

Effect of Cationic Impurities on the Formation of Radiation Defects in Alkaline Earth Fluorides

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Abstract—A new model of photochromic centers formed by ionizing radiation or the additive coloration of alkaline earth fluorides doped with rare-earth ions (La, Ce, Gd, Tb, Lu, and Y) is proposed, based on original experimental results and the literature data.

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INTRODUCTION

All crystals of high-purity alkaline earth fluorides are stable with respect to radiation at room temperature [1, 2]. Doping alkaline earth fluorides with several cation impurities sometimes results in effective radiation coloring. Cation impurities can affect the formation of intrinsic defects in an anionic sublattice through two completely different mechanisms.

The formation of centers containing impurity ions and anion vacancies occurs at temperatures exceeding those of the onset of anion vacancy migration, and the temperature range of these centers' formation is quite wide (from 200 K to room temperature and even higher). The formation of anion vacancies most likely results from the nonradiative decay of autolocalized, relaxed exciton, i.e., from the formation of radiative defects usually observed in nondoped alkaline haloid crystals. Such centers were studied earlier in CaF₂, SrF₂, and BaF₂ crystals doped with divalent cadmium ions, and in CaF₂ and SrF₂ crystals doped with zinc ions [3–5].

The formation of centers with impurity ions and anion vacancies proceeds at the boiling temperature of liquid nitrogen, and their emergence is not controlled by the thermally activated process of anion vacancy migration. Such formation is most likely explained by configuration instability near some rare-earth ions and yttrium when electrons are captured by the excited state of an impurity ion [6]. Such instability results in the formation of so-called photochromic centers that (according to the existing model) contain a trivalent ion, an anion vacancy, and one (PC⁺ center) or two electrons (PC centers) each [7–9].

In this work, we propose a new model of PC centers in which the second electron is not necessary. The PC centers are similar to excited F-centers, and PC⁺ centers most likely include divalent rare-earth ions. The transition between them may be considered as electron

transition from parts of one configuration. This means that the PC-center has a structure of $Re^{3+}F$ (deep trap), the PC⁺-center has a structure of $Re^{2+}v_a$ (small trap), and the transition of electron between them by means of photons ($Re^{3+}F \leftrightarrow Re^{2+}v_a$) is possible.

EXPERIMENTAL

Crystals of alkaline earth fluorides doped with rare-earth ions (La, Ce, Gd, Tb, Lu, and Y) were synthesized using the Stockbarger technique from a melt in an inert atmosphere. Cadmium fluoride was added to the charge in order to prevent the formation of oxygen impurities. Radiation coloration was performed using an X-ray tube with a Pd anode at 20 mA, 40 kV, and exposure times of <60 min. The absorption spectra were obtained on the Lambda 950 UV/VIS/NIR spectrophotometer at the Baikal Analytical Center for Collective Use, Siberian Branch, Russian Academy of Sciences.

RESULTS AND DISCUSSION

The effect different conditions have on the stability of impurity ion valences and the changes in their valence is of both applied and fundamental interest. Trivalent ions (Y, La, Ce, Gd, Tb, and Lu) with low third potential ionization are not reduced to the divalent state; instead, they form photochromic centers. According to the current model, each center has a trivalent ion, an anionic vacancy, and one (PC⁺ center) or two (PC center) electrons [7–9].

In the divalent state, rare-earth ions (La, Ce, Gd, Tb, and Lu) do not form stable compounds with oxygen, fluorine, chlorine, or bromine ions. The ability to form divalent compounds is best analyzed according to the formation of iodides, since an iodide-ion (I⁻) is the best reducing agent among F⁻, Cl⁻, Br⁻, and I⁻.

