

Radiation-Thermal Diffusion Of Cationic Impurities In Sub-Surface Layers Of Ionic Crystals

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Abstract – The paper describes research results of high-temperature diffusion of isovalent (Na) and heterovalent (Mg, Al) impurities in the sub-surface layers of ionic crystals KBr under the conditions of strong electron radiation.

Homogenizing annealing was carried out under the conditions of thermal and electron-beam heating of crystals. Parameters of the used electron bunch ensured both a high input rate of radiation defects and heating of specimens. Annealing temperature span (760–880) K was in accord with the intrinsic diffusion region. Annealing time set for the experiments ensured doping agents' penetration into moderate depth not exceeding (1–2) μm . Depth impurity distribution after homogenizing annealing of crystals was carried out by means of secondary ion mass-spectrometry.

Measured temperature dependencies of diffusion coefficients under thermal (D_T) and radiation-thermal (D_{RT}) heating are described by the following Arrhenius's expression (activation energy of the process is given in eV, and a diffusion coefficient in cm^2/s):

$$\text{for Na in KBr} - D_{T,RT} = 1.2 \cdot 10^{-2} \exp\left(-\frac{1.37}{kT}\right);$$

$$\text{for Al in KBr} - D_T = 1.9 \cdot 10^{-8} \exp\left(-\frac{0.81}{kT}\right)$$

$$D_{RT} = 3.15 \cdot 10^{-4} \exp\left(-\frac{1.45}{kT}\right);$$

$$\text{for Mg in KBr} - D_T = 3.5 \cdot 10^{-9} \exp\left(-\frac{0.74}{kT}\right)$$

$$D_T = 1.5 \cdot 10^{-6} \exp\left(-\frac{1.06}{kT}\right).$$

The results denote intensification of multivalent cations' diffusion in the studied crystals under strong electron radiation. Radiation in the sub-surface layers involves a substantial increase in values of a preexponential number as well as the process activation energy. Analysis of possible causes of radiation impact on the diffusion process.

1. Introduction

Diffusion phenomena in solids have been widely investigated. However, the most important problem of atom diffusion in the region immediately adjacent to the solid surface was given undeservedly little atten-

tion to. Moreover, these are the properties of sub-surface layers and features of doping agent transfer that might limit a rate of diffusion. A sub-surface layer of materials is in a specific physical-chemical state. It is substantially filled up with structural defects (vacancies, dislocations, impurities) and its properties differ from properties of the main bulk. So it is not surprising that a specific state of sub-surface layers might influence kinetics of various processes, including diffusion.

A systematic research in this field has not been practically carried out. A main reason for that was absence of reliable methods for measuring diffusion profiles in sub-surface laminas of condensed mediums. Wide application of various microprobe techniques for element structure analysis of sub-surface layers of materials helps solve this problem. One of these techniques is a method of secondary ion mass-spectrometry (SIMS). Due to a low rate of the surface atomization by ion beam, specimen laminas, first of all, sub-surface layers, length of which depends on the material nature and method for its preparation and preprocessing, are probed. This makes possible to obtain important information on peculiar properties of diffusion phenomena in crystals adjacent to the surface.

This paper presents the research results of the high-temperature diffusion of isovalent Na and heterovalent Mg, Al impurities in sub-surface layers of ionic crystals KBr and its change under the conditions of strong electron radiation.

2. Experimental technique

During experiments a makeup chipped surface of crystals was covered with films of proper diffusants (doping agents) by thermal vacuum evaporation. Within a set of research experiments on diffusion of heterovalent ions in potassium bromide the surface was covered with metal films of aluminum or magnesium. Due to a high hygroscopicity of haloid salts of the noted elements their use was not possible. Use of other similar doping agents was mapped out as the used mass-spectrometer did not allow us to reliably register and select proper signals. To study sodium diffusion in potassium bromide sodium chloride films were used.

Homogenizing annealings were carried out under the conditions of thermal and electron-beam heating of crystals. Analogously to the experiments described

in paper [1], an electron accelerator *ELV-6* with the electron energy of 1,4 MeV and the continuous bunch current density of $2,5 \mu\text{A}/\text{cm}^2$ was used for radiation heating-up of specimens. Annealing temperature span was set as 760 – 880 K, which was in accord with intrinsic diffusion region.

Annealing time was so that it provided for penetration of doping agents into moderate depths. The information mainly related to processes in crystal sub-surface layers. Obtained diffusion profiles were approximated by solution of the Fik's equation. This helped estimate representative values of sub-surface diffusion coefficients.

