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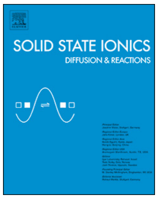

Luminescence of defect clusters in the disordered anion sublattice of CaF_2 crystals

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ABSTRACT

The fast quenching of CaF_2 crystals preheated up to 1000 °C allows to stabilize the high-temperature disordering of anion sublattice typical for the superionic state of the crystal. Such procedure results in the formation of structured ultraviolet to vacuum ultraviolet (UV–VUV) absorption with a lengthy long-wavelength tail stretching into the visible spectral range. Such absorption in the quenched crystals cannot be related to any local center and testifies to the presence of nano-sized complexes of displaced anions, the electron structure of which is drastically changed as compared with a regular lattice. Possibly, these clusters are frozen dynamic clusters that were discovered earlier in the superionic state with quasi-elastic diffuse neutron-scattering technique. Four luminescence bands in near UV and visible spectral range correspond to four low-energy absorption bands. Unlike absorption bands that are of zone nature, the luminescence occurs from the localized state that arises due to strong electron-vibration coupling in the clusters. Absorption and luminescence states are divided by a potential barrier that is responsible for the spacing between corresponding excitation and emission bands as well as the temperature quenching of luminescence. The luminescence study reveals the features of the electronic structure of clusters within preheated/quenched CaF_2 crystals. The quenching method allows to study the high-temperature superionic state of crystals with fluorite structure using a wide set of experimental techniques.

1. Introduction

The lattice of crystals with fluorite structure, space group $Fm\bar{3}m$, may be viewed as a simple cubic array of anions with alternate cube centers occupied by cations (i.e. the crystal structure may be also considered as a “3D-chessboard”). The feature of this structure is a high lability of anion sublattice stipulated by the presence of unoccupied anion cubes. The typical structure defect of the crystals is an anion Frenkel pair – an interstitial fluoride and an anion vacancy. Pair dissociation results in the appearance of mobile defects that provide the ionic conductivity of the crystals. The increase of defects concentration with temperature, e.g., thermally induced disorder in the anion sublattice is responsible for a Schottky-type anomaly in the specific heat at temperature T_c well below the melting temperature T_m of the crystal ($T_c \approx 0.8\ T_m$) [1]. This “superionic” state is characterized by a high ionic conductivity comparable with that in melting salts and a strong modification of physical properties of the crystal, e.g., elastic constants. In other words, this state may be considered as the melting of anion sublattice.

Since the fast-ion conductivity displays itself at relatively high temperatures, fluorite-type crystals, excluding PbF_2, are not used in practice. Nevertheless, due to the simplest structure they are fine model systems for the study of ionic conductivity in crystals (see, e.g., [2–12]). Of particular interest is the opportunity to modify the chemical composition of fluorite-type crystals without altering the overall crystal structure (see, e.g., [9,13]). It should be also noted that electrochemical energy systems, rechargeable solid-state fluorine-ion batteries are attractive devices owing to their high theoretical energy density [14,15]. The recent study of mechanocaloric effect in fluorite-type crystals supports the fact that fast-ion conductors constitute a new family of materials showing great promise for prospective solid-state refrigeration applications [16].

The important experimental technique for studying the high-temperature disordering of anion sublattice of crystals with the fluorite structure is a coherent diffuse quasi-elastic neutron scattering (QES) which is related to both the instantaneous picture of anion positions

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and their variation with time (see, e.g., [2,3]). The analysis of QES in fluorite-type crystals led to the conclusion that the strong disorder of anion sublattice in the superionic state is accompanied by the formation of short-lived nano-sized clusters each of which comprises true anion interstitials, anion vacancies and displaced anions [17–19]. At the temperature typical of anomaly in the specific heat, the lifetime of these clusters is about 10^{-12} s [19]. Computer simulation technique is also used for the clarification of a cluster structure [19–21]. It was concluded that QES experiments are in good agreement with cluster models containing one or two anion Frenkel defect pairs and displaced near-neighbors (nn) and next near-neighbors (nnn), whereas true interstitial anions are displaced along ⟨110⟩ directions, nn and nnn anions – along ⟨111⟩ directions [19]. Note that the model suggests no relaxation around fluorine vacancies and the location of cations at their regular sites.

Since clusters formation is bound with the dynamical disordering of anion sublattice, their existence at room temperature seems impossible. However, it has been revealed recently that the preheating to 600–1000 °C and subsequent quenching of CaF_2 crystals causes the appearance of the structured absorption starting in the vacuum ultraviolet (VUV) spectral range with a giant, several eV long, low-energy tail spreading through the visible range [22]. Such induced absorption cannot be ascribed to any single or aggregate center with the transitions typical of local centers, while similar absorption spectra are typical for semiconductors with indirect optical transition. One may suppose that the observed absorption is due to some nano-sized complexes, the electron structure of which is radically reconstructed; as compared with that of a regular CaF_2 lattice. Such reconstruction is possible for sufficiently small (nano-sized) complexes/clusters. These clusters may be identical to those observed in QES experiments if their dimensions correspond to that of high-temperature clusters. The attempts to estimate experimentally the size of clusters by means of different methods are now in progress.

