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SOLUTE DISTRIBUTION IN CaF_2 CRYSTALS DOPED WITH Pb^{2+} IONS

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Abstract
In this paper, the solute axial distribution in CaF_2 : Pb^{2+} crystals has been experimentally and numerically established, for the 1% - Pb^{2+} doped crystal. It has also been found that the absorption coefficient depends on the Pb^{2+} concentration and this dependence is nearly linear at lower values of the solute concentration (1-3%). An approximate estimation of the segregation and diffusion coefficients has been made. The numerical results are in a quite good agreement with the experimental ones. The longitudinal distribution of the Pb^{2+} solute measured along the crystal shows some oscillations, like in the case of the semiconductors.

1. Introduction

In alkaline-earth fluorides crystal hosts, the Pb^{2+} ions perform interesting optical properties. Their absorption spectra present 4 bands, denoted A, B, C, D (in order of energy increasing). In x-ray irradiated SrF_2 , CaF_2 , BaF_2 crystals doped with Pb^{2+} ions, three other types of axial centres appear: $Pb^{+}(1)$, $Pb^{+}(1)$ - Pb^{2+} and $Pb^{0}(2)$ [1]. Similar with $Tl^{0}(1)$ laser centres in alkali halides [2-4], the $Pb^{+}(1)$ centres in alkaline-earth fluorides are expected to be attractive laser centres [1]. The disadvantage is that the emission band of the $Pb^{+}(1)$ centres overlaps the absorption band of the $Pb^{0}(2)$ centres and so, laser effect based on $Pb^{+}(1)$ centres has not been obtained yet. However, it seems possible to prevent the $Pb^{0}(2)$ centres formation, choosing a proper lead concentration and an adequate irradiation temperature [1]. For this purpose, intending to obtain CaF_2 crystals with the proper Pb^{2+} concentration and very homogeneous, we have experimentally and numerically investigated the solute distribution in CaF_2 crystals doped with Pb^{2+} ions in different concentrations (1%, 2%, 3,66%).

2. Experimental details

The various concentrations (1%, 2%, 3,66%) Pb^{2+} - doped CaF_2 crystals have been grown using vertical Bridgman method [5]. Suprapure grade Merck calcium and lead fluoride were used as starting materials.

The absorption spectra of about 2 mm thin samples (obtained after a transversally cutting of the crystals) have been recorded at room temperature, using a Schimadzu 1650 PC UV – VIS spectrophotometer.

The absorption coefficient has been measured for the absorption band located at 305 nm and then, the solute concentration has been computed by interpolation of the absorption coefficient values for various initial concentrations (1%, 2%, 3,66%) of Pb^{2+} ions in crystals.

The solute axial distribution has been established for the 1% - Pb^{2+} doped crystal, which was transversally cut in 20 parts and the UV - VIS absorption spectra were recorded for each part of this crystal.

3. Experimental results

It has been found that the absorption coefficient depends on the Pb^{2+} concentration and this dependence is nearly linear at lower values of the solute concentration (1-3%). Figure 1 presents the absorption coefficient of the CaF_2 : 3,66 % Pb^{2+} crystal at room temperature.

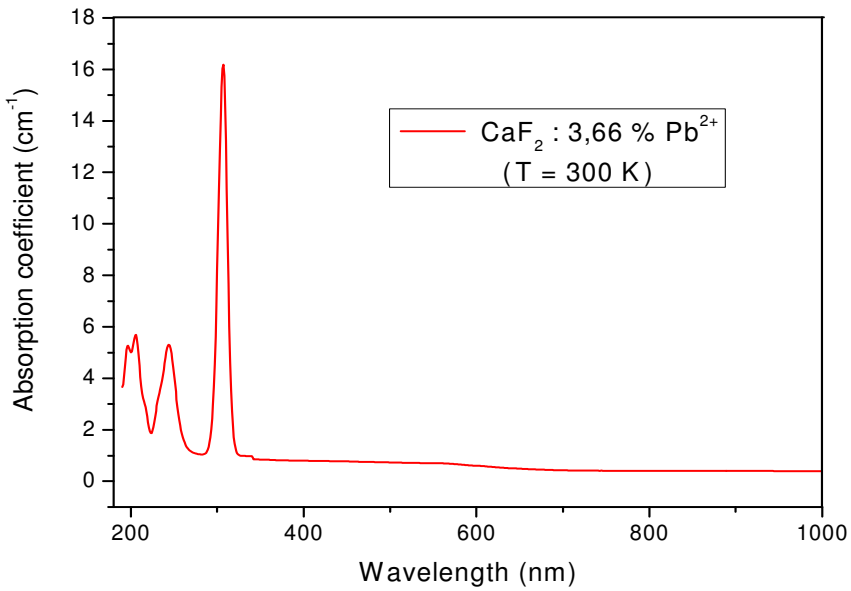

Fig. 1. *The absorption coefficient of the CaF_2 : 3,66 % Pb^{2+} crystal at room temperature.*

4. Numerical simulation

The numerical computation of the solute distribution has been performed with the commercial code FIDAP, using the parameters presented in table 1.

