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Defects induced in fluorides and oxides by VUV radiation

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Irradiation effects of monochromatic VUV were studied in some broad band crystals such as alkaline-earth and perovskite-type fluorides as well as metal oxides. The irradiations were carried out at RT and at LNT and the thermal stability of some radiation-induced defects was studied. Results were compared to effects induced in the same samples by X or β radiation. The various types of investigated crystals showed some interesting common properties. In most materials, essentially the same main TL peaks and with the same thermal activation energies appeared after VUV as after X or β irradiation, indicating that the same traps were induced by the different irradiations. The TL excitation spectra in the various types of crystals generally showed maxima at the long wavelength tail of the fundamental absorption; this fits previous results in various alkali halides. Dosimetric properties and possible application of the materials as dosimeters for the VUV were also investigated.

1 Introduction

The processes of defect formation in alkali halides and other broad band crystals have been studied intensively for several decades. Point defects in alkaline-earth (AEF) and composite fluorides, such as the perovskite type ABF_3 (A=Na, K…and B=Ca, Sr, Ba…) as well as in various metal-oxides were studied by many authors (e.g. [1–3]). These crystals are of interest from both the points of view of basic and applied research and special attention has been given to AEF doped with trivalent, mostly rare-earth (RE) ions. The doped crystals contain F^- interstitial ions compensating for the excess charge of the trivalent ions, which occupy sites of divalent cations in the crystal lattice. The F^- interstitial ions are assumed to be the dominant carriers in these doped fluoride crystals. Most of the previous studies on radiation effects and the formation of point defects concentrated on the effects of higher energy radiation such as γ, β and X-rays, and relatively few works dealt with the effects induced by monochromatic VUV radiation (e.g. [4, 5]). It has previously been shown that in some broad band crystals, the application of monochromatic VUV radiation can be very useful for studying processes of defect formation since it also enables the measurements of the spectral dependence of the production efficiency of the radiation induced defects. In alkali halides, maxima of the F-center production efficiency were observed at the long wavelength tail of the first exciton band and also at the peak of the weak F^+ band; these findings supported the conclusion that an excitonic process is involved in the generation of the radiation induced defects in these crystals [6]. In some metal oxides such as MgO or Al_2O_3, energy of ~50 eV is necessary to eject an ion from its normal position and a high energy radiation such as neutrons or fast electrons is required for knocking out ions from their lattice positions and for generation of vacancies and interstitials. VUV as γ, β or X-radiations, which are effective for creation of vacancies and interstitials in alkali

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and alkaline-earth halides cannot create primary lattice defects in these oxides; but they may produce in these oxides free carriers which may then be trapped at the sites of existing lattice defects or impurities. Much interest has recently been given to applications of various materials as efficient dosimeters; some fluorides and oxides are presently used as radiation detectors and dosimeters mainly for higher energy radiation (e.g. [7–9]).

In the present work effects of monochromatic VUV radiation various broad band crystals were studied and the results were compared to those obtained in the same materials by β or X-rays. The investigated materials included some simple and composed fluorides as well as some metal oxides. The radiation effects were studied by means of optical absorption, X and light induced luminescence (XL and PL) as well as thermoluminescence (TL). Special attention was given to analogous effects and properties in the various types of crystals. Dosimetric properties such as the TL efficiency and dose dependence were also studied and possible application of some materials as dosimeters for the VUV region was investigated.

2 Experimental techniques

Nominally pure and variously doped single crystals have been used for the measurements. The X-irradiations were performed with a W-tube (40 kV, 15 mA), the β-irradiations with a ^{90}Sr source of a 1.5 Gy/min. dose-rate. and the VUV irradiations with a one-meter normal-incident VUV monochromator and an H_2 arc lamp. The TL measurements from RT up were carried out in a TL compartment flushed by N_2 gas; the heating rate above RT was 5 K/sec. For the low temperature TL and OSTL measurements the samples were kept in a liquid nitrogen vacuum cryostat and heated at a rate of 20 K/min. Further experimental details are given elsewhere [8].

