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Time-resolved luminescence of oxygen-vacancy centres in alkaline-earth fluoride and barium fluorohalide crystals

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Abstract. Two decay components of luminescence of oxygen-vacancy centres were observed in alkaline-earth fluoride and barium fluorohalide crystals at 17–300 K. We denoted them as slow and very slow components.

Very slow components are observed in all crystals except for type II oxygen centres in BaFBr. Above 100–150 K the integrated intensity of very slow components decreases in parallel with the decay time with thermal energy 0.1–0.2 eV.

The integrated intensity of the slow component is not decreased from 17 to 300 K, while the decay time decreases from several hundred microseconds to several microseconds. This behaviour is explained by thermal interaction between three closed excited levels with different radiative lifetimes. We tentatively assume that these three levels belong to different oxygen-vacancy centre configurations in the lowest excited state.

1. Introduction

Oxygen-vacancy centres in alkali and alkaline-earth fluoride crystals exhibit an effective luminescence, the intensity of which does not decrease much from liquid-helium temperature to room temperature. Two components of the decay of luminescence were measured in LiF and NaF crystals. These components were ascribed to singlet–singlet and triplet–singlet transitions [2].

The main features of the physical properties of chalcogen-vacancy centres can be explained by the molecular-like model of the centres. The optical transitions in oxygen-vacancy centres were assigned to electron transfer from the oxygen to the anion vacancy and vice versa [3]. We assume that the chemical bond of chalcogen-vacancy centres is similar to the bond of the HF molecule and the states of centres were labelled according to the $C_{\infty v}$ symmetry of HF molecule notation [1]. The validity of this assumption can be verified by studies of excited-state spectroscopy.

In this paper we studied the time-resolved luminescence of oxygen-vacancy centres in alkaline-earth fluoride and barium fluorohalide crystals. At least four triplet excited states are involved in the luminescence from 17 K to room temperature. Experimental results are consistent with the molecular-like model of the centres. Some previous results were published in [7].

2. Experimental details

The light source used for spectroscopy included a home-made flash lamp with W–Th

electrodes. The duration of flash was 0.01–2 μs depending on the value of the capacity (100–10 000 pF). The light from the lamp was passed through the grating monochromator, and the luminescence of the samples was recorded through appropriate filters or a monochromator.

The decay of emission up to 3 μs was measured by the single-photon technique using the CAMAC time-to-digital converter with channel width 0.4 ns. Longer decay of emission was measured using an analogue-to-digital converter. Usually a decay curve was accumulated with 10^6 pulses by the single-photon technique and with 10^3 pulses by the analogue technique.

The crystal preparation has been described elsewhere [5, 6]. Just before the measurement the sample was annealed at 700 °C for 10 min in a closed stainless steel boat and quenched in air.

The luminescence was excited into the lowest-energy absorption bands of oxygen-vacancy centres. Both types of oxygen-vacancy centre with their own optical bands [6] were studied in barium fluorohalides. Type I and type II oxygen-vacancy centres in BaFCl and BaFBr were assumed to occupy the F–X and X–X pair sites, respectively (X \equiv Cl or Br) [6]. The first absorption bands and emission bands of oxygen-vacancy centres in the crystals studied are listed in table 1. The decay time was independent of the photon energy of the excited (or emission) light within the absorption (or emission) band.

Table 1. The low-energy absorption and emission bands of oxygen-vacancy centres in the crystals studied at 80 K [5, 6]. The absorption bands for alkaline-earth fluoride crystals were measured at room temperature.

Crystal	E_{abs} (eV)	E_{emis} (eV)
CaF ₂	6.45	2.60
SrF ₂	5.65	2.65
BaF ₂	5.2	2.38
BaFCl type I	5.0	2.5
BaFCl type II	4.2	2.05
BaFBr type I	4.9	2.30
BaFBr type II	4.5	2.45

3. Results

In the emission data for all crystals no fast-decay components with $\tau < 10^{-6}$ s are distinguished. Inspection of the decay at a longer time shows that at least two components are involved (figure 1). We denoted the observed two components of decay as slow and very slow components.

Very slow components are observed in all crystals except type II oxygen centres in BaFBr. In BaF₂, SrF₂ and BaFBr (type I centres) the emission and excitation spectra of the very slow component are slightly shifted with respect to those of the slow component. These shifts are about 0.1–0.2 eV depending on the crystal. The thermal quenching of very slow components is not related to the increase in the slow component. Therefore at least in these three crystals the slow and very slow components originate from different well separated states.