Table 1

Parameter	Symbol	Value
Crystal radius	R	0,0055 m
Crucible radius	R_C	0,007 m
Crucible length	L	0,07 m
Crucible lowering rate	v	$1{,}1 \cdot 10^{-6}$ m/s
Temperature axial gradient	G_T	2000 K/m
Solidification temperature	T_S	1653 K

The calculus of the doping distribution in crystal needs the simultaneous computing of the following equations:

- the mass conservation equation:

$$\rho \nabla \vec{u} = 0 \tag{1}$$

- the heat transfer equation:

$$\rho c_P \left(\frac{\partial T}{\partial t} + \vec{u} \nabla T \right) = k \nabla^2 T - \nabla \vec{q}_R \tag{2}$$

- the Navier – Stokes equation:

$$\left[\frac{\partial \vec{u}}{\partial t} + (\vec{u} \nabla) \vec{u} \right] = -\nabla p + \mu \nabla^2 \vec{u} - \rho_0 \vec{g} \left[\beta_T (T - T_0) \right] \tag{3}$$

- the diffusion equation:

$$\frac{\partial C}{\partial t} + \vec{u} \nabla C = D \nabla^2 C \tag{4}$$

5. Numerical results

Near the interface, the isotherms are convex, because of the temperature radial variation, due to the difference between the thermal conductivities of the solid and liquid states. Interface deflection is f = 1,3 mm.

The fluid ascents near the crucible walls and descents near the symmetry axis. Maximal convection speed is $u_{\max}$ = 1,5 ·10-5 m/s.

The iso-concentrations are deformed because of the fluid flow, which move the doping near the crucible wall, where the concentration is higher.

6. Discussion

Because the segregation (K) and the diffusion (D) coefficients are unknown for the $CaF_2 : Pb^{2+}$ crystals, an approximate estimation of these constants has been made from the experimental results: $K \approx 0,8$; $D \approx 5 \cdot 10^{-9}\ m^2/s$.

The comparison of the experimental and numerical computed values of the solute Pb^{2+} concentration shows that the numerical values (obtain using the previous values for K and D) are quite smaller then the experimental ones. A better agreement probably can be obtained choosing a more adequate value for the diffusion coefficient. Figure 2 presents the comparison of the experimental and numerical results, for the average radial concentration.

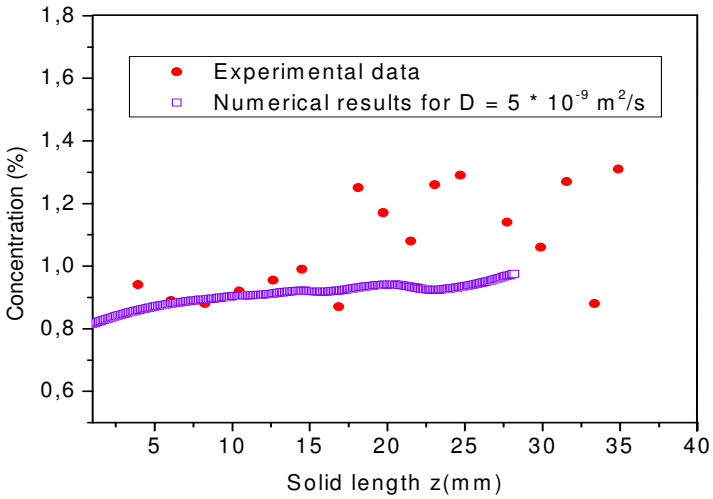

Fig. 2. *The comparison of the experimental and numerical results, for the average radial concentration.*

The longitudinal distribution of the Pb^{2+} solute measured along the crystal shows some oscillations. Such oscillations have also been obtained for other doped crystals, like semiconductors.

7. Conclusions

- An approximate estimation of the segregation and diffusion coefficients for $CaF_2 : Pb^{2+}$ crystals has been made.

- The solute axial distribution has been established for the 1% - Pb^{2+} doped crystal. The numerical results are in a quite good agreement with the experimental ones. A better agreement probably can be obtained choosing a more adequate value for the diffusion coefficient.

- The longitudinal distribution of the Pb^{2+} solute measured along the crystal shows some oscillations, like in the case of the semiconductors.

- We expect to obtain more precise values for the segregation and diffusion coefficients, comparing the experimental and numerical results of the solute distribution of various concentration Pb^{2+} ions in CaF_2 crystals. So, we hope to determine the growth conditions for these crystals, in order to obtain a high doping homogeneous.

8. Acknowledgement

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