

Formation of La-containing microcrystals in KCl and NaCl matrices

T.Demkiv, V.Vistovskyi, P.Savchyn, G.Stryganyuk^{},
A.Voloshinovskii, L.Demkiv^{**}*

I.Franko Lviv National University,
8 Kyryla and Mefodiya St., 79005 Lviv, Ukraine

^{*}Institute for Scintillation Materials, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine,
60 Lenin Ave., 61000 Kharkiv, Ukraine

^{**}I.Franko Lviv National University, 50 Dragomanov St.,
79005 Lviv, Ukraine

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The mechanism of the K_2LaCl_5 and $LaCl_3$ aggregate formation in KCl and NaCl matrices as a result of long-term annealing is discussed. Thermodynamic analysis of formation conditions of such aggregates has been performed. The influence of diffusion processes and the elastic deformation of aggregates by the matrix are considered. It has been shown that Ce and Pr as activator ions penetrate efficiently into aggregates.

Обсуждается механизм образования агрегатов K_2LaCl_5 и $LaCl_3$ в матрицах, соответственно, KCl и NaCl в результате продолжительного отжига. Проведен термодинамический анализ условий формирования таких лантансодержащих микрокристаллов. Учитывается влияние диффузионных процессов и энергии упругой деформации микрокристаллов под действием матрицы на условия фазообразования в исследуемых композитах. Показано, что ионы Ce и Pr эффективно входят в агрегаты K_2LaCl_5 и $LaCl_3$ в качестве активаторов.

The formation of "crystal in crystal" type composites is a promising way to obtain efficient materials for different functional uses [1, 2], in particular, fast scintillators. $K_2LaCl_5:Ce$ and $LaCl_3:Ce$ single crystals are well-known as efficient scintillation materials in the wide spectral range (γ -rays, X-rays, VUV) with high light yield, fast response and high energy resolution [3, 4]. However, those are unstable at normal conditions due to hygroscopicity and oxidation in air. Therefore, the incorporating of K_2LaCl_5 and $LaCl_3$ crystals activated with cerium or praseodymium ions into a weather-resistant insulator host is of a special interest. In order to elucidate the mechanism of K_2LaCl_5 and $LaCl_3$ phase for-

mation during long-term annealing, the thermodynamic analysis of the aggregate formation conditions has been performed.

The bulk crystals of KCl- $LaCl_3$ (1 mol.%) - $CeCl_3$ (0.05 mol.%), KCl- $LaCl_3$ (1 mol.%) - $PrCl_3$ (0.05 mol.%), and NaCl- $LaCl_3$ (1 mol.%) - $CeCl_3$ (0.05 mol.%) composition were grown in quartz ampoules by a modified Bridgman-Stockbarger technique using previously purified salts. The obtained crystals were subjected to long-term (100 h) annealing at about 600 K. As a result of such a treatment, K_2LaCl_5 or $LaCl_3$ aggregates activated with Ce^{3+} or Pr^{3+} ions were formed in KCl and NaCl hosts, respectively.

The crystal microstructure was studied using a scanning electron microscope (SEM JEOL JSM-T220A). The elemental composi-

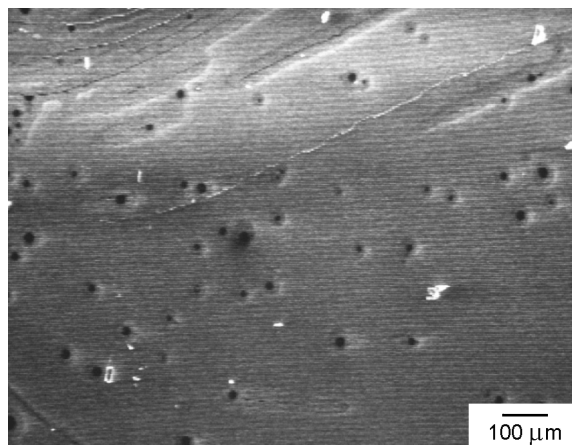


Fig. 1. Micrograph of KCl-LaCl₃(1 mol. %) freshly cleaved surface.

tion of the samples prepared by cleaving in dry atmosphere was studied using X-ray analyzer (dispersion Si (Li) detector). Micrographs were obtained using secondary electron and cathodoluminescence registration modes.

It is well-known that two stable ternary compounds could exist: K₂LaCl₅ (m.p. 636°C) and K₃La₅Cl₁₈ in KCl-LaCl₃ system [5]. In our case, however, the LaCl₃ concentration in a crystal is low (<2 mol. %), so only formation of the K₂LaCl₅ crystalline phase in KCl matrix is possible. The long-term annealing results in formation of K₂LaCl₅ microcrystals in the volume of KCl matrix. This fact is confirmed by the micrograph of a KCl-LaCl₃(1 mol. %) sample freshly cleaved surface (Fig. 1). Dark spots of 10–50 μm size located at a lighter background are clearly seen. The X-ray analysis results indicate that the mass ratio of elements in the dark spots corresponds to K₂LaCl₅ while that in the lighter background, to KCl. At the same time, no lanthanum ions have been revealed outside of dark spots.