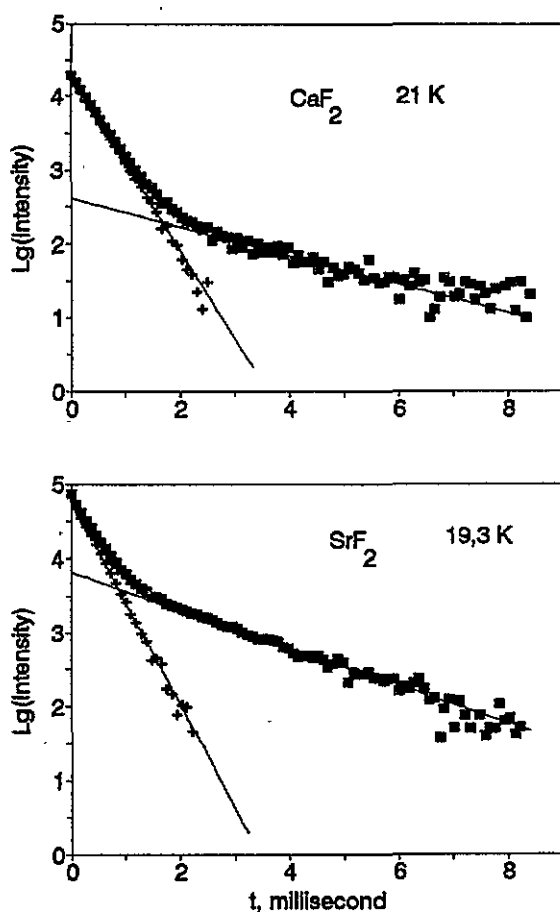


Figure 1. Decay of luminescence of oxygen-vacancy centres in CaF_2 and SrF_2 crystals. The curves are resolved into two exponential components (—) which are denoted as slow and very slow components. The points for the slow component (+) are calculated by subtraction of the very slow component intensity from those of the experimental decay curve.

3.1. Alkaline-earth fluorides

The temperature dependences of the slow and very slow components are different. The decay time of the very slow component takes a constant value below 150 K for CaF_2 and BaF_2 (figure 2). The very slow component appears in SrF_2 emission below 80 K. With increasing temperature the decay time decreases. The integrated intensity of very slow components (product of initial intensity with decay time) shows a similar behaviour (see figure 2). These facts are explained by introducing a thermally activated radiationless decay process, which competes with the radiative transition. In this case, the temperature dependence of the decay time $\tau(T)$ and integrated intensity $I(T)$ are described by the following equation:

$$I(T) \sim \tau(T) = [1/\tau_R + 1/\tau_{NR} \exp(-E/kT)]^{-1} \quad (1)$$

where τ_R and τ_{NR} are the radiative and radiationless decay times, E is the activation energy and k is the Boltzmann constant.

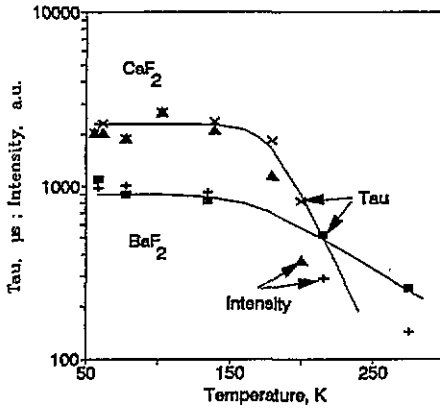


Figure 2. Temperature behaviour of the decay time of the very slow component as well as the light sum (product of initial intensity with decay time) in CaF_2 and BaF_2 crystals (a.u., arbitrary units): —, calculated using equation (1) (see text).

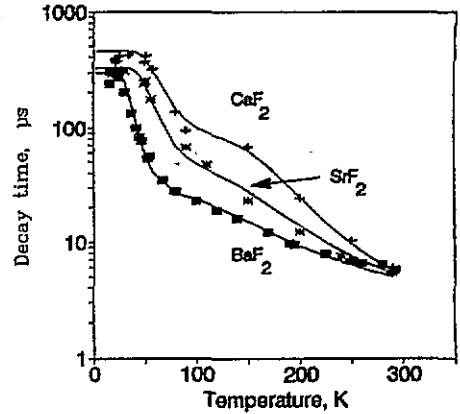


Figure 3. Temperature behaviour of the decay time and integrated intensity of the slow component in alkaline-earth fluoride crystals: —, calculated using equations (2) and (3) (see text).

