Characterisation of oxygen defects in calciumdifluoride

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Abstract

We study the aggregation of oxygen dipoles well dispersed in a CaF_2 crystal upon annealing at temperatures ranging from 370 to 420 K. The concentration of oxygen dipoles is monitored by measuring the intensity of the ionic thermocurrent peak as well as by absorption and luminescence spectroscopies. Results from three methods agree within experimental error and yield an activation energy of (1.2 ± 0.1) eV for the diffusion of isolated oxygen centres in the crystal.
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1. Introduction

The doubly negative oxygen ion is well known to substitute fluorine in the fluorite lattice. To restore charge neutrality, this defect is accompanied by a fluorine vacancy. Oxygen ions are introduced into the crystal during growth and a homogeneous distribution of defects can be obtained by heating the crystal to temperatures above 870 K. An oxygen-vacancy centre has a dipole moment and can be investigated by dipole sensitive techniques like the thermodepolarisation current method (also known as ionic thermocurrent method) [1]. When heating a crystal containing oxygen-vacancy centres, at a certain temperature, the fluorine vacancy is activated to rotate around the oxygen ion. In a thermodepolarisation measurement, this results in a reorientation peak at 151 K [2]. A reorientation peak is not observed in CaF_2 crystals cooled down slowly from high temperatures, but appears if the crystal is quenched [2]. At temperatures above room temperature, oxygen centres become mobile where they can diffuse through the lattice by jumping from one to the next anion vacancy. At high enough defect concentration, diffusion is accompanied by aggregation involving the combination of oxygen dipoles into more stable defect clusters such as dimers, trimers or even larger complexes [3].

The aim of this paper is the comparison of three experimental techniques for monitoring oxygen defects with respect to their suitability for samples with different oxygen concentration. A quantitative analysis of the aggregation of oxygen dipoles into dimers in CaF_2 is performed in a comparative study of the thermocurrent method as well as optical absorption and luminescence spectroscopy methods.

2. Experimental methods

Crystals were grown by Stockbarger and Stöber methods in vacuum in a graphite crucible by P. Figura and V. Ivashechkin at the Institute of Geochemistry, Irkutsk. A few wt% of CdF_2 or PbF_2 were added to remove most of the oxygen from the melt that is present if no reducing substance is added. By adjusting the amount of CdF_2 or PbF_2, the oxygen concentration can be controlled at a level of 10^{-1} mol% or less. Samples have a size of typically 10×10 mm^2 and are cleaved along the [1 1 1] surface plane to obtain a sheet of 1 mm thickness. The oxygen concentration c in the sample is not known a priori or can be deduced from preparation. A formula for the estimation of c has been proposed by Arkhangelskaya [4]

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using the absorption coefficient a at the maximum of the 185 nm oxygen absorption band. Since this photon energy lies outside the range of operation of our absorption spectrometer, we evaluated the oxygen concentration in our samples using the formula given by Molchanov et al. [5] for absorption at 193 nm:

$$a(193\,nm)(cm^{-1}) = (0.002 \pm 0.004) + (0.0033 \pm 0.001)(c/ppm). \quad (1)$$

For absorption measurements on our samples, we used a standard spectrometer providing sample and reference beams in the spectral range of 190–1200 nm. A typical spectrum of a doped sample together with a reference spectrum of a nominally pure sample (VUV quality is the best commercially available quality) is presented in Fig. 1. The spectrum of the doped sample clearly exhibits absorption due to oxygen centres at wavelengths below 220 nm. Before all measurements of aggregation, samples were annealed at 870 K for 15 min to dissolve residual oxygen aggregates possibly left over from previous experiments and then quenched to room temperature within a few minutes.

