mg,Ti DTG-4 single crystals (Nepomnyachikh et al., 1985) produced in the Institute of Geochemistry, Irkutsk,

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Russia, were used in this study. Gamma irradiation was carried out at room temperature with a ^{60}Co source up to 500 Gy. Prior to irradiation, all crystals were annealed for 1 h at 673 K and quenched by cooling down on a cooper plate. Test irradiations (about 0.3 Gy) for measurement of changes in TL sensitivity were carried out with a ^{90}Sr–^{90}Y beta source.

PL measurements were taken with a spectrofluorimeter Fluoromax (SPEX Co). Crystals were mounted on a holder, the temperature of which was controlled by a programmable temperature controller. Emission spectra between 300 and 800 nm were excited by UV light with wavelengths from 200 to 300 nm. To eliminate the influence of second order light, a 300 nm cut-off filter was used. The spectra were corrected for the wavelength response of the spectrofluorimeter and absorption of the cut-off filter.

TL measurements were performed with a Harshaw 4000 TLD system. A linear heating of 1 K/s was used for readout until 643 K, followed by an annealing at this temperature for 10 min.

3. Results

Typical PL emission spectra of irradiated LiF : Mg,Ti as functions both of emission and excitation wavelengths are shown in Fig. 1a. The spectra exhibit a very pronounced well-known Ti emission band with excitation and emission maxima at 200 and 410 nm, respectively (Rossiter et al., 1971). A weak emission between 600 and 750 nm (210–240 nm excitation) is also observed, which may be caused by the initial concentration of the Mg^0 centres in the irradiated crystal. After the irradiated crystal is heated up to 643 K with a heating rate of 1 K/s, the Ti band decreases and an additional emission appears (Fig. 1b). The excitation maximum position at 225 nm (5.5 eV) and the temperature behaviour (see below) of this emission close to the temperature behaviour of the 5.5 eV OA band allowed us to connect this emission with PL of the Mg^0 centres.

To investigate the process of creation and decay of the Mg^0 centres a repeated linear heating, at a rate of 0.1 K/s to increase the temperature from 373 to 653 K with 10 K temperature steps, was performed. The PL emission spectra excited by 225 nm (5.5 eV) UV light were measured after each heating cycle. Fig. 2a shows an evolution of the emission spectrum measured at room temperature (RT) after subsequent heating. The spectra consist of the Ti band and emission of the Mg^0 centres between 450 and 750 nm. The emission of the Mg^0 centres is very broad and is clearly composed of at least three bands with maxima at about 540 nm (2.3 eV), 620 nm (2.0 eV) and 650 nm (1.9 eV).

The emission spectra consist of several strongly overlapping bands. Our attempts to deconvolute the spectra with Gaussian bands (in eV) have shown that at least six bands (three for Ti and three for Mg^0 emission) are needed. Moreover, we have obtained several sets of bands, which may