3. Experimental results

On the basis of experimental results data on temperature dependencies of coefficients sub-surface diffusion of heterovalent cation impurities in crystals (Fig. 1).

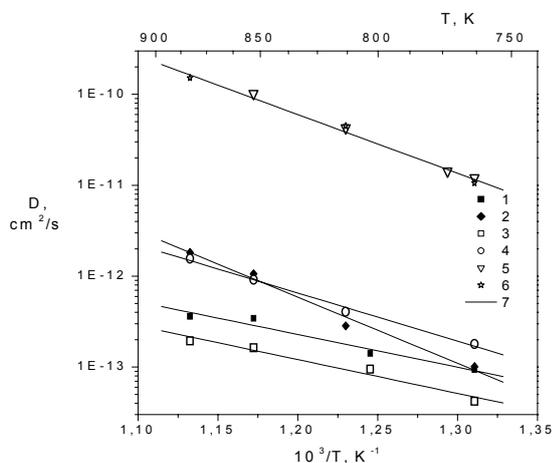


Fig. 1. Temperature dependencies of diffusion coefficients for ions Na, Mg, Al in crystals KBr.

1, 2 – diffusion from aluminum film, under thermal and radiation-thermal annealing, respectively;
3, 4 – diffusion from magnesium under thermal and radiation-thermal annealing, respectively;
5, 6 – diffusion from sodium chloride film under thermal and radiation-thermal annealing, respectively;
7 – straight approximating experimental points

Measured temperature dependencies of diffusion coefficients under thermal D_T and radiation-thermal D_{RT} heating are described by the following Arrhenius's expression (activation energy of the process is given in eV, and a diffusion coefficient in cm^2/s):
for Na in KBr –

$$D_{T,RT} = 1.2 \cdot 10^{-2} \exp\left(-\frac{1.37}{kT}\right) \quad (1)$$

for Al in KBr –

$$D_T = 1.9 \cdot 10^{-8} \exp\left(-\frac{0.81}{kT}\right) \quad (2)$$

$$D_{RT} = 3.15 \cdot 10^{-4} \exp\left(-\frac{1.45}{kT}\right) \quad (3)$$

for Mg in KBr –

$$D_T = 3.5 \cdot 10^{-9} \exp\left(-\frac{0.74}{kT}\right) \quad (4)$$

$$D_T = 1.5 \cdot 10^{-6} \exp\left(-\frac{1.06}{kT}\right) \quad (5)$$

The analysis has shown that in the sub-surface layer (up to 1–2 μm), contacting with the film, an estimated value of coefficients of thermal diffusion D_S for all studied impurities was ever smaller than the known values of diffusion volume coefficients. For univalent cations this difference is about one order of the value, and for polyvalent impurities it is more essential, reaching 2–3 orders.

4. Discussion of the results

It is very hard to interpret of the obtained experimental data on diffusion of impurity cations in the sub-surface layers at this stage of research. This is mainly caused by weak study of the phenomenon and absence of any conceptions about diffusion mechanisms in crystal regions adjacent to the surface. In the first place, it should be focused that as a whole the parameters characterizing the given diffusion process, namely, a preexponential member D_{0S} and activation energy H , greatly differ from the known values typical for a volume thermal heterodiffusion. To compare let us analyze typical experimental values of parameters for a volume diffusion of some impurities in AHC presented in Table 1.

From the Table we can see that D_0 is by a few orders bigger than values D_{0S} , typical for heterodiffusion in sub-surface layers. At the same time the process is characterized by a higher value of activation energy. It should be noted that in contrast to the case of polyvalent impurity cations the parameters representing a diffusion of isovalent impurity of sodium in the bulk and sub-surface crystal region do not differ to a great extend.

Values from Table 1 are easily verified for the purpose of their conformity with the known mechanisms of impurity diffusions in the lattice of AHC. In this connection a physical meaning of the parameters of the Arrhenius's equation D_0 and activation energy H should be analyzed at the level of elementary diffusion event depending on the process mechanism.

