

## Oxygen Defects in Fluoride Crystals

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### Abstract

Oxygen centers as well as some reactions related with the oxygen centers were studied in different fluorite crystals with wide band gap. Aggregation of oxygen-vacancy dipoles was observed in all crystals above 50 - 100°C. Photodissociation by excitation into second or higher energy absorption bands was observed in all crystals but LaF<sub>3</sub>. In several crystals oxygen centers are trap for electrons and holes.

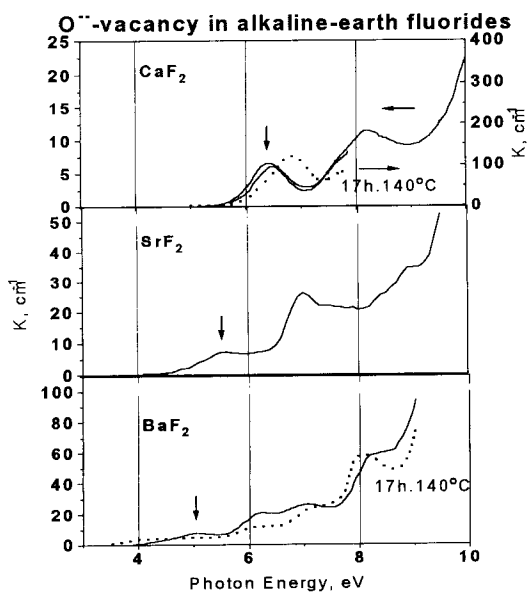
No new absorption bands were observed in well quenched oxygen-doped CeF<sub>3</sub> crystals. Two different types of oxygen defects were observed in LaF<sub>3</sub>. The first type has absorption band near 7.2 eV and three sharp emission lines at 2.36, 2.26, 2.23 eV with rather slow decay time (0.55 ms at 80 K and 13 K). These oxygen centers intensity was a maximum in rapidly quenched samples and was diminished by low temperature (50-200°C) annealing. These defects can be attributed to oxygen-vacancy centers. Another type of defects with broad emission bands near 2.7 eV and much faster decay was attributed to oxygen-vacancy aggregates.

### Introduction

Oxygen ions are very easy penetrated into fluoride crystals during growth or high temperature

annealing. Apart alkali halides where molecular form is predominate the oxygen is introduced into other fluorides as oxygen-vacancy defects. The double charged oxygen ion (O<sup>2-</sup>) is accompanied by anion vacancy for charge compensation. The presence of anion vacancy near oxygen ion leads to effective diffusion of these defects and their photodissociation. Oxygen ions often incorporate with excess charged metal impurity ions. The photoluminescence of oxygen defects is rather effective at room temperature. This property gives easy method for checking of oxygen presence by visible luminescence under ultraviolet irradiation.

In this report we summarize the results of latest investigations of oxygen defects in many fluoride crystals with different structures : alkali fluorides, alkaline-earth fluorides [1], barium fluorohalides [3] as well as new



**Fig.1** Absorption spectra of oxygen-vacancy defects in alkaline-earth fluoride crystals. Dotted curve measured after marked anneal.

results for lanthanide trifluorides.

### Optical transitions

The absorption of oxygen centers in quenched crystals consists of several bands in vacuum ultraviolet region (Fig1., Table 1). The smallest long wavelength absorption band has usually about 0.1 oscillator strength. The luminescence with high yield was observed by excitation into any of absorption bands.

The electronic transitions of oxygen-vacancy centers are well described by a simple model - molecule HF in crystal field [2]. In simple cubic structures such as alkali halides, alkaline earth fluorides the oxygen ion and vacancy probably are the nearest neighbors.

In BaFCl, BaFBr two types of oxygen centers having different absorption and luminescence bands were observed. The first absorption band of the oxygen-vacancy centers is related with the transitions from ground state (mainly oxygen p-orbital) to excited one (mainly vacancy s-orbital). The ground level of the oxygen-vacancy center in alkali halide crystals is not far above of the top of halide valence band. In barium fluorohalide crystal the upper valence band is chlorine or bromine one [4]. The fluorine valence band is lower about 3 eV [5]. The qualitative scheme of zone bands of barium fluorohalides crystals show that the energy of first absorption band of the (F-X) or (F-F) oxygen-vacancy centers have to be larger than that of (X-X) ones (Fig.2).