The solid curves in figure 2 are fitted to the observed points in equation (1). The values obtained for the parameters are $\tau_R = 0.9$ ms for BaF_2 and 2.3 ms for CaF_2 , and $E = 0.1$ eV for BaF_2 and 0.21 eV for CaF_2 . The ratio of the integrated intensity of the slow component to that of the very slow component below 100 K is unity for BaF_2 and two for CaF_2 .

The temperature dependence of the slow component is unusual (figure 3). The decay time takes a constant value below 20–50 K for all three crystals. With increasing temperature the decay time decreases. The striking feature of this process is that the intensity of the slow component has a constant value at all temperatures from 17 to 300 K or slightly increases above 250 K. The intensity of luminescence excited by continuous light decreases about two to three times with increasing temperature from 80 to 300 K. Obviously this decrease is associated with a decline in the very slow component. The temperature dependence of the decay time of the slow component indicates that there are at least three emitting states. The thermal transitions of electrons from the lowest state to the others cause the change in the decay time.

3.2. Barium fluorohalides

The experimental results for BaFBr and BaFCl are mainly compared with those in alkaline-earth fluoride crystals (figure 4). The integrated intensity of the slow component also has a constant value up to room temperature.

4. Discussion

4.1. Model

Two different transitions are expected within the first absorption band of the oxygen-vacancy centres; the transitions started from non-bonding π molecular orbitals (mainly originating from $2p_x$ and $2p_y$ atomic oxygen orbitals) and from σ molecular orbitals, which originated from the $2p_z$ atomic oxygen orbital with some addition of the $1s$ atomic orbital of anion

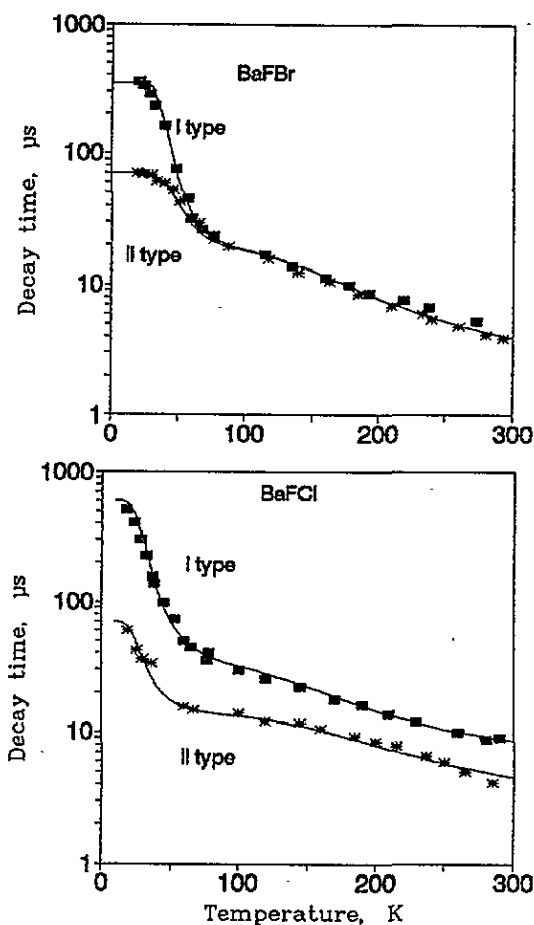


Figure 4. Temperature behaviour of the decay time and integrated intensity of the slow components of type I and type II oxygen-vacancy centres in BaFBr and BaFCl crystals: —, calculated using equations (2) and (3) (see text).

vacancies [1]. Therefore, the first absorption band of oxygen-vacancy centres will consist of two close transitions.

Experimental results show that there are at least two different low-lying excited singlet levels on which the electron transitions are allowed. Then electrons relax into respective triplet states. The radiative transitions from these states have different decay times as well as photon energies. These results and their correlation with the molecular model will be described in the next paper.

The temperature behaviour of the very slow component reflects the radiationless transitions to the ground state through the potential barrier. The behaviour of the slow component is more complicated (see figures 3 and 4).

4.2. The temperature behaviour of the slow component

The intensities of slow components do not vary or slightly increase above 250 K. Therefore, there are no radiationless transitions to the ground state up to 300 K.