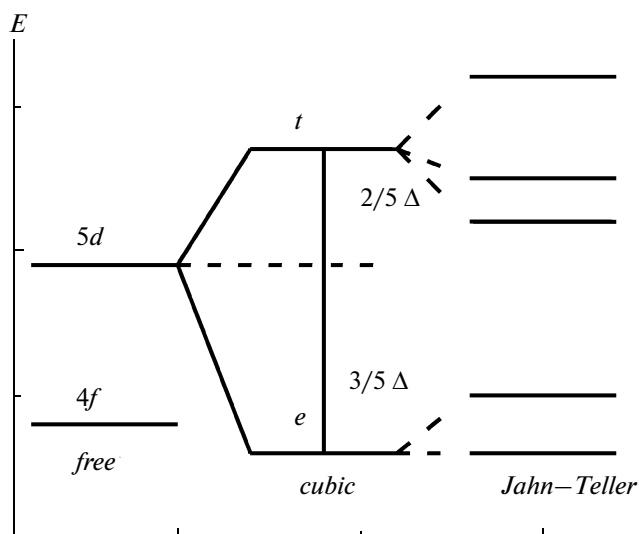


Fig. 1. Splitting of the levels of divalent ions in a crystal field.

Divalent Nd, Sm, Eu, Dy, Tm, and Yb iodides are good dielectrics and form stable compounds, while LaI_2 , CeI_2 , PrI_2 , and GdI_2 acquire metallic lusters and have good electronic conductivities [10]. This shows that the rare-earth ions that form photochromic centers in alkaline earth fluorides cannot retain electrons in the divalent state, and their loss transforms them into the trivalent state.

La^{2+} , Gd^{2+} , and Y^{2+} ions in the free state have the basic configuration d^1 . The basic configuration for Ce^{2+} and Tb^{2+} ions is f^n . However, the $f^{n-1}5d$ and f^n configurations have similar energies. The basic state for Lu^{2+} ($4f^{14}6s$) is close to the $4f^{14}5d$ state in terms of energy. The cubic crystal field in crystals with fluorite-type lattices splits the d state into two states: doubly degenerated (e) with an energy lower by $3/5\Delta$, where Δ is the value of d state splitting by the crystal field, and triply degenerated (t) state with an energy higher by $2/5\Delta$. The lower level is doubly degenerated, so divalent ions Ce^{2+} , Tb^{2+} , and Lu^{2+} in many materials have electron configurations of $4f^15d^1$, $4f^85d^1$, and $4f^{14}5d^1$, respectively. Thus, d^1 is the basic state for these divalent ions and, consequently, two types of transitions are observed in absorption spectra: $d \rightarrow d$ transitions that are similar for all these ions, and $5d^1 \rightarrow f$ transitions for La, Ce, Gd, and Tb that show the valence states of impurities, especially for Ce^{2+} [11].

$d \rightarrow d$ Transitions

The $5d^1$ state is split into two states by a crystal field: doubly degenerated and triply degenerated. Because of this, the ligands around an impurity ion are subject to Jahn–Teller distortion and there is further splitting of the t and e states (Fig. 1). Jahn–Teller lattice distortion

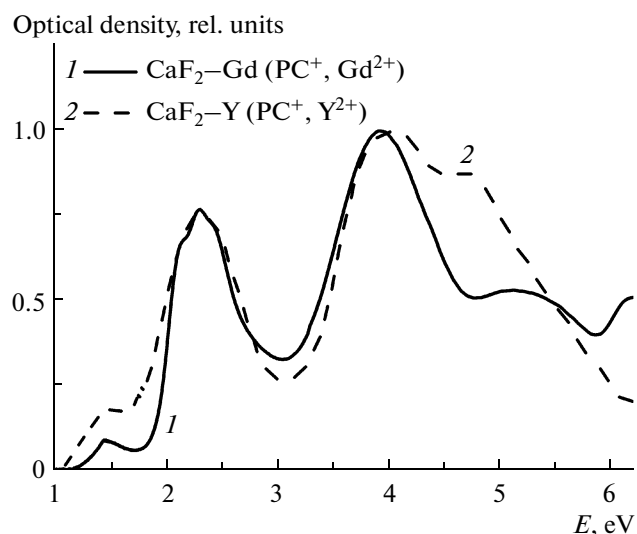


Fig. 2. Absorption spectra of $\text{CaF}_2\text{-Gd}$ (1) and $\text{CaF}_2\text{-Y}$ (2) crystals irradiated with X-rays at 80 K.

allows partial optical transitions within the d envelope.