To justify the obtained experimental results on the K₂LaCl₅ crystalline microphase formation within the KCl matrix, thermodynamic analysis has been performed. We analyzed the temperature behavior of the equilibrium constant for the reaction of K₂LaCl₅ formation from the corresponding components:



The resultant changes of standard enthalpy (ΔH_r^0) and entropy (ΔS_r^0) of this compound formation were taken from [6], where authors had studied the formation of

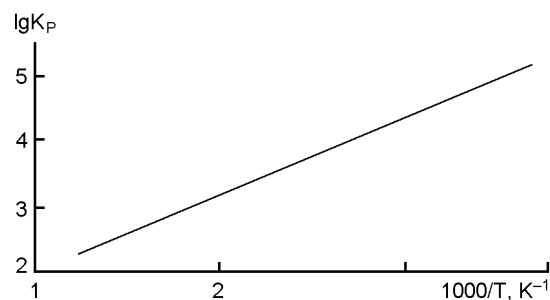


Fig. 2. Temperature dependence of the equilibrium constant K_p for the reaction of K₂LaCl₅ formation.

K₂LaCl₅ compound, analysing the following reactions: $0.6\text{KCl} + \text{LaCl}_3 = \text{K}_{0.6}\text{LaCl}_{3.6}$ and $1.4\text{KCl} + \text{K}_{0.6}\text{LaCl}_{3.6} = \text{K}_2\text{LaCl}_5$. Those (ΔH_r^0) and (ΔS_r^0) values amount – 24.5 kJ/mol and 5.7 J/(mol·K), respectively, at $T = 298^\circ\text{K}$ and $p = 10^5$ Pa. The Gibbs energy for the reaction (1) can be expressed in terms of (ΔH_r^0) and (ΔS_r^0) using Gibbs-Helmholtz equation: $\Delta G_T^0 = \Delta H_r^0 - T\Delta S_r^0$. Finally, the equilibrium constant values have been calculated using [7]:

$$K_p(T) = \exp\left(-\frac{\Delta G_T^0}{RT}\right). \quad (2)$$

As is seen from Fig. 2 the K_p value increases with temperature lowering. This means that the K₂LaCl₅ formation in KCl-LaCl₃ quasibinary system is energetically more favorable process at lower temperatures. At the same time, when the LaCl₃ concentration in KCl-LaCl₃ system does not exceed several mol. %, the diffusion of corresponding components is a necessary factor for the K₂LaCl₅ formation in KCl matrix. It is well known that diffusion occurs via random hoppings of atoms between the states corresponding to the minima of their potential energy, for example, in sites and interstitials. The temperature dependence of diffusion coefficient is defined by Arrhenius equation [8]:

$$D = D_0 \exp(-E_D/k_0T), \quad (3)$$

where D_0 characterizes the fluctuation nature of a particle hoppings; E_D is the activation energy of a diffusion process. Therefore, in order to ensure the K₂LaCl₅ aggregate formation, the activation of diffusion process, that is, the certain temperature, should be provided.

At the same time, there is one more factor that influences significantly the forma-

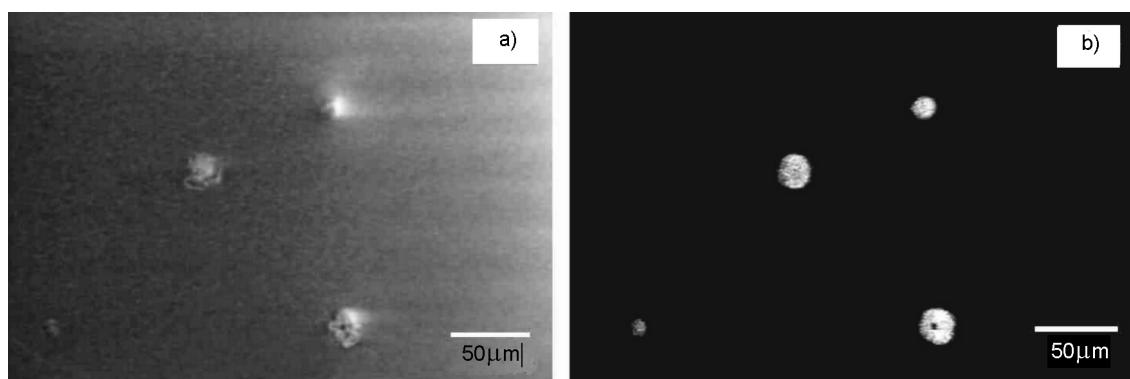
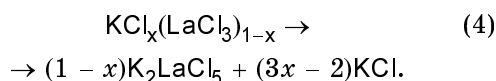