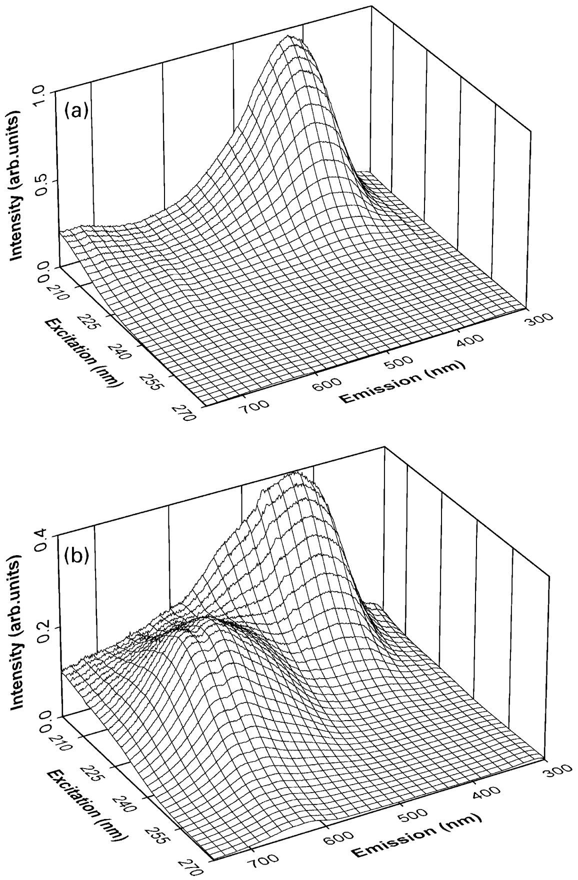

Fig. 1. Isometric plots of the excitation and emission spectra from LiF : Mg,Ti: (a) after gamma irradiation of 500 Gy, (b) after irradiation and following linear heating up to 643 K at heating rate of 1 K/s.

represent any one spectrum with more or less equal precision without any possibility of differentiating one from another. Therefore, in this paper we have tried to divide the Ti and the Mg^0 emission only. The emission spectrum for the irradiated crystal without thermal treatment (spectrum 1 in Fig. 2a) contains mainly the Ti band. The subtraction of this spectrum from the other spectra allows the resolution of the emission connected with the Mg^0 centres. As the intensity of Ti emission depends on the thermal treatment, the subtracted Ti spectrum should be normalized. The average emission intensity between 400 and 410 nm, which seems to be free from the Mg^0 centre emission, was used for normalizing procedure. The results of such subtraction are shown in Fig. 2b. The shape of the emission spectra between 450 and 750 nm is changed after subsequent heating which indicates a different temperature behaviour of the separate Mg^0 bands.

The dependencies of Ti and Mg^0 emission intensity on maximum temperatures of subsequent heating after irradiation are shown in Fig. 3a. The averaged emission intensity

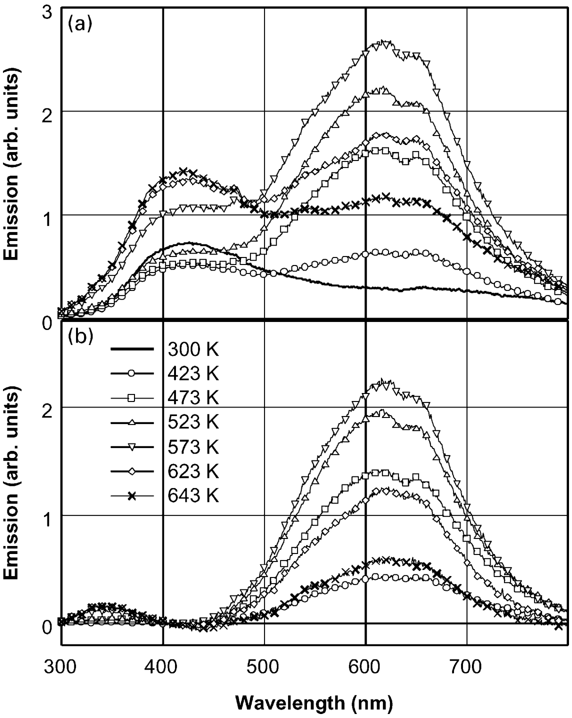

Fig. 2. Emission spectra (excited with 225 nm) of LiF : Mg,Ti gamma irradiated with 500 Gy (curve 1) and after subsequent heating up to temperatures: (2) 423, (3) 473, (4) 523, (5) 573, (6) 623, (7) 643 K. (a) Spectra as obtained. (b) Remaining emission after subtraction of the Ti centres emission (spectrum 1 in Fig. 2a).

