phys. stat. sol. (c) 4, No. 3, 1110–1113 (2007) / DOI 10.1002/pssc.200673855

Irradiation effects in BaF_2:$CuCl_2$ and BaF_2:Mn,Ce crystals

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Received 13 July 2006, revised 16 November 2006, accepted 16 November 2006
Published online 9 March 2007

PACS 61.80.-x, 78.40.Ha, 78.55.Hx, 78.60.Kn, 78.70.En, 87.53.Dq

Effects of X, β and VUV radiation were studied in BaF_2:$CuCl_2$ and BaF_2:Mn,Ce crystals. Methods of optical absorption and of luminescence were applied; X-luminescence (XL), photoluminescence (PL), thermoluminescence (TL), photo-transferred TL (PTTL) and optically stimulated luminescence (OSL) as well as emission and excitation spectra were measured. Optical stimulation for PTTL and OSL investigations was carried out at liquid nitrogen temperature (LNT) in samples that had previously been X or β irradiated at room temperature (RT) and the results were compared to those obtained in nominally pure BaF_2 crystals. The TL excitation spectra showed maxima at the long-wavelength side of the first exciton band. In the VUV induced TL, some of the peaks appeared at the same temperature as in the X-induced TL, indicating that the same radiation-induced traps were created by the different types of radiation. The TL efficiency of some of the crystals was found to be of the same order of magnitude as that of the known TL dosimetric material LiF:Mg,Ti (TLD 100).

1 Introduction The formation of defects in alkaline earth halides by ionizing radiation has been studied for several decades. It is well known that low temperature irradiations cause in these crystals the formation of V-type centers and free electrons; in rare-earth doped samples, the electron may be trapped at the site of a trivalent impurity ion, causing the reduction of the ion to a divalent state, e.g. [1–4]. Most of the previous studies concentrated on higher energy radiations such as β or X-rays; relatively few works dealt with effects of vacuum-ultraviolet (VUV) radiation, e.g. [5, 6]. Effects of VUV radiation in various crystals have been studied in our laboratory, and the results showed that in different crystal systems the same defects are induced by VUV as by the higher energy radiations. The application of monochromatic VUV radiation also enabled the evaluation of the photon energies, most efficient for formation of defects in this crystal, e.g. [7]. In the present work, effects of X, β and VUV radiation on BaF_2:$CuCl_2$ and BaF_2:Mn, Ce, were studied and compared to those induced in nominally pure BaF_2 crystals. Special attention was given to the effects of monochromatic VUV radiation and the effects were compared to those induced in the same samples by X or β radiation. These composed halides appear to be of interest from both the point of view of basic and applied research. Various mixed fluorides such as LiF:Mg,Ti (TLD-100) and CaF_2:Dy (TLD-200) are used as efficient radiation detectors and dosimeters [8, 9]. In the present work dosimetric properties of our Ba-halide crystals were also investigated. Methods of absorption, X-luminescence (XL) and Thermoluminescence (TL) as well as of optically stimulated luminescence (OSL) and of photo-transferred TL (PTTL) were utilized.

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2 Experimental techniques $BaF_2:CuCl_2$, BaF_2:Mn, Ce and nominally pure BaF_2 crystals were used for the measurements. The pure BaF_2 crystals were from Harshaw. The composed Ba-Halides were grown by solid diffusion at 850 °C under protection of carbon powder. The nominal amount of the impurities ($CuCl_2$:Mn,Ce) introduced in the preparation of the samples was 3% in weight for each dopant. X-ray diffraction was measured and the crystal structures were studied by Chen et al. [10]. The X-irradiations were performed with a W-tube (40 kV, 15 mA) and the β-irradiations with a Sr^{90} source of a 1.5 Gy/min. dose-rate. 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 °C/s. For the low temperature TL and PTTL measurements the samples were kept in a liquid nitrogen vacuum cryostat and heated at a rate of 20 °C/min. The ultraviolet (UV) irradiations were carried out with a one-meter normal-incident vacuum-ultraviolet (VUV) monochromator and an H_2 arc lamp. The optical absorption in the infrared (IR), visible and near UV spectral regions was measured with a Cary 17 spectrophotometer and in the far-UV with the normal-incident VUV monochromator. Further experimental details are given elsewhere [7].

3 Results and discussion

3.1 Optical absorption Optical absorption was measured in the visible, near UV and VUV regions. The band-gap of pure BaF_2 crystals is about 10 eV and they are transparent in a broad spectral region from about 130 nm in the VUV to above 15 µm in the IR. The band-gap of the composed Ba halides is slightly smaller (about 8-9 eV). In Fig. 1, the absorption spectra of $BaF_2:CuCl_2$ and BaF_2:Ce,Mn crystals in the VUV region are shown. A steep increase toward the first exciton band was recorded in all measured samples; some weaker absorption bands appeared between 140 and 240 nm.

