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Luminescence and the generation of F-centres by synchrotron radiation in NaF crystals

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Abstract. The excitation of luminescence and the generation of point defects by monochromatic synchrotron radiation at near liquid helium temperature (LHT) was investigated in NaF crystals. Emission bands at 298 and 523 nm are ascribed to the σ and π bands of the intrinsic STE emission. This is supported by the temperature dependence of these bands. The growth of the F-centre concentration during VUV irradiation was monitored by a highly sensitive laser-induced luminescence method. F-centre generation efficiency, as well as the excitation spectra (110–160 nm) of the main emission bands, showed a strong maximum at 123 nm. This excitation maximum coincides with the long-wavelength tail of the first exciton absorption band. A weaker excitation maximum was recorded in the α-band region. These findings agree well with the predictions of the previously proposed model.

1. Introduction

It is now generally accepted that the generation of F-centres by ionising radiation in alkali halide crystals involves a non-radiative recombination of a self-trapped exciton (STE). This recombination at low temperatures results in the formation of a Frenkel pair, consisting of an F and H centre (see for example [1, 2]). It is also widely believed that the intrinsic luminescence emitted during the low-temperature irradiation of these crystals originates from a relaxed excited state of the STE. There are, however, still different opinions regarding the correlation of these two radiation-induced processes. Another question open to debate is the spectral dependence of the production efficiency of the F-centre. Most of the previous investigations on defect formation were carried out by polychromatic radiations, mainly x- or γ-rays. In relatively few works monochromatic radiation has been applied, apparently due to the low intensity of the light sources in the far-UV region and to the difficulty in detecting small concentrations of defects by conventional absorption measurements. In a recent study, the production of point defects by monochromatic x-rays and near-UV radiation has been investigated at LNT [3]. The measurements of the dependence of the yield of the F-centre formation on the energy of the absorbed photon provided valuable information on the formation processes. In the present work the generation of point defects and the excitation of luminescence by monochromatic vacuum ultraviolet (VUV) radiation near liquid helium temperature (LHT) was studied.

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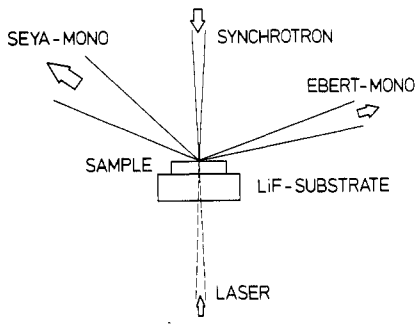

Figure 1. Experimental setup for simultaneous synchrotron and laser irradiations and for the measurement of luminescence emission and excitation spectra. Emission bands in the VUV are recorded by the Seya monochromator, and bands at longer wavelengths by the Ebert monochromator.

2. Experimental techniques

For our investigations, nominally pure (Harshaw) NaF crystals were cooled by a liquid helium (LH) flow cryostat and irradiated with synchrotron radiation from the storage ring BESSY in Berlin, which has been dispersed by a 3 m–normal incidence VUV monochromator [4]. The incident photon flux in the 110–160 nm spectral region was of the order of 10^{11} photons per second for a typical $\Delta\lambda$ of 0.3 nm. The VUV excited luminescence emission spectra were measured with an Ebert grating monochromator and a photon counting system [4]. A highly sensitive method was used for the detection of low concentrations of F-centres, generated by the weak monochromatic VUV radiation. This method involves the measurement of the laser-induced luminescence of the F-centres [3]. The F-centre emission of NaF is known to have a large Stokes-shift of about 2 eV, between the UV absorption at 338 nm and the red emission at about 750 nm [5]. For the excitation of the F-luminescence in the VUV-irradiated samples the 338 nm emission of an excimer-pumped dye laser was used [6]. The F-luminescence was detected by a red-sensitive RCA-C31034 photomultiplier. Stray light and second-order contributions were suppressed by appropriate filters. The growth of the F-centre concentration was also monitored during simultaneous synchrotron and laser irradiations of the specimens. In order to reduce the effects of optical bleaching of the F-centres by the intense laser light, the crystals were exposed to the laser light for short periods, following relatively long periods of sole synchrotron irradiations. A schematic diagram of the experimental setup for the simultaneous synchrotron and laser irradiation and for the luminescence measurements is shown in figure 1. The same setup was also used for the measurements of emission and excitation spectra of the VUV excited photoluminescence (PL).

