Radiation effects in pure and doped Al$_2$O$_3$ crystals

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Abstract

Effects of $\beta$-, X- and UV-radiation on optical properties of nominally pure as well as of variously doped $\alpha$-Al$_2$O$_3$ crystals were studied. Optical absorption, thermoluminescence (TL) and photoluminescence (PL) were measured. The irradiation with wavelengths below 145 nm had essentially the same effects as X-irradiation, indicating that the same defects were formed in both cases. F and F$^+$ emission bands at 410 and 330 nm appeared in the TL and in the PL of all samples. In crystals doped with rare-earth ions the narrow bands, characteristic for these impurities, were dominant. In some of the nominally pure samples also a strong Cr$^{3+}$ band appeared at 698 nm. In the C-doped crystals the TL and PL emissions were relatively strong and dominated by the F and F$^+$ emission bands. These results support previous suggestions regarding a high anion vacancy concentration in the C-doped crystals. A weak emission band appeared near 500 nm with an excitation maximum near 300 nm and is attributed to interstitial Al$^+$ ions. Prolonged UV-illumination with F-light caused a notable increase in the PL yield in the C-doped samples. Irradiation into the Al$^+$ absorption band at 300 nm had a reverse effect and was also efficient for the optical bleaching of the phototransferred TL (PTTL).

1. Introduction

The formation of point defects in Al$_2$O$_3$ crystals has been studied for several decades (e.g. [1–3]). It is well established that in Al$_2$O$_3$ a minimum energy of about 50 eV is necessary to eject an aluminum or oxygen atom from its normal lattice position and that high-energy radiations, such as fast neutrons or electrons, are required for the displacement and the generation of primary defects in these crystals. Ionizing radiation such as X-, $\gamma$-, $\beta$-rays, which are known to be effective for the creation of vacancies and interstitials in alkali halides, may cause in Al$_2$O$_3$ free electrons and holes; these may then be trapped at the sites of existing lattice defects or impurities. Even ionizing UV-radiation is not expected to create new defects in these crystals, but may cause changes in the charge state of impurities or the filling of existing vacancies by free electrons and holes. Effects of vacuum UV (VUV) irradiations on these crystals have previously been investigated in this laboratory [4].
models of some of the absorption and emission bands in the $\alpha$-$\text{Al}_2\text{O}_3$ crystals are well established but others are still discussed. The absorption at 6.1 eV and the emission at 3 eV have been ascribed to F centers; the absorption bands at 5.4 and 4.8 eV, and the emission at 3.8 eV to F$^+$ centers [3]. For the broad 3.8 eV emission band also other models were proposed; some authors attributed this band to the emission of a self-trapped exciton and others to that of an interstitial Al$^+$ ion [5]. An emission band at 2.4 eV and an absorption band at 4.1 eV have also been ascribed to interstitial Al$^+$ ions [6].

In the present work effects of X-, $\beta$- and UV-irradiations on optical properties of pure and variously doped $\alpha$-$\text{Al}_2\text{O}_3$ crystals were studied. These impurities included carbon as well as various rare-earth ions. The anion defective $\alpha$-$\text{Al}_2\text{O}_3$:C crystals have recently become of interest due to their possible application as sensitive radiation detectors [7,8]. Optical absorption, photoluminescence (PL), X-induced luminescence (XL), optically stimulated luminescence (OSL), thermoluminescence (TL) and phototransferred TL (PTTL) were measured in the course of this work. The thermal and optical stability of the defects was also investigated. Results obtained for the variously doped samples were compared to those of the pure $\alpha$-$\text{Al}_2\text{O}_3$ crystals.