Since the emphasis of this work lies on the investigation of aggregation by luminescence spectroscopy, here we comment on the principles of the thermal depolarisation and X-ray optical absorption methods only briefly and describe luminescence measurements in more detail. Thermal depolarisation measurements were performed using an electrometer with a current detection sensitivity of 10^{-16} A. During such measurements, the sample was kept in a vacuum chamber evacuated to 10^{-5}–10^{-6} Torr. For the polarisation of the sample, a voltage of 1–2 kV was applied for 2–3 min at 200 K. The rotation speed of the oxygen-vacancy dipoles at this temperature is high enough
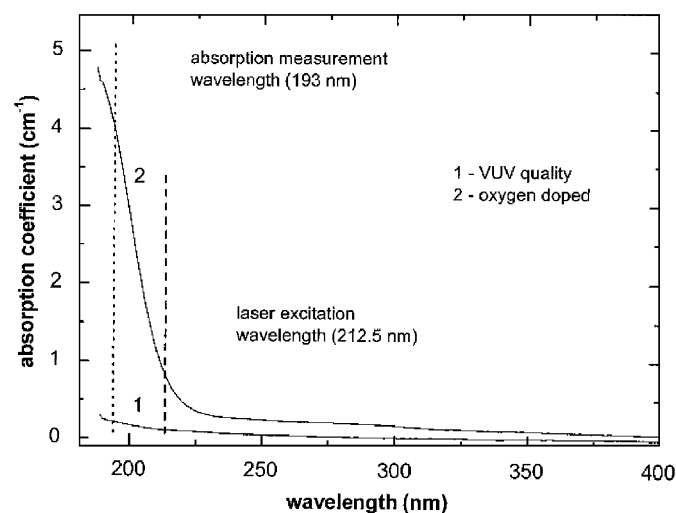
to align almost all dipoles along the electric field. After polarisation, the temperature of the sample was decreased to 80 K and then the high voltage was switched off. The depolarisation current was observed during heating the sample with a rate of $0.2\,K\,s^{-1}$. The height of the thermocurrent peak was measured in several equally performed measurements. Between the measurements, the sample was heated up to a constant temperature in the range of 370–420 K for a certain time. The obtained dependences of thermocurrent peak intensity on heating time at different temperatures can be used to extract the activation energy of the diffusion of oxygen dipoles from an Arrhenius plot [3].

With optical absorption spectroscopy, we monitored F_{2H}^{+} colour centres (double F-centres perturbed by neighboured oxygen) created in oxygen containing crystals by irradiation with X-rays [6]. The irradiation by X-rays was performed with a Pd tube operated at 40 kV and 50 mA for 15 min. The oxygen containing CaF_2 crystals turn slightly red upon X-ray irradiation. The colouration stems from two absorption bands at 2.25 and 3.35 eV belonging to F_{2H}^{+} colour centres perturbed by oxygen ions [6]. It was found that the height of the F_{2H}^{+} absorption peak at 3.35 eV decreases with annealing time at temperatures over 370 K similarly to the intensity of the ionic thermocurrent peak of oxygen dipoles [7]. Therefore, monitoring the 3.35 eV absorption band is an alternative method to study single-oxygen dipoles. The activation energy of oxygen diffusion is obtained like in the method of ionic thermocurrent using the height of the absorption peak.

Earlier investigations have shown that during annealing near 420 K, the oxygen absorption band at 6.5 eV decreases and a band of oxygen aggregates at 6.8 eV appears [8]. Therefore, the strength of oxygen luminescence excited by 5.9 eV photons (Fig. 4a) can be used as a measure for the single-dipole concentration. Oxygen aggregates either exhibit luminescence at higher energies or luminescence is quenched for larger aggregates.

Luminescence was measured with a spectrometer equipped with a liquid nitrogen cooled CCD detector while the sample was irradiated by ultrashort UV laser pulses. To accomplish this, the light from a Ti:sapphire oscillator (100 fs pulses at 80 MHz repetition rate) operated at 840 nm was twice frequency doubled by LBO and BBO crystals to obtain 5.9 eV photons for excitation. The exciting beam was directed perpendicularly onto the sample surface and focused into the volume. The average power of the ultraviolet beam was limited to 1 mW to avoid sample damage, saturation of the luminescence and multi-photon absorption of the exciting light. The luminescence light was collected by a lens under the angle of 45° and coupled into the spectrometer via a quartz optical fibre.