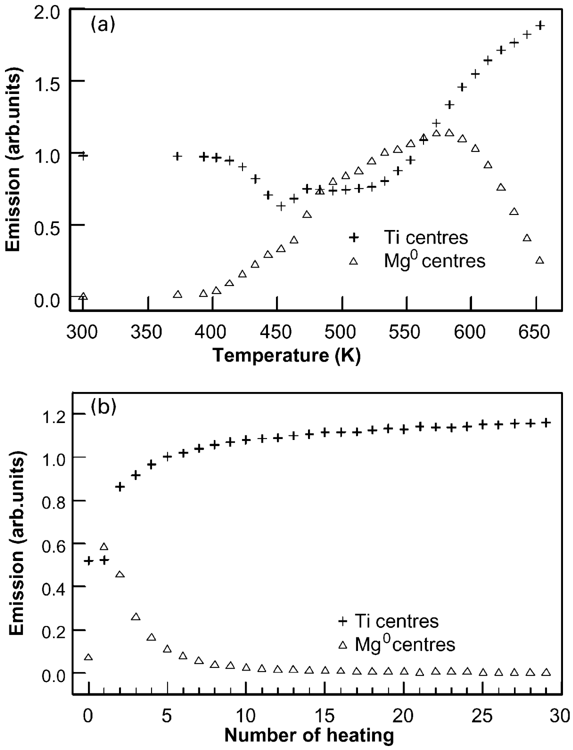

Fig. 3. Behaviour of the Ti and Mg^0 centre emission bands with thermal treatment. (a) Repeated linear heating up to increasing temperatures from 373 up to 653 K with 10 K steps. (b) Repeated linear heating up to 643 K.

between 400 and 410 nm, conveniently normalized (multiplied by integrated emission under the spectrum 1 in Fig. 2a to obtain the same scale as for the Mg^0 band), was taken as the estimation of the Ti emission and the integrated emission between 450 and 750 nm as the evaluation of the emission related to the Mg^0 centres. The Mg^0 emission appears (begin increasing) after heating up to 400 K and continuously increases up to 580 K. Further increase of the maximum heating temperature leads to a fast decay of the band. The growth rate of the Mg^0 emission is not constant and may be compared with the presence of TL peaks (the peaks 3–8 (or 9), as can be seen in Fig. 4a). The maximum growth rate is observed between 460 and 490 K where TL peak 5 appears in the glow curve. The Ti emission displays more complex behaviour. It starts to diminish at 400 K where the TL peak 3 shows up in the glow curve. At 450 K the decreasing stops, the behaviour becomes practically constant between 470 and 530 K, followed by an increase in the emission up to 653 K (in our measurements). It is interesting to note that the same ambiguous behaviour of the Ti band between 430 and 480 K also is observed during heating (these data are not presented here and will be published separately).

To compare the PL behaviour with the sensitivity of the TL peaks, parallel measurements of PL at room temperature after repeated thermal treatments of one crystal without changing its position in the spectrofluorimeter, and subsequent TL readouts of another crystal irradiated with test beta dose of about 0.3 Gy were carried out. The thermal treatment cycle of both crystals consisted of a linear heating up to 643 K at a heating rate of 1 K/s followed by an annealing at this temperature for 10 min. The dependencies of the Ti and Mg^0 centres emission on the number of the heating cycles are shown in Fig. 3b. The first heating (TL readout after 500 Gy irradiation without annealing at 643 K) does not change the Ti emission, but creates the Mg^0 centres. The subsequent heating cycles increase Ti emission and reduce to zero the Mg^0 emission. After 15–20 cycles the Ti emission seems to reach saturation, whereas the Mg^0 centres completely disappear.