Probably the oxygen centers occupied the Br( or Cl) - F and Br-Br (or Cl-Cl) vacancy pairs in these crystals. The third type of oxygen-vacancy centers in barium fluorohalides was not found so far.

### Decay of luminescence

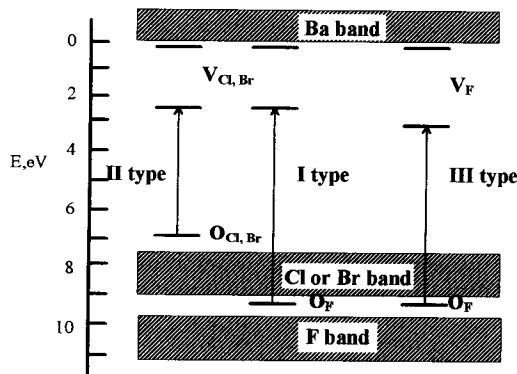


Fig.2 The qualitative scheme of zone bands of barium fluorohalide crystals and energy levels of oxygen-vacancy defects of three different types. The arrows show the allowed transitions which form the first absorption bands.

**Table.1** The absorption and emission bands of oxygen-vacancy centers at 80 K [1, 3]. Absorption bands for alkaline-earth fluoride and LaF<sub>3</sub> were measured at room temperature.

| Crystal          | E <sub>abs</sub> , eV | E <sub>em</sub> , eV      |
|------------------|-----------------------|---------------------------|
| CaF <sub>2</sub> | 6.45, 8.25            | 2.60                      |
| SrF <sub>2</sub> | 5.65, 7.0, 9.4        | 2.65                      |
| BaF <sub>2</sub> | 5.2, 6.05, 7.2, 8.6   | 2.38                      |
| BaFCl I type     | 5.0, 6.3              | 2.5                       |
| BaFCl II type    | 4.2, 5.28, 6.35       | 2.05                      |
| BaFBr I type     | 4.9, 6.3, 7.3         | 2.30                      |
| BaFBr II type    | 4.5, 5.6, 6.5, 7.4    | 2.45                      |
| LaF <sub>3</sub> | 7.2                   | 2.36 (295K)<br>2.26, 2.23 |

The decay curve generally consists of fast components ( in nanosecond time scale) and slow components (in micro-milli second time scale).

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

The temperature dependence of slow component is described by three closed excited levels with

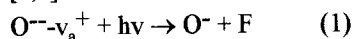
thermal equilibrium between them. We tentatively assume that these three levels belong to different center configurations in the lowest excited state. Some facts point out that the energy surface of oxygen ion in excited state is rather soft and ion can easily move to off-center positions. One may conclude that at low temperatures the oxygen ion occupies an off-center position, which is farther from F center. So radiation probability is rather low. At higher temperatures the oxygen ion moves into on-center position. The intersection between 1s F center and 2p oxygen orbital becomes larger, therefore the decay time is shortened.

### Aggregation

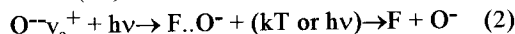
Aggregation of oxygen centers was observed at 50-200°C temperatures. The processes of oxygen accumulation into aggregates and incorporation of oxygen centers with some impurities were observed using changing of absorption and luminescence spectra. Usually normal aggregation leads to shift first absorption band to higher energies (see Fig. 1 top plot). Incorporation of moving  $O^-$ -vacancy centers with some impurities have resulted in low energy shift of first absorption band (see Fig. 1 bottom plot).