3. Experimental results and discussion

The emission spectrum of the PL excited in NaF at 6 K by a synchrotron beam of 1254 Å is shown in figure 2. The emission bands at 298 and 523 nm appear to be identical with the 4.27 eV and 2.4 eV emission bands, previously observed in the luminescence, induced by x-rays in NaF crystals. These bands were ascribed to the σ and π bands of the intrinsic STE emission [7]. The conclusion is apparently supported by the observed steep decay of the luminescence intensity with increasing temperature (figure 3), which resembles the typical temperature quenching of a STE emission. The data for the 298 nm

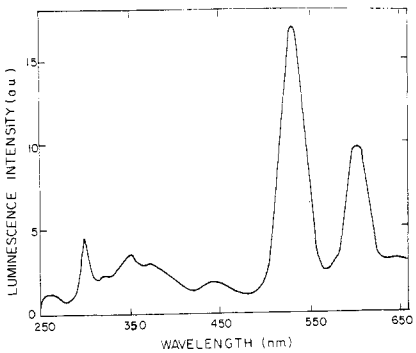

Figure 2. Emission spectrum of NaF, excited at 6 K by synchrotron radiation of 125.4 nm (not corrected for the efficiency of the detection system).

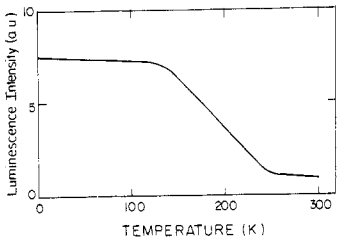

Figure 3. Temperature dependence of the 298 nm luminescence emission of NaF, excited by 125 nm synchrotron radiation. Data were recorded during the cooling of the crystal from 300 to 6 K.

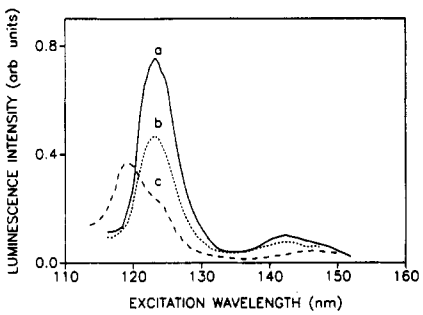

Figure 4. VUV excitation spectra of the (*a*) 298 nm, (*b*) 344 nm, and (*c*) 440 nm emission bands of NaF, recorded at 6 K and corrected for the spectral distribution of the incident photon flux.

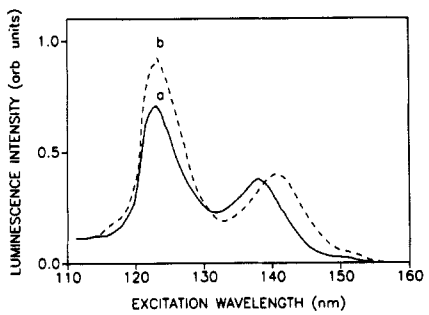

Figure 5. VUV excitation spectra of the (*a*) 525 nm, and (*b*) 595 nm emission bands of NaF, recorded at 6 K and corrected for the spectral distribution of the incident photon flux.

emission band in figure 3 were recorded during cooling of the crystal in order to avoid any overlapping effects from thermoluminescence which may appear during heating of the crystal.

The UV excitation spectra of the main emission bands were measured in the spectral region between 110 and 160 nm and are shown in figures 4 and 5. All emission bands show an excitation maximum at 123 nm. The 523 and 595 nm emission bands have an additional excitation maximum at about 140 nm, and the 440 nm emission band has an excitation maximum near 120 nm.

The production of F-centres by monochromatic VUV irradiation was also investigated in this work. It was found that the 123 nm radiation, which is most efficient for exciting PL in these crystals, was also efficient in the production of F-centres at low temperatures.

The growth of the concentration of F-centres, produced by the synchrotron irradiation at 125 nm, was monitored by illumination into the F-absorption region at 338 nm with the laser and measurement of the Stokes-shifted red F-centre luminescence emission. Irradiation at 125 nm has been used instead of 123 nm because of the somewhat