The splitting of the d state in alkaline earth fluorides is 20000 cm^{-1} [12] and results in an absorption band at $\sim 2.3\text{ eV}$ (18550 cm^{-1}) (Fig. 2) that most likely results from transitions from the lower e to the t state (Fig. 1). The absorption band has a poorly reflected structure, indicating poor splitting of the t state. Photoconductivity is observed in $\text{CaF}_2\text{-Gd}$ crystals when excited by light with an energy of 2.0 eV [19]; i.e., the t state occurs within the conductivity zone. The less intense absorption band at $\sim 1.5\text{ eV}$ (Fig. 2) is most likely explained by optical transitions between the levels within the e state split, due to the Jahn–Teller effect (Fig. 1). A comparison of the absorption spectra for $\text{CaF}_2\text{-Gd}$ and $\text{CaF}_2\text{-Y}$ crystals irradiated by X-ray radiation at 80 K (Fig. 2) shows that they are very similar, as would be expected from the $d \rightarrow d$ transitions. Sometimes the absorption of $d \rightarrow d$ transitions is overlapped by the absorption of $d \rightarrow f$ transitions; however, an absorption band is clearly visible at 2.3 eV (Fig. 3a). The wide absorption band at $\sim 4.0\text{ eV}$ is explained by V_k centers. In the first studies of alkaline earth fluorides with the above impurities in the 1960s [13], the absorption bands registered after radiative coloration were attributed to $d \rightarrow d$ transitions and impurity ions reduced to the divalent state. It would seem, however, that this was not entirely correct, since it was later shown that these ions were not quite like other divalent rare-earth ions. On the one hand, in contrast to other rare-earth ions, they had no cubic symmetry; instead, they had C_{3v} symmetry. On the other hand, they had a clear photochromic effect, due to the presence of anionic vacancies [7–9]. They were labeled PC^+ centers, and the transitions were explained by anionic vacancies.

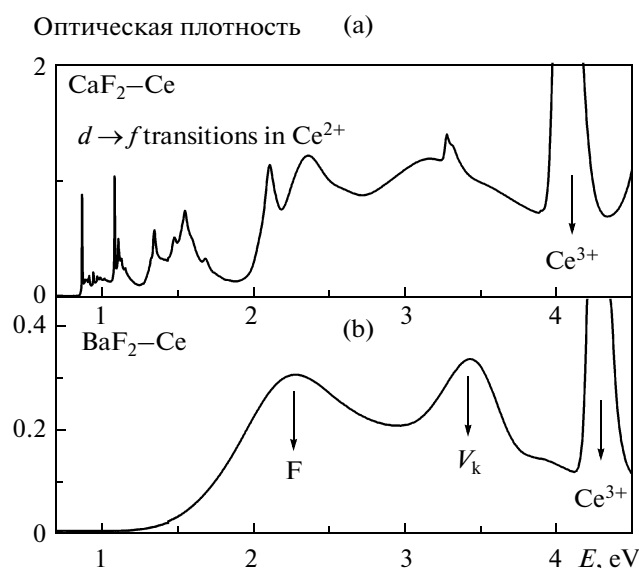


Fig. 3. Absorption spectra of (a) $\text{CaF}_2\text{-Ce}$ and (b) $\text{BaF}_2\text{-Ce}$ crystals at 80 K, irradiated with X-rays at (a) 300 K and (b) 80 K.

$d \rightarrow f$ Transitions

The formation of PC^+ centers, either through the optical destruction of PC centers by ultraviolet light in additively colored calcium fluoride crystals [7–9] or through X-ray coloration of CaF_2 and SrF_2 crystals at 80 K [14–15], was nevertheless accompanied by the formation of divalent ions (La, Ce, Gd, and Tb), as was registered in the form of $d \rightarrow f$ transitions or EPR spectra [16]. Especially vivid absorption spectra were observed for divalent cerium ions.