3 Results and discussion

3.1 Optical absorption

The various investigated crystals were all highly transmitting in a broad spectral range from the near IR to the VUV region up to about 11 eV. Absorption spectra of some samples are shown in Figs. 1–3. The

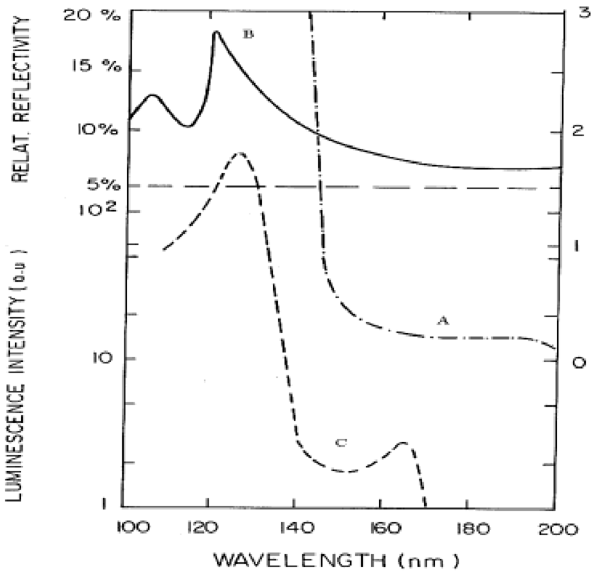

Fig. 1 A) Absorption (optical density), B) reflectance [10], C) TL excitation spectra of synthetic quartz.

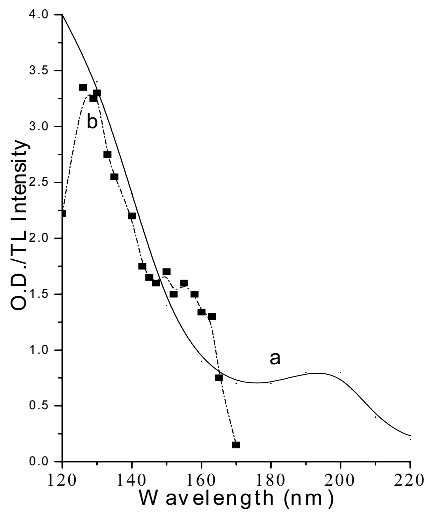

Fig. 2 a) Absorption and b) TL excitation spectra of $RbMgF_3$.

absorption spectra of the doped samples also showed narrow absorption bands, characteristic of the impurity ions and after prolonged irradiation additional absorption bands, related to various color centers were recorded in all samples.

3.2 TL

In all examined crystals TL could be excited by X and β irradiation and in many crystals also by monochromatic VUV radiation in the 110–200 nm region. In Figs. 1 and 2 samples of TL excitation spectra of some oxides and fluorides are shown and compared to the absorption spectra of the same crystals. The results show that in most of the examined alkaline-earth and perovskite-type fluorides as well as in some metal oxides the excitation maxima coincide with the long wavelength tail of the fundamental absorption. These results also agree similar previous results in alkali halides and support the predictions of a theoretical expression for the number of defects formed by the UV radiation which takes into account the radiation dose, the absorption coefficient of the crystal and the penetration depth of the monochromatic light. This expression predicts for a region of high absorbance the appearance of an excitation peak at the long wavelength tail of the strong absorption band rather than at its maximum [6]. The comparison of the TL, induced by VUV radiation with that induced in the same sample by X or β radiation showed that the main VUV excited TL peaks appear in the various examined fluorides and oxides at the same temperatures and with the same thermal activation energies as in the β or X-induced TL in the same crystal; examples are shown in Figs. 3 and 4.