## 2. Materials and experimental procedure

The nominally pure synthetic $\alpha$-$\text{Al}_2\text{O}_3$ crystals were from Insaco, the rare-earth doped samples were obtained from the crystal-growing laboratory of the Hebrew University in Jerusalem and the C-doped crystals were grown by Akselrod and Kortov at the Urals Polytechnical Institute [7]. The X-irradiations were performed with a W-tube (40 kV, 15 mA) and the $\beta$-irradiations with a Sr$^{90}$ source at a 1.5 Gy/min dose-rate. The far-UV irradiations were carried out with an 1 m normal-incident VUV monochromator and a H$_2$ arc lamp. For the UV-illuminations above 200 nm a 150 W high-pressure Xe-lamp and a 0.25 m grating monochromator were used. The incident photon flux was monitored with a pyroelectric radiometer. The irradiations were carried out at various temperatures between 80 and 300 K. The TL was recorded with a 6255 EMI photomultiplier. The heating rate above room temperature (RT) was 5°C/s. For the low-temperature TL and PTTL measurements the samples were kept in an LN vacuum cryostat and heated at a rate of 20°C/min. The TL spectra were simultaneously recorded with an EMI 9789 QA photomultiplier and a 0.5 m grating monochromator, equipped with an electronically controlled fast scanning device. The reciprocal linear dispersion of the monochromator was 3.3 nm/mm; the slit width was normally 0.5 mm. The same setup was used for measurements of the XL and the PL emission spectra. The optical absorption was measured with a Cary 17 spectrophotometer.

## 3. Results and discussion

During X-irradiation of the pure and the variously doped samples luminescence was emitted at RT as well as at LNT. After prolonged X- or $\beta$-irradiation TL emission could be recorded. The XL emission spectra of the nominally pure $\alpha$-$\text{Al}_2\text{O}_3$ crystals showed a main UV emission band centered at about 310 nm. In some of these nominally pure crystals, as well as in samples doped with various rare-earth ions, a narrow red band appeared at 698 nm that was accompanied by weaker side-bands. In the Cr$^{3+}$-doped crystals these red bands were by more than 2 orders of magnitude stronger than in the other samples. These bands are apparently due to the R line and the vibrational side-bands of Cr$^{3+}$ ions; the results indicate that Cr$^{3+}$ impurity ions are present even in nominally pure alumina crystals. In the various other rare-earth doped alumina crystals narrow bands, characteristic for these impurity ions, were dominant and some of these impurity bands were superimposed on a broad emission band centered at 325 nm. In the C-doped $\alpha$-$\text{Al}_2\text{O}_3$ crystals the Cr$^{3+}$ bands could not be recorded. In these C-doped samples the total luminescence and TL intensities were much stronger than in the nominally pure crystals. The $\alpha$-$\text{Al}_2\text{O}_3$:C crystals showed a high-temperature stability and the effects of X-irradiation at RT were
not annealed by heating up to about 1500 K. The PTTL could be re-excited in such samples by low-temperature UV-illumination of appropriate wavelengths. The very high luminescence sensitivity of the C-doped crystals is attributed to the relatively large concentrations of oxygen vacancies [7]. This enhanced vacancy concentration is due to the C content and to the growth of these crystals in a highly reducing atmosphere. This is in accordance with the finding that the XL spectra in these C-doped crystals are dominated by the F band at 410 nm; while in the pure samples a main emission was recorded near 310 nm. In Fig. 1 the XL and TL emission spectra of pure and C-doped samples are given for comparison. Curves a and b show the XL emission at LNT. TL emission spectra recorded at various glow peaks of these samples are given by curves c, d and e. The main 410 and 330 nm emission bands appeared in the 260, 280 and 450 K TL peaks as well as in the PTTL peaks of the C-doped crystals. The TL intensities of the nominally pure samples were much weaker than in the C-doped crystals and the emission maximum of the 280 K peak appeared in the pure crystals at a slightly shorter wavelengths (~310 nm). The 260 K TL peak revealed in the doped samples a complex emission band around 325 nm with two maxima at 330 and 310 nm; an additional weak band appeared near 500 nm. An emission at 500 nm has previously been attributed to the emission of an interstitial Al\textsuperscript{i} ion. This was supported by the measurements of the PL excitation spectra that had a maximum at the absorption peak of an interstitial Al\textsuperscript{i} center near 300 nm [6]. The present results showed that the 500 nm emission appeared in the same cases as the weaker 310 nm band indicating that both bands may be due to the same process.