The slow decay of oxygen-vacancy centres in alkaline-earth fluoride crystals, BaFBr and BaFCl is exponential (at least for two to three decades of intensity) at all temperatures 17–300 K. The exponential decay of the luminescence of molecules when many excited states are involved was explained by assumption that the radiationless transition probabilities sufficiently exceed the radiative transition probabilities [4]. In thermal equilibrium between states the decay time can be written as follows [4]:

$$\frac{1}{\tau} = \sum_i \left(\frac{C_i}{\tau_i} \right) \quad (2)$$

where C_i is the distribution function between excited states ($\sum_i C_i = 1$) and τ_i is the radiative decay time from the i th state to the ground state. For the Boltzmann distribution between excited states we can write

$$C_i = \left[A_i \exp\left(\frac{-E_i}{kT}\right) \right] / \left[\sum_i A_i \exp\left(\frac{-E_i}{kT}\right) \right] \quad (3)$$

where A_i is the relative probability of radiationless transition to the i th level and E_i is the energy of the i th level. The calculated curves are best fitted with experimental data with the parameters in tables 2 and 3. It should be noted that the precision in the calculation of τ_2 is poor, because of the absence of data above 300 K. Therefore we note only the existence of the third excited levels and do not discuss the dependence of τ_2 from the host cations. There is some regular dependence of τ_0 and τ_1 on the host cations. τ_0 and τ_1 decrease from Ca to Ba (see table 2).

Table 2. The best-fit parameters for the decay of oxygen-vacancy centres in alkaline-earth fluoride crystals.

Crystal	A_0	τ_0 (μ s)	A_1	τ_1 (μ s)	E_1 (meV)	A_2	τ_2 (μ s)	E_2 (meV)
CaF ₂	1	450	100	70	35	1500	≈ 1.0	140
SrF ₂	1	330	100	35	33	800	≈ 1.0	110
BaF ₂	1	300	100	22	23	180	≈ 1.0	80

Table 3. The best-fit parameters for the decay of type I and type II oxygen-vacancy centres in barium fluorohalide crystals.

Crystal	A_0	τ_0 (μ s)	A_1	τ_1 (μ s)	E_1 (meV)	A_2	τ_2 (μ s)	E_2 (meV)
BaFBr, type I	1	350	200	17	28	600	1.0	90
BaFBr, type II	1	70	200	17	28	600	1.0	90
BaFCl, type I	1	600	20	25	16	200	4.5	80
BaFCl, type II	1	70	35	12	13	200	1.8	80

At 17 K the decay times of the oxygen-vacancy centres in the crystals studied are about 10^{-3} – 10^{-4} s. The photoluminescence at 2.7 eV that can be excited at 4.6 eV in oxide containing BaFBr is due to triplet emission from the oxide centre [8]. Therefore, these radiative transitions belong to forbidden triplet–singlet transitions. The decay times of

such transitions in light molecules are approximately seconds [11]. The shortening of these transitions in crystals is usually associated with spin-orbital coupling. This interaction mixes the triplet state with the appropriate singlet state and the transition to the singlet ground state becomes more allowable.

At this stage there are two obvious explanations for the existence of three radiative levels; they could originate in three triplet sublevels of one particular morphology or, alternatively, they could originate in three different excited-state morphologies of oxygen-vacancy centres.

4.2.1. Spin-orbital interaction. The spin-orbital interaction is very sensitive to the charge (atomic number) of the nearest nucleus involved. The lifetimes of triplet-singlet transitions of molecules are gradually shortened by the neighbouring heavy atom or ion (the heavy-atom effect) [11]. In the central-field approximation this interaction shortens the lifetimes as the squares of spin-orbital coupling constants [11]. Comparing the decay times with spin-orbital constants for host cations (table 4), one notes that the decay time does not follow the spin-orbital constant. In excited states, the electron of the oxygen-vacancy centre occupies the anion vacancy level. The variation in τ is also much less than that of F-centre spin-orbital constants in the 2p state (table 4).

Table 4. Relative values of the decay time of oxygen-vacancy centres and the inverse of squared spin-orbital constants of metallic ions and F centres (in the 2p state) in alkaline-earth fluoride crystals.