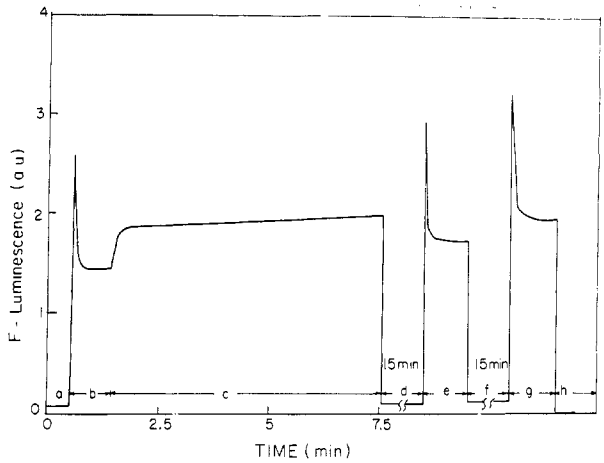

Figure 6. Growth of the laser induced F-centre luminescence emission in synchrotron irradiated NaF crystals at 6 K. Data were recorded in successive steps: (*a*) during sole synchrotron irradiation at 125 nm; (*b*) during sole 338 nm laser excitation (synchrotron off); (*c*) simultaneous synchrotron and laser irradiations; (*d*) 15 min sole synchrotron irradiation (laser off); (*e*) sole laser excitation (synchrotron off); (*f*) 15 min sole synchrotron irradiation (laser off); (*g*) sole laser excitation (synchrotron off); and (*h*) synchrotron and laser off.

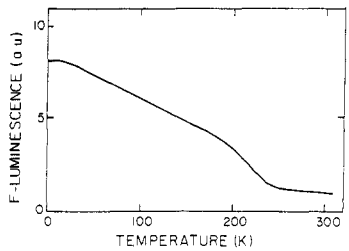

Figure 7. Temperature dependence of F-centre luminescence excited by 338 nm laser radiation in NaF crystals after 30 min of synchrotron irradiation at 6 K.

higher synchrotron light flux at this wavelength. By this sensitive luminescence method, F-centre concentrations as low as 10^{10} cm^{-3} can be detected [3]. In figure 6 the growth of the laser induced F-luminescence during various periods of 125 nm synchrotron irradiation is shown. The intensity of the F-luminescence was found to depend on the dose of the absorbed synchrotron radiation. Exposure of the VUV irradiated samples to the 338 nm laser light resulted at 6 K in the emission of an intense luminescence flash which decayed fast into an almost steady emission level; this level decreased slightly with prolonged exposure to the laser light, apparently due to optical bleaching of the F-centres by the intense laser light. Exposure of the crystals to simultaneous VUV and laser irradiations resulted in a slightly increasing luminescence signal due to the combined effects of generation and optical bleaching by these two radiations. This is demonstrated in the various parts of figure 6. The temperature dependence of the F-luminescence was also investigated. The intensity of the red F-luminescence band near 750 nm was found to increase markedly during cooling from room temperature to LHT (figure 7).

It is assumed that the generation of the F-centres by the monochromatic VUV radiation at 125 nm is due to the well known excitonic mechanism, which involves the production of a self-trapped exciton (i.e. an electron trapped in the vicinity of an F_2^- molecular ion)

by the absorbed VUV photon. Frenkel pairs are then formed at low temperatures as a result of a non-radiative recombination of the STE. The discovery that the 125 nm radiation was highly efficient for the formation of F-centres, as well as for the excitation of 298 and 523 nm intrinsic luminescence emission, is consistent with this assumption. Pure NaF crystals are transparent in the spectral region from about 12 microns to 135 nm. Below this wavelength the intrinsic absorption sharply increases and reaches a maximum at the first exciton peak at 117 nm [8]. The here measured main excitation maximum at 123 nm coincides with the long-wavelength tail of the first exciton band of NaF and the weaker excitation maximum, recorded at 140 nm, is in the region of the α absorption band. These findings agree also with the predictions of the theoretical model, previously proposed for UV excitation in the spectral region of high absorbance [9]. This model takes into account the radiation dose, as well as the absorption coefficient of the material and therefore the penetration depth of the incident UV radiation. In a region of very low absorbance, the incident radiation is obviously not effective. At the peaks of absorbance and reflectance, very few photons will penetrate into the bulk of the crystal and the processes will be restricted to an extremely thin surface layer. Such a surface layer may be strongly influenced by casual impurities and adsorbed surface contaminations, which may provide an alternative channel for de-excitation for electrons and holes. In this thin surface layer, saturation due to exhaustion of halogen traps at high F-centre densities may also occur. Therefore, in a region where the absorbance and reflectance vary from nearly zero to very high values (as at the long-wavelength tail of the first exciton band) the wavelength most effective for excitation will apparently be between these two extremes. The fact that the main maximum appeared on the long-wavelength tail at 123 nm and not at the exciton peak at 117 nm fits these assumptions. Our present results are also in good agreement with recent measurements of the production of F-centres by near-UV light in alkali bromides and iodides [3].

The present investigation clearly demonstrates that the use of synchrotron radiation can provide valuable information on the processes of defect formation in ionic crystals which cannot have been obtained by other means. Of particular importance is the information which can be obtained regarding the dependence of the efficiency of defect formation on the photon energy, by tuning this continuous radiation source over a broad spectral range from the UV to the x-ray region. Such experiments will provide relations between efficiencies of luminescence excitation and of defect formation.

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