Diffusion mass transfer in ionic materials under intense electron irradiation

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Abstract. The results of studies on the impact of an electron beam with the energy of 1-2 MeV on diffusion processes in materials with ionic bonds are presented in the paper. Used electron beam intensity is allowed to provide heating of the material to temperatures of 1600 K. Diffusion of Na, Mg, Al ions into single crystals KBr in the temperature range 573-883 K, Al ions in the NiO-AlO system at 1373-1573 K, was studied. Diffusion annealing carried out under thermal and radiation-thermal heating of the samples. Then diffusion coefficients were determined. It was found stimulating action of irradiation on diffusion processes of Mg, Al ions in Kbr and Al ions in the NiO-Al_2O_3 system, which consists in increasing the diffusion coefficients at radiation-thermal annealing. The observed effect is achieved by increasing the effective rate of diffusion jumps.

1. Introduction

Concentrated streams of energy can be used for processing organic and inorganic materials [1-4]. Several authors [5-9] proposed a method based on the use of high-intensity beam of the high-energy electrons to heat and to activate the process of sintering of ceramic materials. A beam of the high-energy electrons (1.4-2.0 MeV) transfers its energy to the entire volume of irradiated material at the same time. Thereby, the thermal conductivity factor limiting the process rate is eliminated. Apart from the purely thermal effect of heating speed, it may have a phenomenon of the radiation-thermal activation of the diffusion processes underlying ceramic production. Therefore, research directed on revealing the impact of the irradiation on mass transfer, are of great interest.

This report summarizes the studies of high-temperature diffusion carried out by us in several ionic compounds under irradiation of accelerated electrons beam, providing both a high rate of radiation defects, and heating of the samples. Here we studied the effect of the irradiation on different types of diffusion processes.

Diffusion crystals doping of the impurities examined by the example of the most simple in composition and structure of alkali halide crystals (AHC). Diffusion limiting solid phase synthesis was investigated by conducting the reaction leading to the formation of spinel $NiAl_2O_4$ by the interaction between the nickel oxide and alumina.

2. Experimental results and discussion

2.1. Research of heterodiffusion under intense electron irradiation in AHC

Single crystals of potassium bromide were used in the experiments. It was studied the diffusion of impurity ions with different charge state: Na^+, Mg^{2+}, Al^{3+}. Diffusion annealing carried out under conditions of thermal and electron beam heating of the crystals. We used electron accelerator ELV-6 (INP SB RAS, Novosibirsk) for radiative heating of samples with the electron energy of 1.4 MeV and the continuous beam current density of 2.5 mA/cm^2.

The depth profiles of impurity ions were investigated by secondary ion mass spectroscopy (SIMS). The technique of the profiles measurement, excluding the effects of the crater and the charging surface, is described in [10-12].

2.1.1. Diffusion of ions Na^+.
Diffusion carried from the thin film of NaCl (200-400 nm thickness) deposited on the surface KBr single crystal by thermal evaporation under vacuum. Diffusion annealing of the different samples was performed in the temperature range of 573-883 K for 20 min. In the semi-logarithmic coordinates the temperature dependence of the coefficients of thermal (D_T) and radiation-thermal (D_{RT}) diffusion of sodium ions in KBr lattice approximated by two temperature portions with different activation energy of the process (the activation energy is given in eV):

$$D_T = 1.3 \cdot 10^{-7} \cdot \exp(-\frac{0.51}{kT}) + 7.3 \cdot \exp(-\frac{1.68}{kT}), \text{ cm}^2/\text{s};$$

$$D_{RT} = 2.3 \cdot 10^{-7} \cdot \exp(-\frac{0.55}{kT}) + 3.8 \cdot \exp(-\frac{1.67}{kT}), \text{ cm}^2/\text{s}.$$

Irradiation did not affect on the diffusion process of isovalent impurity over the entire temperature range.

Mechanisms of impurities thermal diffusion in AHC analyzed at the literature [13]. It is found, that the impurities homologues diffusion, as well as self-diffusion is performed by the vacancy mechanism. In accordance with these views the low-temperature portion is likely caused by the migration of sodium on the biographical origin cation vacancies, the concentration of which is determined primarily crystal contamination of multivalent cationic impurities. The concentration of these vacancies (N_{imp}) was estimated by us on the basis of the ion conduction measurements of used crystals. According to the calculations the measured diffusion coefficients were provided by the original defectiveness of the cation sub-lattice at 10^{-7} mol. fractions in the low-temperature area. The activation energy of diffusion in this area is close to the activation energy for migration of the cation vacancies, which is consistent with the considered model of the process. Diffusion limited thermodynamically equilibrium vacancies at higher temperatures.