Fig. 3. Micrographs of KCl-LaCl_3 (0.5 mol. %)– PrCl_3 (0.05 mol. %) freshly cleaved surface obtained using the electron beam analysis technique in the secondary electron mode (a) and in the cathodoluminescence mode (b).

tion of aggregates in the matrix. Since the parameters of K_2LaCl_5 and KCl crystalline structures are mismatched, the crystal region where the formation of an aggregate occurs is strained. The energy of an aggregate elastic strain depends on its size and results in an increased potential well energy and thus to slowed diffusion hoppings of atoms to the aggregate formation region. As a result, the aggregate size is confined.

The K_2LaCl_5 formation reaction in a quaternary $(\text{KCl})_x(\text{LaCl}_3)_{1-x}$ system is defined as:



It is worth noting that (4) is valid at $x = 0.67$ to 1 and the K_2LaCl_5 formation is possible only in the composition range corresponding to the region of ternary compound existence on the phase diagram [5].

The free energy change of the system where K_2LaCl_5 aggregates are formed, accordingly to (4), is expressed as:

$$\begin{aligned} \Delta F = \int & \left\{ [(1-x)(H_{\text{K}_2\text{LaCl}_5} - TS_{\text{K}_2\text{LaCl}_5}^0) + \right. \\ & + (3x-2)(H_{\text{KCl}} - TS_{\text{KCl}}^0)] - \\ & - [(1-x)(H_{\text{LaCl}_2} - TS_{\text{LaCl}_2}^0) + \\ & \left. + x(H_{\text{KCl}} - TS_{\text{KCl}}^0)] \right\} dV + E_{el\ def}, \end{aligned} \quad (5)$$

where the first term defines the energy of K_2LaCl_5 phase formation and the second one, $E_{el\ def}$, the energy of an aggregate elastic strain due to the matrix. The formation of aggregates is possible at $\Delta F < 0$ [7]. The growth of an aggregate is stopped when the elastic strain energy $E_{el\ def}$ compensates the compound formation energy.

The diffusion transfer of the K_2LaCl_5 components from the matrix volume into

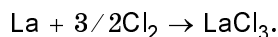
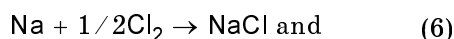
the aggregate formation region and the deformation thereof due to the matrix causes the existence of the temperature range where the K_2LaCl_5 formation is possible. The lower limit of that temperature range is due to the need for the diffusion activation of K_2LaCl_5 components and the upper one, to the compensation of the energy of the elastic straining of an aggregate in the KCl matrix. The growth of an aggregate continues until the compound formation energy will be compensated by the elastic strain energy.

The KCl-LaCl_3 (0.5 mol%)– CeCl_3 (0.05 mol. %), KCl-LaCl_3 (0.5 mol. %)– PrCl_3 (0.05 mol. %) crystals were grown adding CeCl_3 or PrCl_3 into the charge, respectively. As a result, the $\text{K}_2\text{LaCl}_5:\text{Ce}$ and $\text{K}_2\text{LaCl}_5:\text{Pr}$ aggregates embedded in KCl host were formed. The diffusion migration of Ce or Pr ions through the crystal results in the accumulation of these elements in the regions where the K_2LaCl_5 aggregates are formed. The micrographs of such composites in the secondary electron mode and in the cathodoluminescence one are shown in Fig. 3. Those confirm the activation of K_2LaCl_5 microcrystals by Ce or Pr ions. As is seen, only the aggregates emit the light, that is possible in the case of the impurity penetration into microphase. Thus, Pr ions enter mainly the K_2LaCl_5 microphase. A similar situation is observed in the case of Ce ions.

The formation of only LaCl_3 crystallites in NaCl-LaCl_3 (1 mol. %)– CeCl_3 (0.05 mol. %) crystal comes from the phase diagram of NaCl-LaCl_3 system [9], where the solid solution of raw compounds exists in the whole range of their concentrations. Thus, it is sufficient to compare the equilibrium constant values for the reactions:

Table. Thermodynamic data at $T = 298$ K and $p = 10^5$ Pa [11, 12]

Compound	ΔH^0 , J/mol	ΔS^0 , J/mol·K	C_p , J/mol·K
KCl	-435900	82.56	51.29
LaCl ₃	-1070700	144.3	98.031
NaCl	-411100	72.12	49.71
Na	0	51.45	28.16
La	0	57.3	27.6
Cl ₂	0	222.9	34.94

