Deep traps in $KMgF_3$ and $LiBaF_3$ crystals

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The influence of the high temperature annealing in air to the deep traps formation in $KMgF_3$ and $LiBaF_3$ fluoroperovskites was the subject of this study. An additional absorption and blue emission connected with O^{2-} ions presence in annealed crystal were revealed. The thermal destruction of colour centres in x-irradiated samples is accompanied by intensive recombination luminescence in high temperature TSL peaks. This phenomena was explained by pyrohydrolysis of crystal surface and oxygen diffusion into the crystal volume. Hydrolysed crystals were found to store the energy under UV irradiation.

Работа посвящена изучению влияния высокотемпературного отжига на воздухе на образование глубоких ловушек в флюороперовскитах $KMgF_3$ и $LiBaF_3$. Обнаружено, что в отожженных кристаллах возникает дополнительное поглощение и "синее" свечение, связанное с присутствием O^{2-} ионов. Термическое разрушение центров окраски в образцах, облученных рентгеновским излучением сопровождается интенсивной рекомбинационной люминесценцией, проявляющейся в высокотемпературных пиках ТСЛ. Это явление может быть объяснено пирогидролизом поверхности и диффузией кислорода в объем кристалла. Показано, что гидролизованные кристаллы запасают энергию при УФ облучении.

It is known that in the thermally stimulated luminescence (TSL) analysis reproducibility of results at multiple use of the dosimetric material is of particular significance. Ionic processes stimulate the aggregation of defects during irradiation and further heating. That is why in practice it is customarily to perform an intermediate annealing of samples at temperatures sufficient for the recovery of structure to the initial state. In a number of cases such thermal treatment is carried out in air. Annealing of fluorides (LiF, CaF_2, MgF_2, etc.) may result in pyrohydrolysis, i.e. enrichment of the subsurface layer by the products of the matrix interaction with air (O^{2-}, H^-, H_2O, CO_3^{2-}, etc.) [1–4]. Multiple experiments on the study of absorption characteristics of fluorides showed that in the hydrolysed crystals formed the impurity (oxygen and hydrogen containing) defects that have an essential effect on energy storage in the process of posterior ionizing irradiation [1, 2]. Elucidation of the role of high temperature annealing in air in the deep trap formation in fluoroperovskites $LiBaF_3$ and $KMgF_3$ has been the subject of the present paper.

Nominally pure and Eu, Mg and oxygen doped $LiBaF_3$ and $KMgF_3$ crystals were grown by the Stockbarger method. The impurities were introduced into melt in the form of corresponding fluorides and oxides. The control of transparency was realized by measuring the absorption spectra in the IR region (spectrometer UR-10) and in the UV/VIS range (spectrometer SPECORD-M40). The emission and thermoluminescence spectra ($0.2°Cs^{-1}$ in air) were obtained using the mentioned above devices [5]. Annealing of crystals was carried out in air in the temperature range of 500–700°C. X-ray

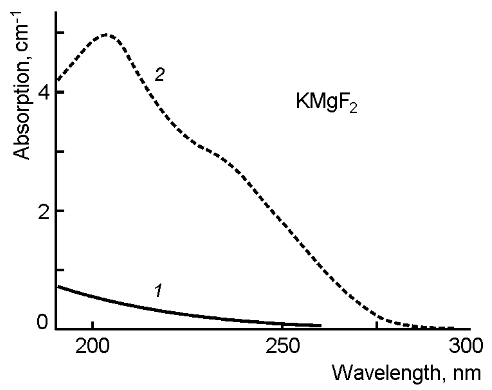

Fig. 1. UV-absorption of as growth (*1*) and hydrolysed (*2*) $KMgF_3$ crystals. Heat treatment 700°C, 6 h in air.

irradiation was carried out at room temperature at a dose rate of 600 Gy·h^{-1}.

Fig. 1 shows the absorption spectra of initial and subjected to high temperature annealing in air $KMgF_3$ crystals. Hydrolysis of crystals is accompanied by the appearance of additional absorption bands in 200–280 nm region. Simultaneously, the bands corresponding to oxygen radicals are at 3555–3605 and 3400 cm^{-1}. The value of the radiation induced by the ionizing radiation absorption depends on the hydrolysis products presence in crystals (Fig. 2). The additional absorption increases in the region of 190–220 nm and a new band at 330 nm arises.