The effect of the heating cycles on TL is shown in Fig. 4. Fig. 4a shows an evolution of glow curves after subsequent heating cycles. The first curve displays the TL due to the 500 Gy gamma irradiation on which peaks 3, 4, 5 (peak 2 is not present because of the delay of the TL measurement after irradiation) and several unresolved high temperature peaks show up. The other curves in Fig. 4a were obtained after test beta irradiation. These curves consist of peaks 2–5, one or two high temperature peaks (with relative

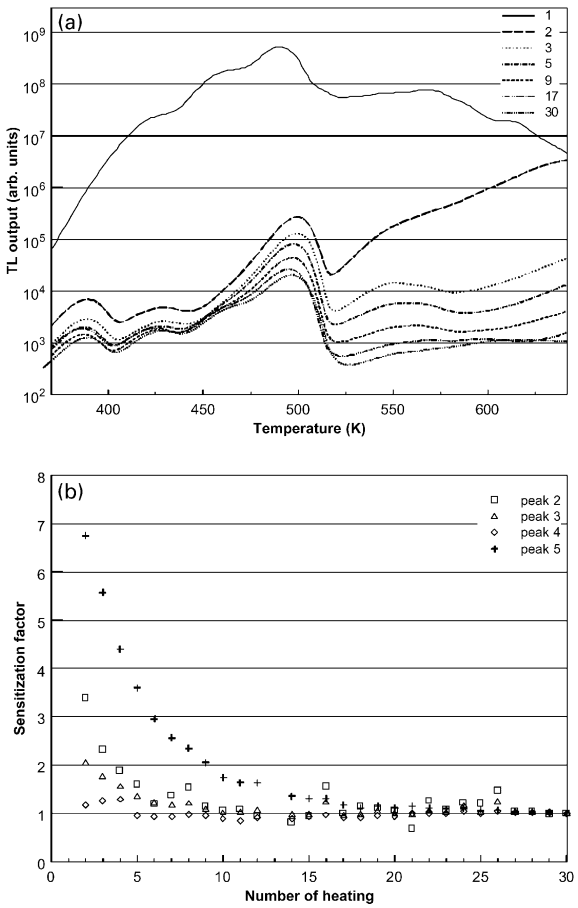

Fig. 4. Effect of the repeated linear heating up to 643 K on TL sensitivity of LiF : Mg,Ti gamma irradiated with 500 Gy. (a) The glow curves, taken at 1 K/s (number 1 corresponds to heating after 500 Gy irradiation; the others correspond to heating after test beta irradiation, done after the number of heating cycles seen in the legend). (b) The sensitization factor as a function of the number of heating cycles.

intensities different from that of curve 1) and a tail of peak 10, reminiscent of the 500 Gy gamma irradiation, the intensity of which decreases rapidly with the heating cycles. Fig. 4b shows changes of sensitivity factors for TL peaks 2–5. The TL sensitization factors were obtained by the normalizing peak areas to their values after 30 heating cycles. The peak areas were extracted from the glow curves by a deconvolution procedure. The TL sensitization factors decrease constantly after heating cycles for all peaks except for peak 4 that does not display supralinearity and sensitization. The dependency of the TL sensitization factors and the Mg^0 emission on heating cycles look very similar. This supports the point of view that the Mg^0 centres are connected with the TL sensitization mechanism, and that the precursors of the Mg^0 centres are the competitors in the TL process.

4. Summary

PL emission at RT related to the Ti and Mg^0 centres and their changes after thermal treatments have been measured on LiF : Mg,Ti crystals gamma irradiated with 500 Gy. The behaviour of the Mg^0 centre emission during subsequent heating to higher temperatures clearly indicates that the Mg^0 centres are created simultaneously with the emptying of TL peak traps. The disappearance of the Mg^0 centre emission due to repeated heating cycles followed by 10 min annealing at 643 K coincides with the decreasing of the TL sensitization factors of peaks 2, 3 and 5. Both facts support the position (McKeever, 1990; Issa et al., 2000) that the precursors of Mg^0 centres act as competitive traps during TL readout and determine temperature and dose dependencies of the supralinearity and sensitization factors.

The behaviour of the Ti-related emission was found to be unexpectedly complex. Noticeable changes of the Ti band shape and non-monotonous growth of the Ti emission during subsequent heating cycles are not unequivocal and require an additional investigation.

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