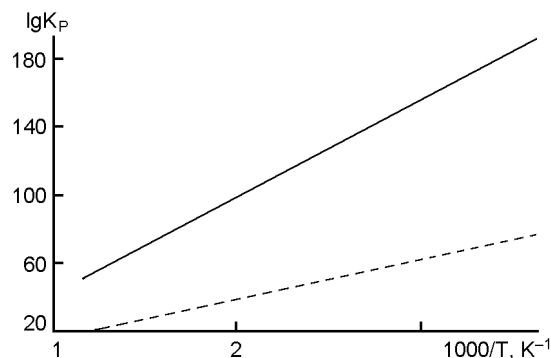
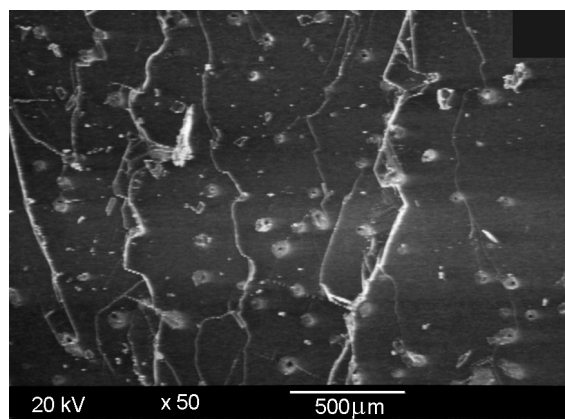


The temperature dependence of Gibbs energy has been obtained in the first Ulich approximation [7]. The data used in calculation are shown in the Table. The calculation results of the temperature dependence of equilibrium constants are presented in Fig. 4. It is seen from the Figure that the equilibrium constant values of LaCl₃ formation exceed those for NaCl. This indicates the higher priority of the aggregation process of the La-containing phase. Since the aggregation occurs due to the diffusion, our previous suggestions about the formation mechanism of K₂LaCl₅ in KCl matrix are valid for the NaCl–LaCl₃ system as well. In addition, similar to the case of KCl–LaCl₃ system, embedded LaCl₃ aggregates are strained due to the mismatch between the LaCl₃ and NaCl crystalline structure parameters. The elastic strains arising at this condition causes the size confinement of aggregates.

The diffusion migration of Ce ions through the crystal results in formation of LaCl₃:Ce aggregates embedded in NaCl, similar as in the case of K₂LaCl₅ aggregate formation. In the NaCl–LaCl₃ crystals activated with Ce ions, it is also expected that the diffusion behavior of Ce ions is similar to that of La ions.

The surface microstructure of NaCl–LaCl₃(1 mol. %)-CeCl₃(0.05 mol. %) crystal (Fig. 5) evidences the formation of LaCl₃:Ce aggregates in NaCl. The embedded aggregates are clearly seen in this micrograph and they emit light in the cathodoluminescence mode [10]. The results of the qualitative X-ray analysis indicate that the embedded aggregates contain La and Cl elements in the ratio corresponding to the LaCl₃ compound. The luminescence of these aggregates shows that Ce ions enter mainly LaCl₃ microcrystals.

To conclude, in KCl–LaCl₃ (1 mol. %) and NaCl–LaCl₃ (1 mol. %) systems, K₂LaCl₅

Fig. 4. Temperature dependences of equilibrium constants for LaCl₃ (solid line) and NaCl (dashed line) formation.Fig. 5. Micrograph of NaCl–LaCl₃ (1 mol. %)-CeCl₃ (0.05 mol. %) freshly cleaved sur-

and LaCl₃ microcrystals embedded in KCl and NaCl matrices, respectively, are formed as a result of long-term annealing. Such a formation has been confirmed by the scanning electron microscopy and X-ray microanalysis. Thermodynamic analysis of the La-containing microcrystals formation conditions and taking into consideration the diffusion of components and the strain of aggregates made it possible to explain the existence of the optimal temperature range where the formation of such aggregates is energetically favorable process. Ce and Pr ions have been found to penetrate efficiently K₂LaCl₅ and LaCl₃ microcrystals embedded in KCl and NaCl hosts as a consequence of long-term annealing.

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Формування лантановмісних мікрокристалів у матрицях NaCl та KCl

Т.Демків, В.Вістовський, П.Савчин, Г.Стриганюк, А.Волошиновський, Л.Демків

Обговорюється механізм утворення агрегатів K_2LaCl_5 та $LaCl_3$ у матрицях KCl та NaCl, відповідно, внаслідок тривалого відпалу. Проведено термодинамічний аналіз умов формування таких лантановмісних мікрокристалів. Враховується вплив дифузійних процесів та енергії пружної деформації мікрокристалів зі сторони матриці та умови фазоутворення у композитах, що досліджуються. Показано, що іони Ce та Pr у ролі активаторів за малих концентрацій і тривалого відпалу ефективно входять в агрегати K_2LaCl_5 та $LaCl_3$.