Table I. Representative parameters of the Arrhenius's equation for volume heterodiffusion in intrinsic region in alkali-haloid crystals (AHC) [2]

Crystal	Doping agent	Temperature span, K	D_0 , cm ² /s	H , eV
KCl	Na ⁺	850–950	33	1.975
KBr	Na ⁺	850–950	4.23	1.64
NaCl	Co ⁺²	820–1090	$7.6 \cdot 10^{-2}$	1.33
KCl	Co ⁺²	820–1090	$1.2 \cdot 10^{-1}$	1.27
NaCl	Ca ⁺²	950–1060	$1.3 \cdot 10^{-1}$	1.55
NaCl	Sr ⁺²	870–1020	$4.13 \cdot 10^{-2}$	1.36
KBr	Pb ⁺²	700–850	$1.6 \cdot 10^{-1}$	1.16

For this purpose we have used sufficiently proved functional dependences of impurity diffusion coefficients in AHC on temperature and process thermodynamic parameters obtained on the basis of thermodynamic approach [2]. Their type is determined by a doping agent type and a diffusion mechanism. A diffusion coefficient of isovalent cation impurity in the intrinsic temperature span is:

$$D(Me^+) = 4a^2 \cdot f \cdot \nu_0 \cdot \exp\left(\frac{S_m + \frac{S_s}{2}}{k}\right) \exp\left(-\frac{H_m + \frac{H_s}{2}}{kT}\right) \quad (6)$$

where ν_0 – Debye-like vibration frequency, a – lattice parameter, k – Boltzmann spacing, H_s and S_s – enthalpy and entropy of Schottki pair formation, H_m and S_m – enthalpy and entropy of migration, respectively.

For diffusion coefficients of heterovalent cations in the intrinsic region the following expression takes place:

$$D(Me^{+2}) = 4a^2 \nu_0 f \exp\left(\frac{S_s/2 + S_{m++} - S_a}{k}\right) \exp\left(-\frac{H_s/2 + H_{m++} - H_a}{kT}\right) \quad (7),$$

where H_a и S_a – enthalpy and entropy of associations of an heterovalent cation with a cation vacancy.

In formulas (6) and (7) a product of multipliers independent on the temperature is nothing but D_0 . As result of calculation numerical values of D_0 and H have been obtained for the above mentioned cases. They coincided with the values given in Table 1 in the range of one-two orders. This coincidence can be reckoned satisfactory, taking into consideration estimated character of calculations and absence of sufficiently accurate values of thermodynamic parameters. Values of enthalpy and entropy representing a diffu-

sion process in KBr, borrowed from paper [2], were the following: $S_s = (6.5-7.18) k$; $S_m = (2.54-2.9) k$; $S_a = (1.82-2.5) k$; $H_s = (2.13-2.37) \text{ эВ}$; $H_m = (0.6-0.7) \text{ эВ}$; $H_a = (0.5-0.6) \text{ эВ}$.

Thermodynamic parameters representing a diffusion process in disrupted sub-surface layers are likely to differ from the values typical for the lattice bulk. It is not inconceivable that this factor with reference to an isovalent impurity is of crucial importance concerning change of its diffusion activity in these layers. Moreover, change in the values of thermodynamic parameters within reasonable limits (even under their most unfavorable combination) does not provide for obtaining experimental values of parameters D_{0s} and H_s , representing diffusion of heterovalent cations in crystal sub-surface layers.

The conducted analysis has shown that basic models and equations, normally used to describe a bulk diffusion of heterovalent impurities, agree with experimental results rather well and, at the same time, do not represent an objective physical essence of the phenomenon in sub-surface layers of AHC. It is obvious that a diffusion mechanism of polyvalent cations under the experimental conditions cardinally differ from the bulk diffusion. This distinction is likely to be concerned with a manner of a doping agent penetration into sub-surface layers. Under the condition of heating and contact with air impurities might interreact with oxygen with the following formation metal oxides. It is not inconceivable that an impurity cation in bound state penetrates in sub-surface layers in the form of compound stiff molecular oxide complexes.

Data, presented in Fig. 1, illustrate that coefficients of thermal diffusion of sodium ions are almost three orders differ from polyvalent impurity cations in potassium bromide. Experimental research emphasize a variant character of radiation thermal impact on a sub-surface diffusion of the considered impurities in crystal. The rate of high-temperature heterodiffusion of isovalent cations is practically the same both in the radiation filed and in the absence of it. However, a sub-surface diffusion of heterovalent cations in AHC under strong irradiation accelerates noticeably. It should be pointed out that in this case a radiation impact involves

rise of both preexponential member in the Arrhenius's equation and activation energy of the process.

4. Conclusions

Comparison of the data on radiation impact on the diffusion of isovalent and heterovalent impurities in potassium bromide brings to the conclusion that high-intensity bunches of accelerating electrons are not capable to activate fast diffusion processes in subsurface layers of ion crystals, but might provide for ac-

celeration of heterodiffusion processes that, as a rule, have a low rate.

References

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