Crystal	τ_0	τ_1	A_M^{-2}	A_F^{-2}
CaF ₂	1.5	3.18	50	13.0
SrF ₂	1.1	1.59	4	1.86
BaF ₂	1	1	1	1

Other striking features are the increases in E_1 and E_2 in the row from BaF₂ to CaF₂ (see table 2). From components of the triplet state that are split by spin-orbital coupling, one expects a reverse dependence of splitting. The spin-orbital splitting has to be smallest for CaF₂ and largest for BaF₂. The value of splitting is also too high for spin-orbit coupling. For example the zero-field splitting of triplet sublevels of excitons in alkali iodides is less than 1 meV [9].

For these reasons we do not believe that these three levels belong to triplet sublevels, which are split by spin-orbital coupling. Possibly the spin-orbital splitting effects will be resolved at temperatures lower than 17 K.

4.2.2. Vibronic distortion of the excited state. Earlier three different IR emission bands for Se²⁻-vacancy and Te²⁻-vacancy centres were explained as follows [12]. The double-negative chalcogen ion Ch²⁻ after absorbing a photon becomes ionized into a single-negative ion Ch⁻ and quasi-free electron. The Ch⁻ forms a weak homopolar bond with one of six neighbouring alkali ions. Because of the nearby anionic vacancy this leads to three different potential energy curves in the excited state depending on the relative positions of the vacancy and homopolar bond [12].

This model is also suitable for our case. At low temperatures the system falls into the lowest minimum. At higher temperatures the system can move into higher minima and emission with a different lifetime occurs. In the row from BaF₂ to CaF₂, one expects an

increase in energy difference between excited states (see table 2) because the lattice becomes closer.

However, the off-centre position of the O_{Br}^- defect was not found in alkaline-earth fluorides [15] nor in BaFBr [14] and BaFCl [13]. The ESR spectrum of the O^- ion in alkaline-earth fluoride crystals is tetrahedrally distorted by the Jahn-Teller interaction [15]. Nevertheless the calculations indicate that the O_{Br}^- ion moves off the bromide site along the c axis towards the nearest Ba^{2+} ion plane in the BaFBr crystal [16]. The oxygen ion in the O^- -vacancy centre in CaF_2 can easily jump to a nearby anion vacancy with an energy of about 0.01 eV [17]. This defect is created when the V_k centre is captured by the O^{2-} -vacancy centre [18]. The activation energy for the orientation of the S^{2-} -vacancy dipoles in KI in the lowest excited state is small in comparison with that in the ground state [19]. These facts indicate that the energy surface of the oxygen ion in the excited state is rather soft and ions can easily move to off-centre positions.

The exciton in alkali halide crystals has different configurations of excited states. In KI and RbI crystals the energy differences between on-centre and off-centre exciton configurations are equal to 81 meV and 36 meV, respectively. Thermal transformation of on-centre excitons into off-centre excitons was observed above 120 K [20]. The energy differences in our case are in the same range (see tables 2 and 3). Therefore several minima of the adiabatic potential surface of the lowest excited state of oxygen-vacancy centres are not impossible.

The problem has similarities with the Ag^+ centre in alkali-halide crystals. The adiabatic potentials of the ground states are distorted owing to electron-phonon coupling. At low temperatures the ions are displaced in the $\langle 111 \rangle$ or $\langle 100 \rangle$ directions. This leads to splitting of the $d-s$ ion absorption bands. At temperatures above 70 K the ions move into the on-centre position and absorption bands become unsplit [21]. Obviously in our case we observed similar interactions but in the excited states.

τ_0 for the oxygen-vacancy centre in barium fluorohalides is several times less for type II centres than for type I centres (see table 3). The possible explanation for this is the following. In the lowest excited state the electron occupies the orbital, which mainly consists of a 1s F-centre orbital with a small addition of the $2p_z$ oxygen orbital [1]. Shortening of the decay time is obviously related to the spin-orbital interaction with heavier surrounding ions. The type II (X-X) centre is surrounded by heavier ions (Ba and Cl or Br) than is the type I (F-X) centre. Therefore, the type II centre must have an emission lifetime shorter than that of type I owing to spin-orbital coupling with surrounding ions.

5. Conclusions

Slow and very slow components of decay time are observed in the luminescence of oxygen-vacancy centres in alkaline-earth fluoride and barium fluorohalide crystals. The temperature dependence of the integral intensity and the decay time of very slow components indicates that, in this state, electrons transfer through the potential barrier to the ground state.

The temperature dependence of the slow component is described by three closed excited levels with thermal equilibrium between them. We tentatively assume that these three levels belong to different centre configurations in the lowest excited state.

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