During the measurement, samples were heated up to a constant temperature in the range of 370–420 K for a certain time then cooled down rapidly and the luminescence was recorded at room temperature. This procedure

Fig. 1. Absorption spectra of oxygen-vacancy dipoles in CaF_2 of the VUV quality sample (1) and oxygen-doped sample (2). Both crystals were measured to estimate the oxygen concentration according to formula (1) given in [5] at 193 nm (dotted line). The oxygen-doped sample was used for aggregation studies with the luminescence method using laser excitation at 212.5 nm (dashed line).

was repeated several times with cumulative annealing time at a constant temperature. The entire cycle was repeated for several temperatures. The reason of measuring luminescence at room temperature and not continuously during annealing is the strong quenching of the luminescence with temperature. Without this measure, intensity changes of the luminescence due to temperature quenching would dominate over the slow intensity changes due to oxygen aggregation and strongly diminish experimental accuracy. However, the effectiveness of the aggregation process significantly increases for samples with high oxygen concentration. This effect puts a severe limitation for the measurement of samples with high oxygen concentration with the luminescence method. Since it is impossible to quench the sample instantly, a part of defects aggregate before the sample reaches room temperature. It leads to a large offset of initial luminescence intensity and following luminescence intensities measured in the experiment. On the other hand, the luminescence method is far more sensitive than the other methods, for both, mobile and trapped oxygen-vacancy defects contribute to the luminescence signal. Due to this fact, even a large concentration difference between samples investigated by the luminescence and other methods leads only to a small parallel shift of the curve in the corresponding Arrhenius plots. The high sensitivity of the luminescence method opens the possibility to analyse samples with 1 to 2 orders of magnitude less oxygen concentration than in our studies, for example crystals of high purity, designed for the use in deep vacuum ultraviolet laser lithography. The technical simplicity of the luminescence method is a further advantage in comparison to thermodepolarisation and X-ray-induced optical absorption methods.

3. Aggregation model

To model the process of aggregation of oxygen centres in CaF_2, we apply a kinetic formalism previously developed for the description of Me^{2+}—cation vacancy (Me^{2+}—Sr, Pb, Mn, Mg) dipoles aggregation which has been thoroughly studied in alkali halides [9,10] and for RE^{3+}—interstitial fluorides (RE—rare earth elements) dipoles investigated in the fluorite lattice [11–13]. Here, we consider the aggregation process as a result of diffusion through the crystal lattice in contrast to a dipole rotation. The diffusion of dipoles differs from a rotation significantly in terms of the respective activation energy and takes place at much higher temperatures than the rotation. We can also neglect thermally induced dissociation of aggregates which starts at about 600 K, i.e. at much higher temperature than the range of 370–420 K that we cover for diffusion studies [14].

Starting annealing at $t = 0$ and assuming a dipole concentration of $n = n_0$, we assume a rate equation for the aggregation process of the form [9]

$$(n_0/n)^{\alpha-1} = (\alpha - 1)n_0^{\alpha-1}Kt \exp(-E/kT) + 1. \tag{2}$$

Here α is a coefficient describing the order of the kinetics, E is the activation energy for the process, T the sample temperature, t the elapsed time for diffusion and K the reaction rate constant. Here we observe the aggregation in terms of the formation of simplest aggregates, i.e. dimers consisting of two dipoles for which the second-order kinetics ($\alpha = 2$) would satisfy Eq. (2). For second-order kinetics and plotting $(n_0/n) - 1$ versus time one obtains a straight line with different slopes at particular constant temperatures following the Arrhenius equation

$$(n_0/n) - 1 = n_0 Kt \exp(-E/kT) \tag{3}$$

Former experimental results for alkali halides show that the equation fits well for short annealing times [15]. At longer annealing times, there is a deviation of the decay curve from the straight line. In general cases, K is a time-dependent function of molecular parameters of the system [16]. For bimolecular reactions, effects like pair correlation and distribution of the reactants may play a significant role. However, the use of the simple kinetic model is justified under the assumption that the aggregation follows simple $A + B \rightarrow AB$ type reaction and second-order kinetics at short annealing times. We assume, furthermore, that the formation of larger aggregates which grow by addition of new dipoles to smaller aggregates does not affect the order of the kinetics for short annealing times.