In accordance with the mechanism of Dienes-Damask [14], the main condition for the stimulation of diffusion processes in radiation fields is the excess of the stationary concentration of radiation vacancies (N_{irr}) over the thermodynamically equilibrium concentration (N_{th}) and N_{imp}. The calculations of these values show that it does not hold in the realized experimental conditions. N_{th} was determined according to the formula proposed by Lydiard [15], and N_{irr} in accordance with the kinetic model Dienes-Damask. The rate of radiation defects was set equal to 10^{-3}-10^{-9} s^{-1}. Thus, the results of the study suggest that the Dienes-Damask mechanism of the radiation diffusion stimulation is ineffective at high temperatures.

2.1.2. Diffusion of heterovalent impurities in the KBr.
The thin metallic films of aluminum or magnesium were deposited on the crystal surface by thermal evaporation under vacuum in this series of experiments. The diffusion profiles were measured by SIMS. The results in Table 1 indicate the intensification of heterovalent impurities diffusion in potassium bromide under electron irradiation.

Temperature dependence of ion diffusion coefficients of Al^{3+} and Mg^{2+} for thermal and radiation-thermal annealing are described by expressions (the activation energy is given in eV):

$$D_T^{Al}(T) = 5.58 \cdot 10^{-7} \exp(-\frac{1.03}{kT}), \text{cm}^2/\text{s}; \quad D_{RT}^{Al}(T) = 1.18 \cdot 10^{-2} \exp(-\frac{1.68}{kT}), \quad \text{cm}^2/\text{s} \quad (1)$$

$$D_T^{Mg}(T) = 4.18 \cdot 10^{-6} \cdot \exp(-\frac{1.2}{kT}), \text{cm}^2/\text{s}; \quad D_{RT}^{Mg}(T) = 3.81 \cdot 10^{-3} \cdot \exp(-\frac{1.6}{kT}), \text{cm}^2/\text{s}. \quad (2)$$

Table 1. The diffusion coefficients of heterovalent cations in KBr.

Temperature, K	Mg^{+2} ions		Al^{+3} ions	
	D_T, cm²/s	D_{RT}, cm²/s	D_T, cm²/s	D_{RT}, cm²/s
673	$5.4 \cdot 10^{-14}$	$4.8 \cdot 10^{-14}$	$2.65 \cdot 10^{-14}$	$3.0 \cdot 10^{-14}$
763	$1.0 \cdot 10^{-13}$	$1.3 \cdot 10^{-13}$	$9.3 \cdot 10^{-14}$	$9.8 \cdot 10^{-14}$
813	$1.3 \cdot 10^{-13}$	$3.8 \cdot 10^{-13}$	$2.1 \cdot 10^{-13}$	$4.9 \cdot 10^{-13}$
853	$3.2 \cdot 10^{-13}$	$1.4 \cdot 10^{-12}$	$4.45 \cdot 10^{-13}$	$1.2 \cdot 10^{-12}$
883	$6.2 \cdot 10^{-13}$	$3.6 \cdot 10^{-12}$	$8.3 \cdot 10^{-13}$	$3.5 \cdot 10^{-12}$

Equations (1) - (2) show that radiation exposure causes an increase in the activation energy of the diffusion process and the pre-exponential factor D_0. In this respect, the situation is radically different from the characteristic of the impurity monovalent ions diffusion where these parameters are insensitive to the effects of the irradiation. Obviously, the observed effect of the stimulation of the magnesium and aluminum ions diffusion under electron irradiation is associated with their charge state different from the charge matrix ions. Multiply charged cations interact effectively with the generated electron-hole pairs in the lattice of AHC in the field of radiation. However, they can change their charge at the electron localization and make the diffusion jumps in different charge states. Perhaps for this reason there is an increase the activation energy of diffusion. The growth D_0 shows an increase in the frequency of jumps under irradiation, which is naturally related to the concentration of vacancy defects. As shown above, the Dienes-Damask mechanism implementation is not able to significantly affect this value. Theoretically, one can assume the existence of spatial correlations between diffusing ion and the cation vacancies accumulated in the surrounding area, which may increase the probability of ion hopping. However, quantifying the contribution of this process to increase the parameter D_0 is not yet possible.