Colour centres (CC) in the initial samples are completely destroyed at 150–200°C while in the hydrolysed crystals both intrinsic and additional CC turn to be thermally stable up to 300 °C. Investigation of the induced by annealing in air defects using the thermostimulated luminescence method showed the following (Fig. 3). In the initial $KMgF_3$ crystals the intensity of TSL is low and the glow curve consists of two peaks: the main at 86°C and very weak at 200°C. The TL spectrum represents a band with maximum at 590 nm corresponding to the well known luminescence of F_2-centres (Fig. 3.1). The pre-irradiation high temperature annealing of the samples (T = 540°C, from 0.5 to 4 hours) evokes a strong rise of the TSL intensity (Fig. 3.2). Straight after finishing the irradiation at RT there appears an afterglow in the green part of the spectrum (500–550 nm) take place. The effect becomes more pronounced if the annealing duration is elongated, for instance, tree times as much after 1 hour and

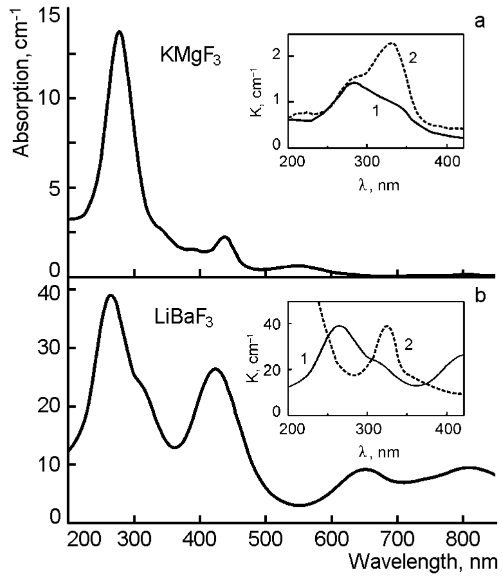

Fig. 2. Optical absorption of x-ray irradiated $KMgF_3$ (a) and $LiBaF_3$ (b) crystals. Dose 300 Gy. Insets: induced absorption in initial (*1*) and annealed at 540°C, 1 h (*2*) crystals.

300 times after 4 hours. In the hydrolysed samples the TSL peaks at 460°C and 560°C with the green luminescence similar to that observed right after irradiation are clearly discriminated.

High temperature TSL peaks typical for annealed in air undoped sample reveal in the oxygen doped $KMgF_3$ crystal. In case of oxygen and europium co-dopant the TL spectrum becomes more complicated and f-f luminescence (the line 359 nm) of Eu^{2+} ion is clearly defined (Fig. 3.3). The ratio between intensities of f-f Eu^{2+} emission (the line 359 nm) and green luminescence essentially depends on the content of europium in the crystal and dramatically increases if Eu_2O_3 concentration exceeds 0.1 %. As it was shown earlier the light sum which is released in TSL process in $KMgF_3(Eu_2O_3)$ is hundreds times higher than in LiF(Mg,Ti) [6].

TSL in $LiBaF_3$ crystals was described in [7]. Similar to $KMgF_3$, CC bleaching in pure crystals occurs in the region of 100–150°C. In Li_2O doped crystals there appears a TSL peak at 200°C and CC become more stable. In case, of oxygen and Mg^{2+} co-doping the process of radiative release of energy becomes quite different. There appears an intensive peak at 330°C with the luminescence at 600 nm. Colour centres are thermally stable and revealed in the absorption spectrum even after annealing up to 300°C. It should be noted that in the hydrolysed

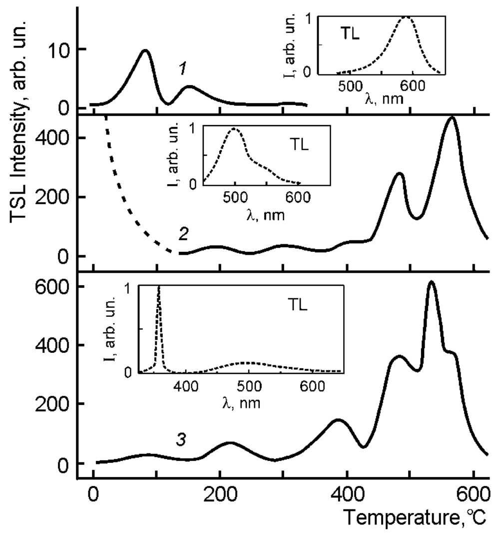

Fig. 3. Thermostimulated luminescence of x-ray irradiated $KMgF_3$: undoped initial (*1*) and hydrolysed (*2*) Eu_2O_3 doped (3) crystals. Insets: TL spectra of high temperature peaks.

$KMgF_3$ energy storage process takes place not only under ionizing irradiation but also at UV-exposure [5]. Co-doping by oxygen and europium leads to increase of UV sensitivity even to a higher extent as compared to hydrolysis.