The presence of several VUV–UV absorption bands may be bound up with the transitions between the valleys in the reciprocal lattice space of reconstructed valence and conduction bands of the *single cluster* (see Section 3). The maximum intensity of low-energy absorption bands is achieved for a direct transition that excites the multi-phonon state of the valence-band valley. The indirect transition into the bottom of this valley (a zero-phonon state) has very low intensity; its energy is smaller than that of the direct transition by several eV. This is the reason of a lengthy short-wavelength absorption tail of absorption in preheated/quenched crystals.

It was found that preliminary heating of crystals in the reduction atmosphere of calcium vapor (additive coloring procedure) introduces some quantity of anion vacancies and electrons into the crystal bulk. Their recombination and aggregation results in the formation of various color centers as well as calcium precipitates, colloids (see, e.g., [23]) and rods [24]. The precipitates are formed at sufficiently high concentration of vacancies/electrons introduced in the crystal during coloring procedure. Vacancies/electrons are "stored" in color centers and calcium precipitates. Their decomposition at preheating liberates both components. The neutral color centers comprise equal quantity of vacancies and electrons, and center destruction injects these components into the lattice. As for precipitates, a calcium metal has the same Bravais lattice as a CaF_2 crystal, and the mismatch of lattice parameters is only about 0.2%. The colloid/rod decay during heating leads to filling-up the voids in Ca lattice by neighboring fluorine atoms according to reaction $Ca + 2F \rightarrow Ca^{2+} + 2F^{-}$ restoring the CaF_2 structure; anion vacancies and electrons remain in crystal layers adjacent to the destructed Ca precipitates. The vacancies produced under preheating of additively colored crystals trigger and intensify the process of anion sublattice disordering. For the crystal colored in intensive coloring regime, the concentration of vacancies/electrons introduced by this procedure is $\sim 3.3 \times 10^{17}\ cm^{-3}$, whereas the concentration of Frenkel defects at $T = 1000$ °C equals $3.5 \times 10^{18}\ cm^{-3}$. Thus, about 10% extra-vacancies quadruple increase the cluster absorption/concentration in the sample preheated/quenched to this temperature [22].

In addition to optical absorption, anion clusters manifest themselves via the luminescence. In the present paper, the analysis of the luminescence excited by photons in the region of the absorption bands induced by the preheating/quenching of as-grown and additively colored CaF_2 crystals is presented.

2. Samples and methods

The VUV grade fluorite single crystals were obtained from INCROM Ltd. (St. Petersburg, Russia). The crystals are grown from high-purity charging mixture and are not contaminated with oxygen because of reduction conditions of growth technique. Sample *A* was cut out from an as-grown crystal. The samples *B*, D_2,[1] and *E* were cut off the crystals subjected to additive coloring procedure. Set-up, in which coloring was executed, and the process itself were described in [25,26]. The quantity of vacancies/electrons introduced into the crystal depends on two parameters: calcium vapor pressure *p* and temperature *T*. Sample *B* was cut out from the crystal that was colored using mild regime at $p = 3 \times 10^{-4}$ Torr and $T = 830$ °C. Samples D_2 and *E* were prepared from the crystals colored using very hard regimes either by pressure ($p = 5.7 \times 10^{-1}$ Torr and $T = 815$ °C, sample D_2) or temperature ($p = 3 \times 10^{-2}$ Torr and $T = 870$ °C, sample *E*). The vacancy concentration in samples D_2 and *E* is higher than in sample *B* by the orders of magnitude. All samples were preheated at $T = 1000$ °C and then rapidly quenched. The plates of $10 \times 10\ mm^2$ area and thickness from 0.33 mm (sample *E*) up to 1.72 mm (sample *A*) were used. Therefore, the absolute values of luminescence intensity in different samples are not comparable.

The spectra of optical absorption were measured using a high-absorbance double-beam spectrometer JASCO V-660 with a double monochromator (1.5–6.5 eV) or a laboratory setup based on a vacuum monochromator VMR-2 (4.5–10.0 eV). In the latter case, the constant number of incident photons of different energies from the hydrogen discharge in a flow capillary tube was achieved by varying the slit width of the vacuum monochromator and using the constant signal from sodium salicylate for normalization.

In photoluminescence experiments, the samples were mounted on the sample holder and placed into a closed cycle helium cryostat provided by ARS (Advanced Research System, Inc.) with temperature controller, Lake Shore Model 355; the measurements were performed in a temperature range from 6 to 295 K. The UV-VUV excitation light from a Hamamatsu L1835 water-cooled deuterium discharge lamp (150 W) was selected via a Seya-Namioka McPHERSON 234/302 monochromator. The luminescence was analyzed using an Andor SR 303i-B grating monochromator equipped with an iDus 416 CCD (Andor) detector or a Hamamatsu H6240-01 photon counting head. Emission spectra were corrected for the spectral response of the detection system. The excitation spectra were normalized to equal the quantum intensities of the exciting photons falling onto the crystal, a sodium salicylate was used as the reference signal. All measurements were controlled by means of LabView based software.

To exclude sample pollution by oxygen at heating procedure, the sample was placed into a porcelain boat and heated in a flowing argon atmosphere (6 N purity level) inside a quartz reactor of a high-temperature furnace from room temperature to $T = 1000$ °C. The sample was kept for 15 min at this temperature automatically controlled by an *S*-type rhodium-platinum thermocouple and then cooled down by moving the reactor out of the furnace.

Both nanometers and electron volt units are used in the description of luminescence and absorption/excitation spectra.

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[1] The absorption spectra of samples *A*, *B*, and D_2 were studied in [22]. We retained the denotation of these samples in the present paper as well.