### Photochemistry

Photodissociation of oxygen-vacancy centers above 200 K follows the reaction [6,7]:



Similar to other fluorides the photodissociation of the oxygen defects in BaFCl crystals also occurs by irradiation into second (and higher) absorption bands (Fig. 3). The creation of  $O^-$  ions substituting  $F^-$  ( $O_F^-$ ) as well as  $O_{Cl}$  centers was observed in BaFBr, BaFCl crystal by UV irradiation (4.5-5.7 eV region) at room temperature [9]. During the photodissociation process of the I type oxygen-vacancy centers in BaFCl, BaFBr the perturbed  $F(X^-)$  centers were created as well as unperturbed ones. It is reasonable to assume that the perturbed  $F(X^-)$  centers are the intermediate defects on way of creation of unperturbed  $F(X^-)$  centers. Then we can write:



Here the  $F..O^-$  means F and  $O^-$  centers, which are spaced by few interionic distances. Similar F centers perturbed by neighboring sulfur ions were observed in NaBr- $S^{2-}$  crystals [10].

In alkaline earth fluorides the created F centers are incorporated with other oxygen-vacancy defects resulting in perturbed F centers [1].

### Charged oxygen centers

The main effect of presence of oxygen impurity is the enhancement of efficiency of X-ray coloration [9]. The  $V_k$  as well as perturbed  $F(Br^-)$  centers are produced by X-irradiation of BaFBr at

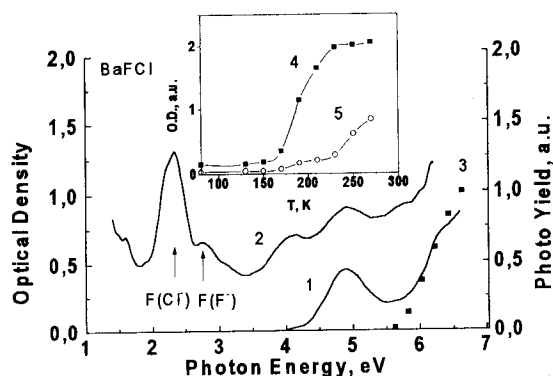
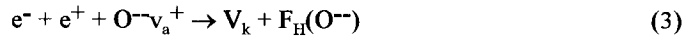


Fig.3 Absorption spectra of BaFCl at 295 K after quenching (1) and subsequent ultraviolet irradiation (2). (3) - formation spectrum of  $F(Cl^-)$  centers. The upper set show temperature dependence of efficiency of photochemical production of  $F(Cl^-)$  centers (4) and F-aggregates (at 1.5 eV) (5).

**Table 2.** The known low energy absorption bands of  $F_H(O^-)$  centers in various halide crystals at 80 K compared with those of F centers.

| Crystal          | $F_H(O^-)$ , eV | F, eV     |
|------------------|-----------------|-----------|
| LiF              | 5.0 [11]        | 5.1 [12]  |
| NaCl             | 2.68 [11]       | 2.77 [12] |
| CaF <sub>2</sub> | 2.85, 3.2 [11]  | 3.3 [13]  |
| SrF <sub>2</sub> | 2.45, 2.77      | 2.85 [13] |
| BaFBr            | 2.08            | 2.15 [14] |
| BaFCl            | 2.18            | 2.28      |

low temperature ( $T < 150$  K). Under X- irradiation the free electrons and holes are produced in crystal. At low temperature part of electrons is captured by oxygen centers and the relevant part of holes is self trapped. This process follows the reaction [11]:



The additional electron is captured on states that originated mainly from anion vacancy. It leads to production of F center disturbed by neighboring  $O^-$  ion (Table 2). Due to the oxygen ions, absorption band of  $F(Br^-)$  centers is slightly shifted to lower energies. The  $V_k$  and  $F_H$  centers are completely converted back to oxygen-vacancy centers if the crystals were irradiated into  $V_k$  band at 80 K. When crystal was heated,  $V_k$ -band disappears above 160 K and the near half  $F(Br^-)$  band was remained. It means that the part of moving  $V_k$  centers is trapped by some defects and cannot reach the  $F_H$  centers. Perhaps these  $V_k$  centers in BaFBr were trapped by oxygen-vacancy centers as it was observed in  $CaF_2$  earlier [15].

Above 200 K the reaction of dissociation of oxygen-vacancy centers begins to play a main role in coloration of  $CaF_2$  crystals [11]. In calcium fluoride crystals the X-ray coloration takes place by means of the same reactions as photochemical ones [1]. The increase of X-ray [16] and photochemical coloration of oxygen doped BaFCl at 180-300 K region (see Fig.3) as well as the parallel creation of  $O^-$  ions and F centers in BaFBr by X irradiation [9] show that the dissociation of oxygen-vacancy centers is the main reason for X-ray coloration at room temperature.