The plot of the logarithmic slope values of the decay lines versus the inverse temperature yields the Arrhenius plot with a slope equal to $-E/k$ and allows us to extract the activation energy E for the dipole diffusion from experimental data.

4. Results

4.1. Absorption measurement

Fig. 1 shows absorption spectra of a VUV quality CaF_2 crystal and the oxygen-doped sample from luminescence studies in the spectral range of 190–400 nm. The excitation wavelength of the laser used for luminescence studies is marked by a dashed line and lies in the lower energy part of the first absorption band of the oxygen-vacancy dipole. The edge of the absorption band is in good agreement with literature data [4]. The absorption coefficient at the wavelength of 193 nm was $0.193\ cm^{-1}$ for the VUV quality sample and $3.43\ cm^{-1}$ for oxygen-doped sample. This converts to oxygen concentrations of 52 ± 20 and 952 ± 340 ppm, respectively. The value for the pure crystal is in the concentration range of the samples used in Ref. [5].

4.2. Ionic thermocurrent

We observe the reorientation peak of oxygen dipoles at 150 K in oxygen containing crystals quenched from 870 K. Undoubtedly the peak we measure is the same as the oxygen dipole peak at 151 K found earlier [2]. During annealing at 350 to 450 K, the intensity of the peak continuously decreases with cumulative annealing time.

The higher the annealing temperature, the faster is the decay of the peak. The decrease of the oxygen dipole peak due to annealing directly reflects the decrease of the single-oxygen dipole concentration due to their aggregation.

For an analysis of the oxygen dipole aggregation, decay curves were plotted in appropriate coordinates according to Eq. (3); respective results are shown in Fig. 2a.

The straight line of dependence in Fig. 2a points out that dimers are the first aggregates of the dipoles. Using the slopes of the lines presented in Fig. 2a we may plot their values on a logarithmic scale versus the reciprocal temperature and obtain the Arrhenius plot presented in Fig. 3. The activation energy for the dimerisation process is calculated from the slope and found to be 1.31 ± 0.12 eV.

Similar to ionic thermocurrent, Fig. 2b shows straight lines obtained by the luminescence method which we explain in detail in Section 4.4.

Fig. 3. Arrhenius plots of the decrease rates for thermocurrent peak intensity (1) optical density data of the F_{2H}^+ absorption peak of X-irradiated samples (2) and luminescence (3). The parallel shift between plots results from different initial oxygen concentrations of the samples used in different methods. The concentration of oxygen was 0.092 mol% for sample (1), 0.054 mol% for sample (2) and 0.005 mol% for sample (3). The activation energies calculated are 1.31 ± 0.12 eV (1) 1.21 ± 0.15 eV (2) and 1.12 ± 0.1 eV (3).

4.3. Optical absorption

The CaF_2 crystal without oxygen doping remains colourless after X-irradiation at room temperature or at 80 K. As a result of X-irradiation of oxygen-doped CaF_2, the F_{2H}^+-color centres with absorption bands at 2.25 and 3.35 eV are created. The colouration of oxygen containing CaF_2 crystals by X-rays depends on the thermal history of the crystal. The annealed and quenched to room temperature sample have the highest colouration ability. If the sample is heated afterwards at temperatures above 370 K, the height of X-ray created absorption peaks decreases with time. It was found that the optical density of the created peaks decreases with the cumulative annealing time similar to the intensity of the oxygen dipoles ionic thermocurrent peak at 150 K [7]. Therefore, we use the height of the 3.35 eV absorption band as a value which is proportional to the oxygen dipole concentration. Based on this procedure, we measure the aggregation of oxygen dipoles via absorption created by X-irradiation. The activation energy derived from optical absorption measurements is 1.21 ± 0.15 eV and coincides well with the one obtained from ionic thermocurrent measurements (see Fig. 3).