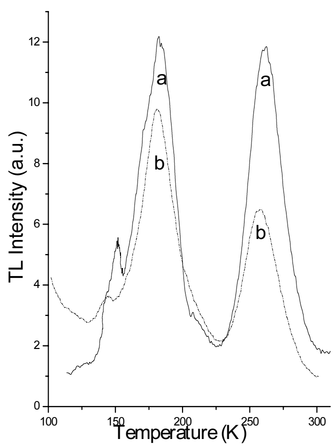

Fig. 3

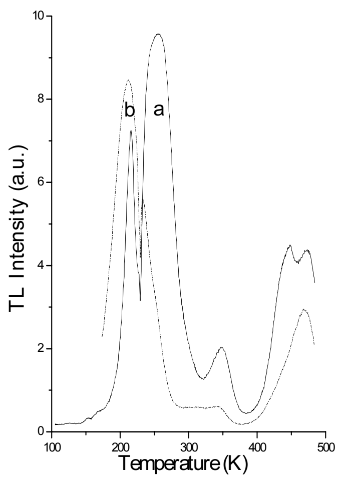

Fig. 4

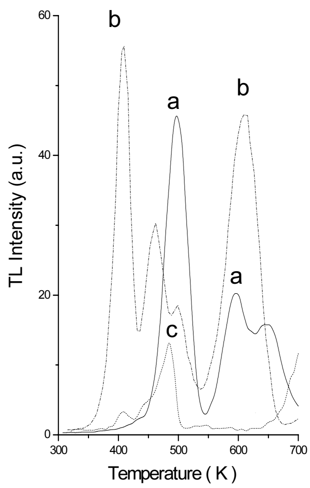

Fig. 5

Fig. 3 Comparison of TL induced in zircon by: a - X and b – 225 nm irradiation at LNT.
Fig. 4 Comparison of TL induced at LNT in $KMgF_3$: Eu^{2+} by a) 215 nm and b) X radiation.
Fig. 5 Comparison of TL sensitivity of: a) CaF_2:Pr^{3+}, b) SrF_2:Pr^{3+}, c) TLD100 (all after 90Gy β irradiation at RT).

3.3 XL, PL and OSL

The X-induced luminescence (XL) of the doped samples differed generally from that of the pure crystals. The emission of the doped samples was stronger than that of the pure crystals and dominated by the characteristic bands of the various impurity ions. In samples which had previously been exposed to ionizing radiation, PL could also be excited by illumination with longer wavelengths that could not excite any PL in non-irradiated samples. These emissions are therefore attributed to processes of optically stimulated luminescence (OSL) In the TL, PL and OSL emission essentially the same spectral bands appeared as in the XL.

3.4 Dosimetric properties

Dosimetric properties and possible application of the materials as radiation detectors and TL dosimeters for the VUV region were also investigated. Among the presently investigated materials some Pr^{3+} doped fluorides showed a relatively high TL sensitivity. The sensitivity of Pr^{3+} doped CaF_2, $LiKYF_5$ and $CsGd_2F_7$ was found to be of the same order as that of the known LiF:Mg,Ti (TLD-100) phosphor [7] and the sensitivity of $SrF_2:Pr^{3+}$ was by more than an order of magnitude higher (Fig. 5). The $SrF_2:Pr^{3+}$ crystals were also found to have a relatively high TL sensitivity by VUV excitation; but reached saturation for relatively low UV doses. Some of these crystals, like $KMgF_3$ are also thermally stable to above 1300 K. The dependence of the TL intensity on the β dose of $LiKYF_5:Pr^{3+}$ was found to be linear up to ~ 2000 Gy, that of $CsGd_2F_7:Pr^{3+}$ to ~ 6000 Gy and that of the 188 °C TL peak in $SrF_2:Pr^{3+}$ was nearly linear up to above 27000 Gy.

4 Summary

The results of this comparative study revealed some interesting common properties in the different types of the investigated broad band crystals,

The TL excitation spectra of the various fluoride and oxides showed generally maxima at the long wavelength tail of the fundamental absorption.

The main VUV induced TL peaks appeared in most crystals at the same temperatures and with the same thermal activation energies as the β or X- induced TL peaks, indicating that the same defect levels are responsible for the TL in these cases.

The fact that different emission bands were recorded at the same TL peaks of doped and pure crystals indicates that the emissions at these peaks are due to different luminescence centers.

A comparison of the investigated materials showed that some Pr^{3+} doped fluoride crystals have a relatively high TL sensitivity and some also show a linear dose dependence up to high radiation doses of above 27000 Gy.

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