Both ESR and optical dichroism results show that in  $CaF_2$   $F_H(O^-)$  center consists of F center disturbed by an oxygen ion in the second fluorine shell (110) site around the F center [17].

## Trifluorides

### $CeF_3$ oxygen centers

The 3.75 eV absorption and bright 2.3 eV emission bands were observed in slowly cooled ("as-grown") cerium fluoride crystals containing oxygen. The decay time of this emission was near 30 ns at 80 K. The short annealing at 600°C transforms this band to 3.6 eV band, and 2.3 eV emission disappeared. The following annealing at 600°C lead to decrease 3.6 eV absorption and increase the edge absorption near 4.4 eV. The annealing above room temperature restored the 3.6 eV absorption band; then the 3.6 eV band diminishes while the 3.75 eV increased. The 2.3 eV emission band was restored also ( Fig. 4).

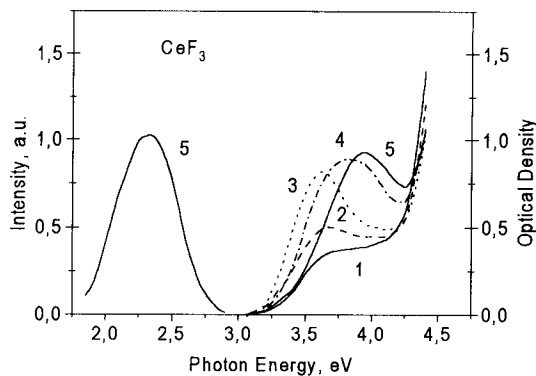


Fig 4. Absorption and emission spectra of  $CeF_3$  crystals contained oxygen impurity quenched from 600°C (1) and annealed. 2- 32 min 65°C; 3,4,5 - anneal at 100°C for 5, 10 and 44 min.

Obviously these 3.6 and 3.75 eV bands belong to some oxygen aggregates. The absorption band of single oxygen center is above the edge absorption of  $CeF_3$  crystals.

It is reasonable to evaluate the position of oxygen vacancy centers in lanthanide trifluoride crystals (Fig.5). The 4f levels are empty for  $LaF_3$  and partially filled for other trifluorides. The 2p oxygen level is believed to be about 1 eV above the top of valence band. The 1s level of anion vacancy lies 2-2.5 eV below the bottom of conductivity band. The 1s-2p levels of anion vacancy

can be considered as the 1s-2p levels of F center (2.1-2.6 eV [18]). The lowest energy absorption band of oxygen center is considered to be near 7 eV in lanthanide trifluorides. These transitions can be seen only in  $\text{LaF}_3$ , in other trifluorides they will be hidden by 4f-5d, 6s transitions of lanthanide ions.

This simple evaluation is in the line with the observation of oxygen absorption at 7.2 eV in  $\text{LaF}_3$  and with absence of oxygen absorption in  $\text{CeF}_3$ .

#### $\text{LaF}_3$ oxygen centers

Usually the  $\text{PbF}_2$  was added to reduce oxygen contamination. When  $\text{PbF}_2$  is not enough the impurity absorption above 6 eV and two groups of emission bands were observed. This fact shows that the absorption above 6 eV and several emission bands related with oxygen impurity.

The sharp green bands are largest in quenched samples (Fig.6) and they decrease with annealing above  $100^\circ\text{C}$ . The easy diffusion of oxygen defects above room temperatures indicates that the oxygen ion is accompanied by the anion vacancy. We may tentatively suggest that the "green" bands belong to oxygen-vacancy centers, while the broad blue emission band belongs to some oxygen aggregates. We cannot observe well-defined absorption bands of oxygen defects. There is continuous absorption growth up to  $\sim 100\text{ cm}^{-1}$ , while in excitation spectrum and in difference absorption spectrum due to  $\sim 100^\circ\text{C}$  annealing the band near 7.2 eV was observed.