4.4. Luminescence

Assuming that the luminescence intensity is proportional to the oxygen concentration, according to Eq. (3), during annealing the luminescence should decrease to zero. However, after some time, the intensity of oxygen luminescence reaches a saturation level as shown in
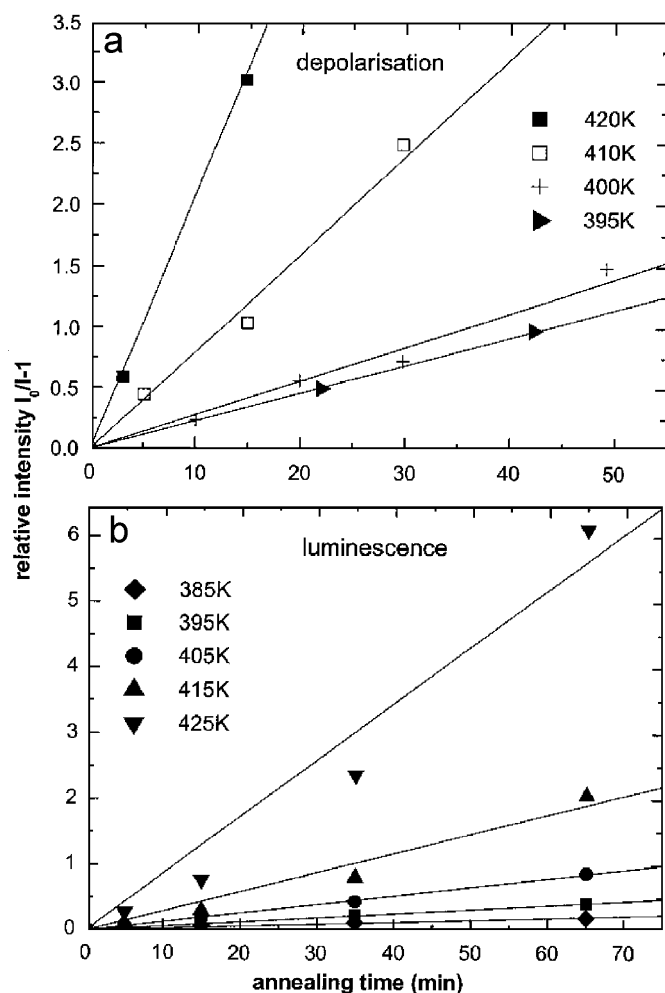