2.2. Investigation of the diffusion controlling the solid-phase synthesis under electron-beam heating.
To study the nickel aluminate spinel synthesis reaction was chosen. This reaction is characterized by a number of advantages that make it suitable for use in diffusion experiments. $NiAl_2O_4$ is the only product of the reaction between the starting oxides, the production rate constant $NiAl_2O_4$ is relatively large and there is practically no mutual solubility between the α-Al_2O_3 and NiO. Experiments were carried out as follows. A thin nickel film with thickness 0.25-0.30 microns was deposited by thermal evaporation in vacuum on a polished surface of the aluminum oxide crystals. Subsequently nickel film was oxidized to NiO in air at the temperature of 1073 K insufficient for spinel formation. Then, solid-phase synthesis of the compound was carried out at higher temperatures by thermal and radiation-thermal heating. The irradiation was made by the accelerator ILU-6 (INP SB RAS, Novosibirsk) with the electron energy of 2.0 MeV. Absorbed dose rate is 20-60 kGy/s. The layer thickness of the spinel formed on the side of NiO was measured with a micro-interferometer MII-11 after removing from sample of unreacted NiO by hydrogen reduction at 823K for three hours and then selectively dissolving the metal in 10% nitric acid solution. The reduction temperature was chosen to 80-90 K below start temperature of the recovery $NiAl_2O_4$.

The growth kinetics of the spinel layer under irradiation as well as in the thermal heating obeyed the parabolic law $x^2 = k \cdot t$, where x is the thickness of the product layer; k - parabolic constant of

formation rate of NiAl$_2$O$_4$; *t* - time. Based on this law, it was calculated the values of *k*, and set their temperature dependence for the compared methods of sample heating (the activation energy is given in eV):

$$k_T = 2.7 \times 10^5 \exp\left(-\frac{5}{kT}\right), \text{cm}^2/\text{s}; \quad k_{RT} = 1.8 \times 10^6 \exp\left(-\frac{5}{kT}\right), \text{cm}^2/\text{s}.$$

It is seen that the irradiation does not alter the activation energy of the process. Radiation-stimulated growth constant *k* is caused by an increase in pre-exponential factor, suggesting an increase in the frequency of cations jumps.

To quantify the diffusion process, the thermodynamic theory of solid-phase reactions [16, 17] should be used, which is based on the following provisions:

1. The reaction rate is limited by diffusion of ions through the product layer.

2. The product layer is compact and its non-equilibrium defects (dislocations, grain boundaries) do not make a decisive contribution to the ion mobility.

3. The reactions at the phase boundaries occur more rapidly than diffusion processes. Hence, local thermodynamic equilibrium is established at the phase boundaries.

4. Individual ions move independently. There is electroneutrality at any cross section of the product.

According to [18] the rate of NiAl$_2$O$_4$ formation is limited by Al^{3+} ions diffusion through the product. Parabolic *k* and rational ($k_1 = k/2V$, where *V* - equivalent volume of spinel) reaction constant directly related to diffusion coefficient of the limiting reaction ions. In the case of oppositely directed diffusion fluxes of positive ions, subject to the conditions of $D_A^{2+} \gg D_B^{3+} \gg D_O^{2-}$ the theory gives the following expression relating the average value of the diffusion coefficient of the limiting reaction ions with a rational reaction rate constant:

$$k_1 = z_i \cdot C_i \cdot \overline{D_i} \cdot \frac{4\Delta G}{3RT}, \text{where } Z_i; C_i; D_i \text{ - ion charge, its equivalent concentration and the average}$$

value of the diffusion coefficient, respectively; *ΔG°* - standard Gibbs free energy of formation NiAl$_2$O$_4$, equal 12.6±1.7 kJ/mol. The calculation results showing an increase in the diffusion coefficient of ions in the radiation field are presented in table 2.

Table 2. The diffusion coefficients Al^{3+} ions in NiAl$_2$O$_4$.

T, K	1373	1423	1473	1523	1573
D_T, cm^2/s	$2{,}4 \cdot 10^{-15}$	$1{,}0 \cdot 10^{-14}$	$4{,}2 \cdot 10^{-14}$	$1{,}7 \cdot 10^{-13}$	$3{,}1 \cdot 10^{-13}$
D_{RT}, cm^2/s	$1{,}3 \cdot 10^{-14}$	$7{,}1 \cdot 10^{-14}$	$2{,}3 \cdot 10^{-13}$	$9{,}6 \cdot 10^{-13}$	$3{,}8 \cdot 10^{-12}$

3. Conclusions

Thus, a plurality of the above results is evidence of the stimulating action of intense irradiation on different types of diffusion processes in dielectric materials. This effect is achieved by increasing the effective rate of diffusion jumps.

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