The presented results testify to the fact that in ternary fluorides ($LiBaF_3$, $KMgF_3$) the interaction of crystals with air components leads to the variation of dosimetric characteristics of the material: appearance of new TSL peaks, rise of energy storage efficiency, redistribution of energy between different traps. These changes are initiated by the process of air components' diffusion into the crystal. At high temperatures in air an efficient hydrolysis of the fluoroperovskite surface takes place. It becomes apparent in the emergence of additional absorption bands in the IR and UV regions. The closeness of the induced by pyrohydrolysis absorption and thermoluminescence properties to those formed due to oxygen doping allows to assume that it is just O^{2-} ions play the decisive role in the formation of additional absorption centres and fluorescence as well as deep trapping levels and centres of radiative recombination.

Excitation of the hydrolysed or oxygen doped crystals at 230–250 nm stimulates "blue" luminescence (380–420 nm) related to O^{2-} ions [5–7]. Analogous processes take place in the described experiments too. It should be noted that removal of the surface layer from the hydrolysed samples does not eliminate completely the spsific absorption and thermoluminescence. This points to the fact that (the same way as in LiF crystals [1]) products of pyrohydrolysis and first of all O^{2-} ions which are formed on the surface of fluoroperovskites diffuse into the lattice volume during annealing.

One more effect connected with the presence of O^{2-} ions in $KMgF_3$ crystals is formation of deep carrier traps. A possibility of making super high temperature TSL dosimeters based on such crystals was mentioned elsewhere [6]. The highest energy store efficiency could be provided by simultaneous doping with oxygen and Eu^{2+} (radiative f-f transition in Eu^{2+} is not quenched up to 600°C).

Obtained results show that the problems of energy storage instability in fluoroperovskites can be surmounted. Stabilization of the high temperature TSL peaks' parameters can be achieved by means of purposeful preliminary doping of crystals with oxygen ions. Stability of high temperature TSL peaks in $KMgF_3$(Eu,O) at their high temperature annealing in air means that the additional number of oxygen ions that has a significant effect on energy storage in pure crystals is insignificant for the doped (Eu,O) perovskites. The similar effect was also observed for $LiBaF_3$ crystals containing Mg^{2+} and O^{2-} ions [7].

The energy storage effect at UV-exposure is of particular interest, this effect was found in hydrolysed $KMgF_3$ as well as in $KMgF_3$(Eu,O) crystals. Besides, TSL after UV-irradiation was recently detected in hydrolysed $LiCaAlF_6$:Ce crystals [8]. As it was mentioned above the similar effect is known for CaF_2 and MgF_2 based dosimeters [3, 4]. To understand the nature of phenomenon the further investigations are required. However, even now it can be assumed that responsible for the said effect are the products of pyrohydrolysis, first of all, O^{2-} ions, and possibly H^- ones, which create trapping and radiative recombination centres in the subsurface layers of fluoride crystals.

The studying of deep traps formation in annealed in air $KMgF_3$ and $LiBaF_3$ perovskites allow formulating several basic conclusions. After thermal treatment there appears an additional absorption in IR and UV region and luminescence connected with O^{2-} centres. Destruction of colour centres during the thermal activation process is accompanied by intensive recombination luminescence which is manifested in the form of high temperature glow curve peaks. TSL instability is explained by pyrohydrolysis of the crystal surface and diffusion of the reaction products (mainly oxygen) into the volume. The formed defects stipulate deep trapping levels of charge carriers and radiative recombination centres. Purposeful doping of crystals with oxygen allows stabilizing the dosimetric parameters of traps and making them independent on the annealing atmosphere. The hydrolysed crystals were found to be able to store energy under the UV-radiation.

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Глибокі пастки у кристалах $KMgF_3$ і $LiBaF_3$

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Роботу присвячено вивченню впливу високотемпературного відпалу на повітрі на утворення глибоких пасток у флюороперовскітах $KMgF_3$ і $LiBaF_3$. Виявлено, що у кристалах після відпалу виникає додаткове поглинання і "синє" світіння, яке пов'язане з присутністю O^{2-} іонів. Термічне руйнування центрів забарвлення в зразках, опромінених рентгенівським випромінюванням, супроводжується інтенсивною рекомбінаційною люмінесценцією у високотемпературних піках ТСЛ. Це явище може бути пояснено пірогідролізом поверхні та дифузією кисню в об'єм кристала. Показано, що гідролізовані кристали накопичують енергію під дією УФ опромінення.