A broad 3.8 eV (326 nm) emission band has previously been reported in Al\textsubscript{2}O\textsubscript{3} and different models have been suggested for this emission [5,6]. Some authors ascribed this 3.8 eV band to an F\textsuperscript{+}-center emission, and others to the emission of a self-trapped exciton or of an interstitial Al\textsuperscript{i} ion [5]. Our results have shown that this broad band is composed of two spectral components at 310 and 330 nm, which we attribute to two different processes, probably to the emission of interstitial Al\textsuperscript{i} ions and of F\textsuperscript{+} centers.

Effects of UV-irradiations were also investigated in this work. In the pure pristine alumina crystals TL could be excited only by VUV-radiation of wavelengths shorter than 145 nm. TL and PL could, however, be induced by near UV light in pure samples, which had previously been exposed to ionizing radiation and subsequently heated to about 500°C. The PL and TL are attributed in this case to processes of optical stimulation and of phototransfer. In C-doped samples TL could be excited by near UV light even without any previous exposure to ionizing radiation. The UV excited PL of these samples also showed main emission bands at 410 and 330 nm with excitation maxima near 200 and 260 nm.

The luminescence efficiency of the 410 and 330 nm emission increased after exposure of the samples to X or β-radiation. Prolonged UV-irradiation into the region of the F absorption band near 200 nm had a similar effect on the emission intensities of these bands. This increase may be due to the capture of excited electrons by existing anion vacancies and the formation of additional F and F\textsuperscript{+} centers, perhaps via an intermediate impurity level. In Fig. 2 a schematic diagram of the energy levels and the transitions is given. The possibility of such a “two step” transfer process is supported by our finding that simultaneous illuminations with 3.5 and 6 eV photons cause an additional increase of the luminescence intensity in these crystals of 9.5 eV band gap; while sole illumina-

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**Fig. 1.** Emission spectra of: (a) XL at LNT of nominally pure Al\textsubscript{2}O\textsubscript{3} (enlarged by a factor of 300); (b) XL at LNT of Al\textsubscript{2}O\textsubscript{3}:C; (c) TL at 260 K peak of Al\textsubscript{2}O\textsubscript{3}:C; (d) TL at 280 K peak of Al\textsubscript{2}O\textsubscript{3}:C crystal; (e) TL at 280 K peak of pure Al\textsubscript{2}O\textsubscript{3} (enlarged by a factor of 30).
nation with 3.5 eV photons had no effect on these emission bands. The 500 nm emission was not affected by these irradiations, but prolonged illumination into the interstitial Al band at 300 nm had a reverse effect.

Investigations of optical bleaching showed that prolonged exposure of the samples to UV light in the 250–400 nm region resulted in a notable decrease of the PTTL intensities. In Fig. 3 the intensities of the 450 K peak are given as a function of exposure time to monochromatic UV light of various wavelengths. After normalizing these results for the relative intensities of the incident monochromatic light beams, wavelengths of 260 and 300 nm were found to be most efficient for the optical bleaching of the PTTL. It should be noted that prolonged illumination into the Al\(^{i+}\) absorption band at 300 nm, which caused a decrease of the PTTL, was also effective for the desensitization of the 410 and 330 nm PL emission. This desensitization may be due to the transition of optically stimulated holes from the interstitial Al\(^{i+}\) ions to the F and F\(^{\ddagger}\) centers (see Fig. 2). This is supported by the finding that during heating the F\(^{\ddagger}\) and Al\(^{i+}\) absorption bands decreased simultaneously between 260 and 280 K and that this thermal decay was accompanied by a strong TL emission. This decay is attributed to an analogous process of thermal release of holes from Al\(^{i+}\) ions and their transition to F\(^{\ddagger}\) centers.

References