Fig. 2. (a) Decrease of the relative intensity of the ionic thermocurrent peak at 150 K as a result of annealing at different aggregation temperatures plotted in appropriate coordinates according to Eq. (3) for the sample with 0.092 mol% of oxygen. (b) Decrease of the relative intensity of luminescence at room temperature as a function of annealing time at different aggregation temperatures shown in appropriated coordinates according to Eq. (3) for the sample with 0.005 mol% of oxygen.
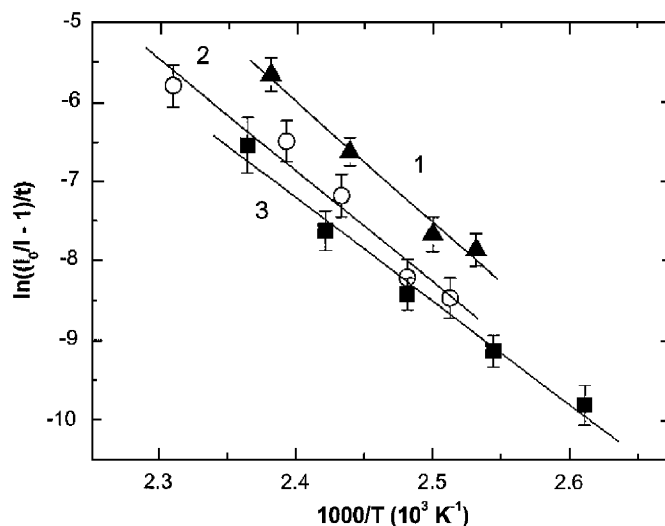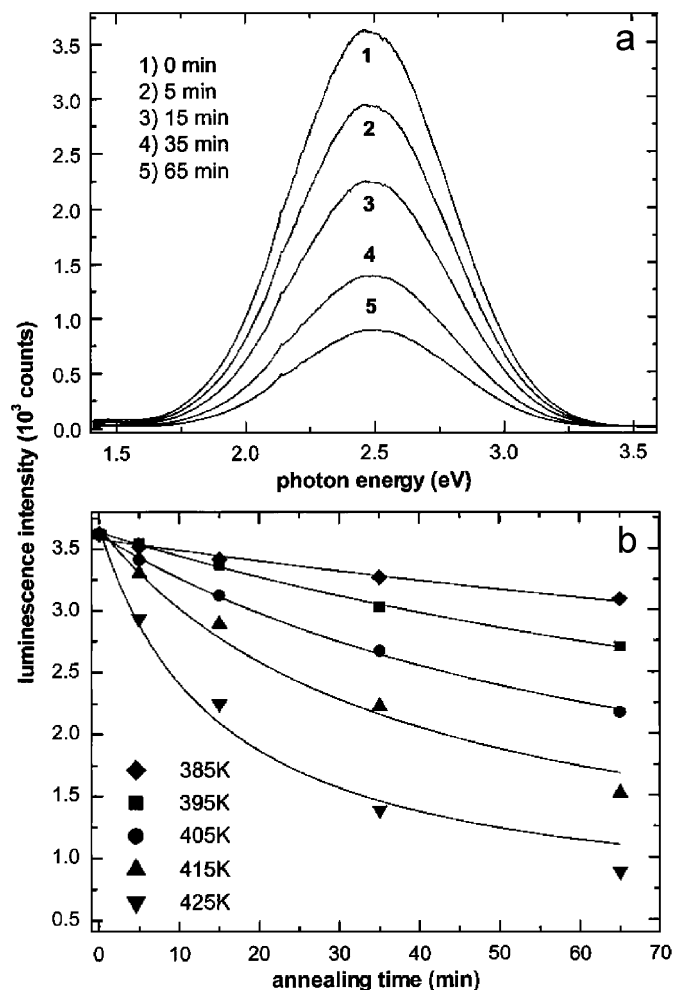
Fig. 4. (a) Luminescence spectra of oxygen-vacancy dipoles in CaF$_2$ at different annealing times taken during the aggregation process. (b) Decrease of the luminescence intensity for the sample with 0.092 mol% oxygen as a result of annealing at different aggregation temperatures.

annealing time while the coefficient B is obtained by transforming Eq. (3). For determining the activation energy, we use calculated slopes from fits to the data in Fig. 2b. The Arrhenius plot for the luminescence measurement is included in Fig. 3. We obtain an activation energy of 1.12 ± 0.10 eV that is the same within experimental error as obtained from the other methods.

5. Discussion

Oxygen-vacancy dipoles and dimers in CaF$_2$ crystals have been studied ab initio recently [14]. The calculated dipole reorientation barrier is 0.64 eV and the activation energy for diffusion of the dipoles is 1.61 eV [14]. We have measured the activation energy by three different methods and the activation energies determined from samples of different oxygen concentration are identical within experimental error where the mean value is 1.21 ± 0.15 eV. The ab initio calculated energy value is in fair agreement but not identical with the experimentally observed energy of aggregation of oxygen dipoles.