The decay of "green" bands consist of two components with decay time 0.24 and 0.70 milliseconds at 295K and 200K. Only one component with decay time 0.55 ms within two orders of intensity was observed at 80K and 13 K. The decay characteristics of well separated 2.26 and 2.36 eV bands were the same near room temperature. Decay times were the same for both 2.23, 2.26 eV bands at 78 and 13 K. The decay of broad "blue" emission band is much faster.

It is very interested to know the reason of narrowing the emission band. Narrow emission bands were also observed for  $F_A(\text{II})$  centers in alkali halides in comparison with "normal" F centers or  $F_A(\text{I})$  centers. Three main differences were observed. The Stokes shift for  $F_A(\text{II})$  centers was twice larger, halfwidth of emission band was twice lesser than for F centers and decay time was six times lesser than for F centers (see review of F.Luty in [12]). For oxygen defects in  $\text{LaF}_3$  the Stokes shift is 1.5 times larger, the halfwidth is nine times lesser than for oxygen-vacancy defects in alkaline-earth fluorides. In contradiction the decay time is in the same range. Generally the shift of oxygen ion into saddle-point position between two anion vacancies in soft fluorine sublattices of trifluorides is rather possible. Three types of fluorine sites may lead to different emission bands.

#### Comparison with excitons

Other defects with large Stokes shift and effective luminescence are self trapped excitons in halide crystals. Generally it is proposed that several minima on adiabatic potential surface can be realised [19]. There are two main features which join the oxygen-vacancy defects and excitons. First similarity is luminescence decay. The singlet-singlet transitions for oxygen-vacancy centers were observed in LiF, NaF, NaCl [20]. The singlet emission bands of excitons were observed in NaF and NaCl, the situation with LiF is questionable [19]. The only triplet-singlet slow transitions

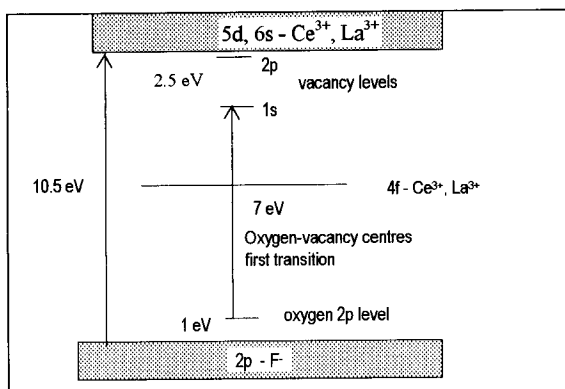


Fig.5 The simplified scheme of zone bands of lanthanide trifluoride crystals. The valence band is formed from 2p fluoride states, the oxygen 2p level is usually about 1 eV higher of top of valence band. The vacancy atomic like levels for the first approximation are situated at the same depth as those of F center.

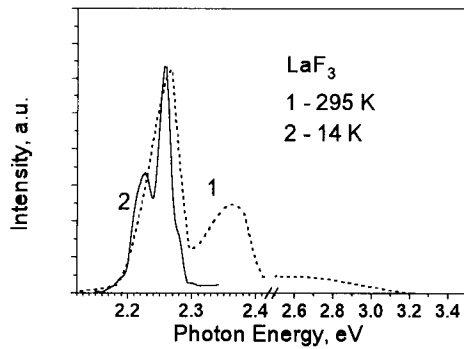


Fig.6 Emission of oxygen contained  $\text{LaF}_3$  crystals under 7-8 eV excitation.

ity in the luminescence decay of both centers.

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were observed in  $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaFCl}$ ,  $\text{BaFBr}$  for oxygen-vacancy centers [20,21] as well as for excitons [19,22].

Second similarity is electronic structure of excited state. The excited electron in oxygen-vacancy centers occupies the level of anion vacancy, so the excited center can be simply considered as F center near O<sup>-</sup> ion (or hole occupied nearest oxygen ion). The exciton in some cases can be considered as F center near hole trapped on (halide)<sub>2</sub> molecule on one anion site (so called H center) [19]. Obviously this similarity in the electronic structure leads to the similar-

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