Fig. 3a shows the absorption spectra of $\text{CaF}_2\text{-Ce}$ crystals subjected to X-ray radiation at room temperature. Narrow lines associated with the $d \rightarrow f$ transitions of Ce^{2+} are observed in the infrared area. This line structure is also typical of $\text{SrF}_2\text{-Ce}$ crystals irradiated at 80 K [17]. The Ce^{2+} centers in these crystals are destroyed when heated up to room temperature.

PC^+ and divalent ions for the above mentioned ions in alkaline earth fluorides are always formed simultaneously, even though (according to the existing model) they are independent of one another. Neither PC^+ nor the divalent ions of these series are formed in barium fluoride, although other rare-earth divalent ions are formed during radiative coloration. Fig. 3b shows the absorption spectra of $\text{BaF}_2\text{-Ce}$ crystals irradiated at 80 K. It is evident from Fig. 3 that X-ray coloration results in the formation of F- and V_k -centers, as in nondoped barium fluoride crystals [18]. However, the spectrum does not show the absorption of PC^+ centers, and there are no lines related to the formation of divalent cerium ions in the infrared area. At present, we can say that this situation is paradoxical. On the one hand, radiative or additive coloration in CaF_2 and

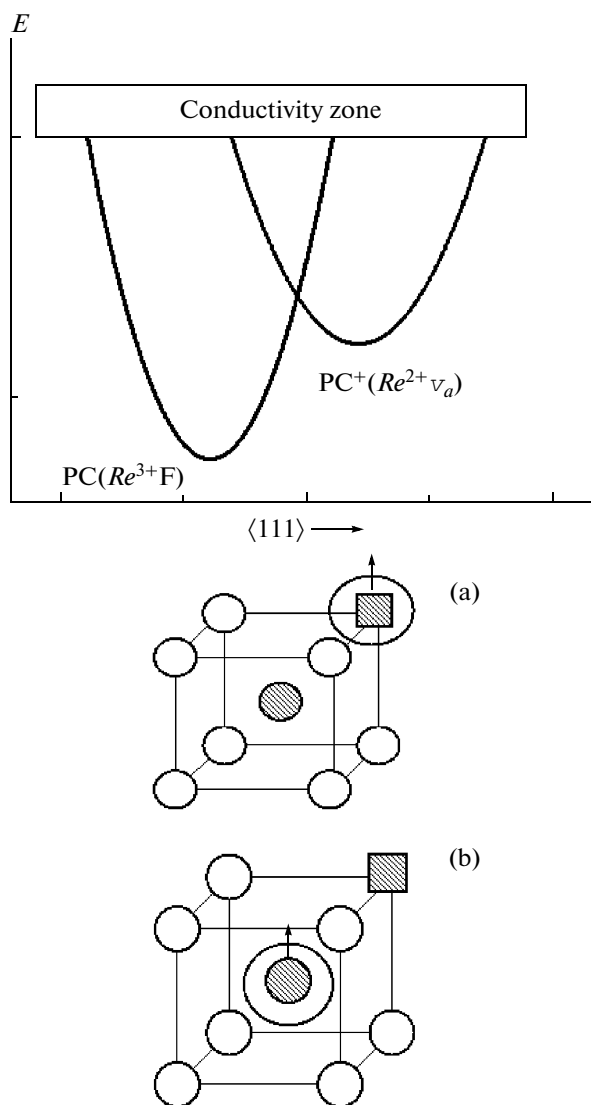


Fig. 4. Models of PC (a) and PC^+ (b) centers and energy scheme of their position in relation to the conductivity zone.

SrF_2 crystals doped with trivalent ions (Y, La, Ce, Gd, Tb, and Lu) produces photochromic PC and PC^+ centers, making the divalent states of these ions unstable. On the other hand, EPR studies and the observed $d \rightarrow f$ transitions clearly show that the divalent ions are also formed simultaneously with the PC^+ centers.