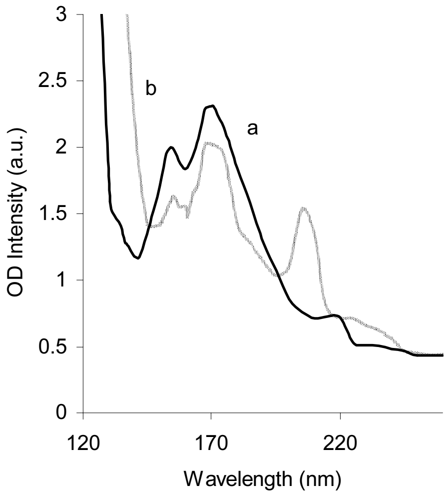

Fig. 1 Absorption of a) BaF_2:Mn,Ce; b) $BaF_2:CuCl_2$ in the VUV region at RT.

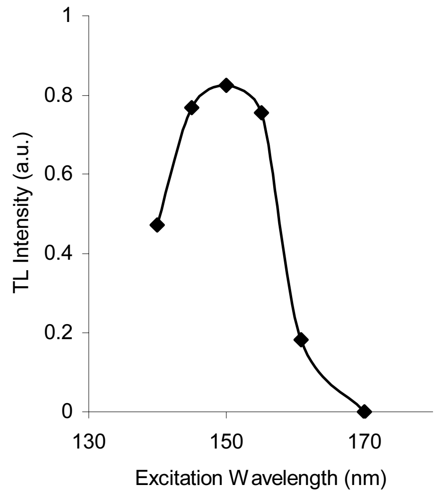

Fig. 2 TL excitation spectrum of $BaF_2:CuCl_2$, in the VUV region measured at the 180 K peak after LNT irradiation.

3.2 TL and PTTL After X or β irradiation, a notable TL emission was recorded in all samples during heating. TL could also be excited by monochromatic VUV radiation in the 130-200 nm region. The TL excitation spectra showed maxima on the long wavelength side of the first exciton band. These results also fit similar previous data on the formation of point defects in alkali halides by VUV photons [5]. The BaF_2:Mn,Ce crystal shows maximal excitation at about 130 nm, which is located on the long wavelength tail of the first exciton band. The $BaF_2:CuCl_2$ crystal had an excitation maximum at 150 nm, which coincides with a weak absorption band. In Fig. 2, the TL excitation spectrum of a $BaF_2:CuCl_2$ crystal is shown. The TL induced by the VUV radiation was compared to the TL induced in the same crystal by X or β radiation.

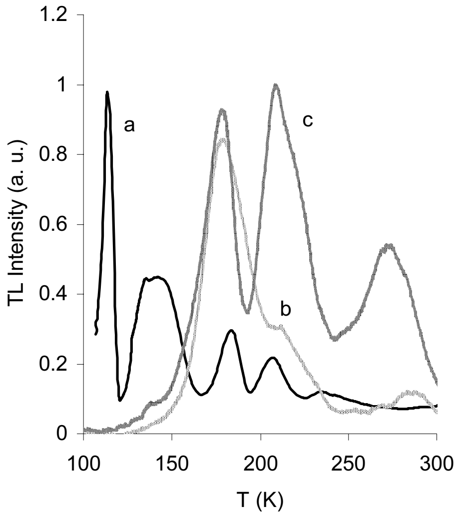

Fig. 3 TL induced at LNT in BaF_2:$CuCl_2$ by a) X -rays, b) 150 nm and c) in BaF_2:Mn,Ce by 130 nm.

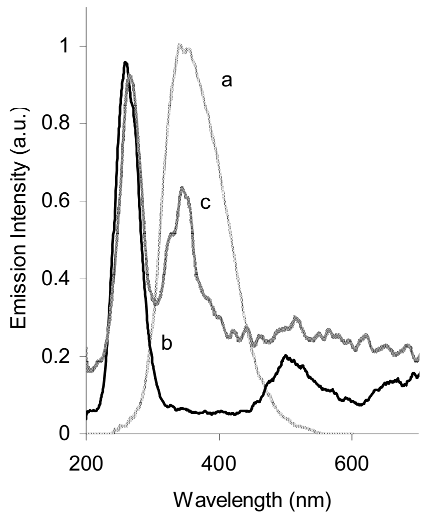

Fig. 4 Emission spectra of BaF_2:$CuCl_2$ crystal, measured at a) XL at LNT, b) 345 K-TL peak, c) PTTL peak after β irradiation and subsequent 400 nm stimulation at RT.