The oxygen concentrations for the samples used in thermodepolarisation and absorption methods differ remarkably from the one used in luminescence method. In our comparative study, we find that the luminescence method does not work for samples with high oxygen concentration, whereas the thermodepolarisation and optical absorption methods do. The reason for this may be slightly different quenching conditions at room temperature since the quenching was performed separately for each particular sample. Another reason may be that in crystals with high oxygen concentrations the dipoles are in a pre-captured state [16] due to the short distance between them. This may affect luminescence properties but possess no limitations for the reorientation of dipoles in the thermal depolarisation method. However, the luminescence method turned out to be much more sensitive than the other methods suggesting that it is best suited to investigate the aggregation process in highest purity crystals used in laser lithography optics.

There are several factors which can influence the accuracy of aggregation measurements that should be considered. It is known that oxygen-vacancy dipoles in CaF$_2$ dissociate either under X-ray irradiation at low temperatures or under irradiation with UV-photons in the 8.4 eV absorption band [8]. The excitation leads to the dissociation of oxygen-vacancy dipoles and subsequent formation of F_{2H}^+ centres, with specific absorption bands at 2.25 and 3.35 eV. The 5.9 eV photons we use for excitation do not have enough energy to initiate such dissociation directly. However, the oxygen luminescence is known to have slow components reaching up to the millisecond range [17] due to a forbidden transition of the luminescence from the excited triplet state to the singlet ground state. This means that there is still a significant number of electrons in the excited state left at the time when the next laser pulse reaches the sample (12.5 ns). Due to this fact, higher

Fig. 4b. The saturation intensity is specific for a particular sample and may reach up to 0.5 of the initial oxygen luminescence intensity. The reason for this behaviour is that some of the oxygen dipoles are trapped by impurities and do not take part in further aggregation as it has been suggested earlier [8]. If we assume for simplicity that the quantum yield of luminescence of free and trapped oxygen dipoles is the same, we may simply subtract the saturation luminescence intensity from the total one and analyse the remaining part of intensity in terms of the aggregation process. On the other hand, the luminescence analysis allows a study of the trapped centres and reveals that indeed a large number of defects are trapped.

Fig. 4b shows experimentally obtained luminescence decay and fit curves according to Eq. (3). An additional term representing trapped oxygen dipoles was subtracted from luminescence data and like in case of the thermodepolarisation method, plots were fitted by a linear function of the type $A+Bt$ (Fig. 2b) where, t is the

excitation from the first excited state can occur which can cause the oxygen dipole to dissociate with following creation of F_{2H}^+-centres. Therefore, irradiation with high repetition rate ultraviolet laser pulses would dissociate oxygen-vacancy dipoles and decrease the number of luminescence centres and the luminescence intensity. Since the luminescence signal is used as a measure for the dipole concentration in the sample, one has to take into account that dissociated dipoles do not contribute to the luminescence signal. Further consideration regards annealing where two processes take place simultaneously, aggregation of oxygen dipoles into dimers and larger complexes and dissociation of the part of F_{2H}^+-centres, the mechanism of which is yet not known and recombination of dissociated parts with singly charged oxygen ions in the lattice and the formation of initial oxygen-vacancy defects. From our experience, the dissociation of oxygen-vacancy dipoles leads to a decrease of the activation energy. In our experiments, precautions have been made to take this into account and to eliminate the influence of dissociation and recombination processes on measuring the activation energy. A detailed investigation of dissociation and recombination processes will be presented in a forthcoming publication.

The activation energies for aggregation of single oxygen dipoles to dimers were found to be 0.85 eV in KCl and 0.79 eV in RbBr [3,18]. These energies are about 1.4 times higher than reorientation energies of oxygen dipoles. For CaF_2 the reorientation energy was found to be 0.46 eV while we measured the aggregation energy of 1.21 eV. The aggregation energy is about 2.7 times higher than the reorientation energy. The difference is obviously related to the different crystal lattices. The fluorite lattice is considerably more rigid than lattices of alkali halides causing a higher diffusion barrier.

Acknowledgements

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