We may thus assume that divalent impurity ions are part of the PC^+ structure, and all absorption bands can be explained by the $d \rightarrow d$ and $5d^1 \rightarrow f$ transitions of divalent ions. On the other hand, PC^+ centers contain anionic vacancies, and a center's structure can be envisioned as a divalent ion near an anionic vacancy: $\text{Re}^{2+}v_a$ (Fig. 4). The photochromic effect results from the thermal or photonic migration of electrons from divalent ions to anionic vacancies and vice versa: $\text{Re}^{3+}\text{F} \leftrightarrow \text{Re}^{2+}v_a$.

Positions of the levels of divalent ions in relation to the conductivity zone, according to photoconductivity (eV) measurements

	CaF ₂	SrF ₂	BaF ₂		CaF ₂	SrF ₂	BaF ₂
La ²⁺				Gd ²⁺	2.0 [19]		
Ce ²⁺	1.6 [23]	1.3 [23]	1.1 [23]	Tb ²⁺			
Pr ²⁺				Dy ²⁺	1.76 [22]		
Nd ²⁺				Ho ²⁺	1.75 [22]		
Pm ²⁺				Er ²⁺			
Sm ²⁺	1.7 [25]			Tm ²⁺	2.75 [22]	2.08 [22]	1.5 [22]
Eu ²⁺	3.8 [25]	3.8 [26]	2.9 [26]	Yb ²⁺	4.22 [25]	3.0 [24]	
				Lu ²⁺			

All of the experimental data can thus be explained by photothermal transformations within a single center $Re^{2+}v_a$, instead of three formally independent centers (PC, PC⁺, and divalent ions Re^{2+}). We may assume that the metastable state $Re^{2+}v_a$ is a shallow trap (Fig. 4). Experimental results on photoconductivity in CaF₂–Gd crystals show that PC⁺ centers are 2 eV from the conductivity zone, while PC centers are 3.1 eV from it, since they are deeper traps (Fig. 4) [19].

Note that in addition to alkaline earth fluorides, there are only a few crystals in which the divalent states of these impurity ions have been studied. Direct and inverse optical transformations of divalent lanthanum (La²⁺) ions into F centers have been studied in BaFCl:La and SrFCl:La crystals by optical means and EPR. Although the explanation of the authors of [20–21] differs from our interpretation, the similarities between them are worthy of attention.

CONCLUSIONS

As was mentioned above, the chemical instability of divalent rare-earth ions (La, Ce, Gd, Tb, Lu, and Y) is explained by their inability to retain an electron, the loss of which returns them to the stable trivalent state [10]. The formation of such stable divalent ions as La, Ce, Gd, Tb, Lu, and Y (PC⁺ centers) in CaF₂ and SrF₂ crystals during radiative or additive coloration occurs via the formation of charged anionic vacancies $Re^{2+}v_a$ near divalent ions, which lowers the basic state of a divalent ion relative to the conductivity zone, thus favoring the retention of electrons near impurity ions.

Table shows the position of the levels of divalent rare-earth ions in relation to the conductivity zone obtained by measuring of photoconductivity. It is evident from Table 1 that the divalent ions Eu²⁺ and Yb²⁺ have the deepest levels in relation to the conductivity zone. From Eu²⁺ and Yb²⁺ to La²⁺ and Gd²⁺, the level position should gradually approach to the conductivity zone [27]. However, it is evident that the level for Gd²⁺ is deeper than that for Dy²⁺ and Ho²⁺, and the depth for Ce²⁺ is comparable with that for Sm²⁺.

Note that the PC⁺ centers ($Re^{2+}v_a$) are formed after radiative coloration at 80 K [14, 15] by the mechanism proposed in [6]. A necessary condition for such formation is that the d^1 state is the basic state for all of the above divalent ions (La, Ce, Gd, Tb, Lu, and Y).

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