The results showed that some of the VUV excited TL peaks appear at the same temperatures as in the β- or X-induced TL indicating that the same defect levels are responsible for the TL in these crystals. In Fig. 3, the TL glow curves, induced at LNT in a BaF_2:$CuCl_2$ crystal by X-rays and 150 nm and in a BaF_2:Mn,Ce crystal by 130 nm VUV radiations are shown. The X-induced TL peaks at 110 and 140 K did not appear after 150 nm irradiation, but the peaks in the 180-210 K region appeared at the same temperatures after VUV as after X irradiation. The low temperature TL peaks in various BaF_2 crystals have previously been ascribed to the thermal release of holes from V-centers and recombination with trapped electrons [1, 2]. TL could not be excited in these crystals by photon energies below ~6 eV, but samples that had previously been exposed to X or β radiation at RT and were subsequently illuminated at LNT with light of energy lower than 6 eV, showed during heating from LNT to RT a TL emission that could not be excited in non pre-irradiated samples. These glow peaks are attributed to a process of optical stimulation or photo-transfer (PTTL). In this process, carriers that were trapped by the ionizing radiation in deep traps are then stimulated at lower temperatures by the near UV or visible light and transferred to shallower traps, which are not stable at the temperature of exposure to ionizing irradiation. PTTL glow peaks may appear during re-heating, when the carriers are thermally released from the shallow traps and recombine radiatively with carriers of opposite sign. PTTL stimulation spectra were measured; in BaF_2:$CuCl_2$ the wavelength of 400 nm was most efficient for the stimulation.

3.3 XL, PL and OSL The X-induced luminescence (XL) was measured in the various crystals. The main XL bands appeared in BaF_2:Mn,Ce; at LNT at 310-335 nm, in BaF_2:$CuCl_2$ at 340-355 nm and in pure BaF_2 at 308 nm. 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 and even by wavelengths longer than those of the emitted luminescence. These emissions are attributed to a process of optical stimulation. Optically stimulated luminescence (OSL) is a process where exposure to high-energy radiation results in the accumulation of stored charges such as in color centers.

These stored charges can then be stimulated by visible or near IR light and produce measurable OSL emission. In the emission spectra of the OSL, TL and PTTL appeared some of the same spectral bands as in the XL of the same crystal indicating that the same luminescence centers are involved. In Fig. 4 XL, TL and PTTL emission spectra of a BaF_2:$CuCl_2$ crystal are shown. Dosimetric properties and possible applications of these materials as TL radiation detectors and as dosimeters for the VUV region were also investigated. The main emission bands are in a wavelength region where the common photomultipliers are most sensitive. Some of these composed Ba- halides showed a relatively high luminescence intensity and the TL sensitivity of these crystals was of the same order as that of the known dosimetric material LiF:Mg,Ti (TLD-100). In Fig. 5 the TL sensitivities of the tested Ba-halides are compared to that of TLD -100.

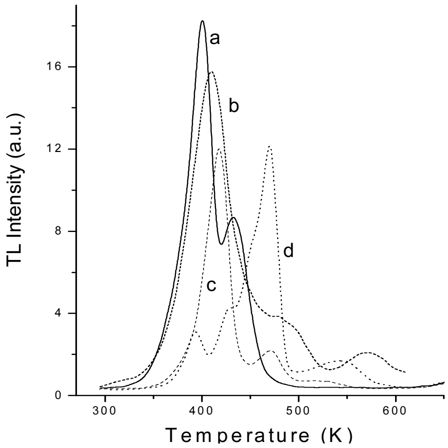

Fig. 5 Comparison of TL sensitivities: a) BaF_2:Mn,Ce, b) BaF_2:$CuCl_2$, c) pure BaF_2,d) TLD-100, after exposure to equal β-doses (90 *Gy*) at RT.

4 Summary The band-gap of these composed Ba-halide crystals is ~8-9eV. Thermoluminescence could be excited by X-rays as well as by monochromatic VUV irradiation. Excitation maxima were on the low wavelength tail of the exciton absorption bands. The results indicate that some of the same defect levels were induced by monochromatic VUV and X-radiations. UV and visible light could stimulate notable PTTL and OSL in pre-irradiated samples. Some emission bands that appeared in the TL and PTTL also appeared in the XL and OSL, indicating that these emissions are due to the same luminescence centers. Some of the composed Ba-halides crystals showed a good XL, OSL and TL efficiency. The mentioned features make these crystals good candidates for solid-state dosimeters.

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