Influence of an initial chemical state of bivalent cation impurities on their diffusion activity in alkali-halide crystals

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Abstract. Influence of an initial chemical state of bivalent cation impurities on their diffusion activity in alkali-halide crystals is investigated. The effect of an intensive electron beam on diffusion of magnesium impurity in crystals of fluoride of lithium is studied.

1. Introduction

Diffusion phenomena in alkali-halide crystals (AHCs) have been addressed in a large number of experimental and theoretical works [e.g., 1–3]. Most of classical experiments on diffusion in AHCs have been carried out using films of halide compound impurities deposited onto crystals. The thus obtained data on the ion transport characteristics of the base material and foreign particles are well reviewed in numerous studies. Furthermore, now we are aware of most physical concepts of the mechanisms of diffusion mass transfer in AHCs. This fundamental knowledge largely predetermines the use of these crystals as model materials in the solution of an urgent and practically important problem of stimulating high-temperature diffusion in dielectric structures with ion-type bonding by ionizing radiation.

We have to admit, though, that the studies on diffusion in ionic dielectrics under radiation are very sparse [e.g., 4-7]. Impurity diffusion investigations in those works were performed from halide impurity compounds using low-power ionizing-radiation sources. No acceleration of high-temperature diffusion was observed.

The present work deals with a critical issue of the influence of the initial chemical condition of bivalent cations of the impurity on their diffusion activity and its variation in the field of a high-power beam of accelerated electrons.

2. Material and experimental methods

To study the influence of the initial chemical condition of bivalent cations of the impurity on their diffusion activity, the following experiments have been performed.

1.   Diffusion was achieved following a conventional pattern from films of halide salts.

2.   A thin metal film was deposited onto the surface of crystals, which was followed by thermal oxidation of this film. The resulting sandwich system was then subjected to annealing in air. A principal difference from the experiment of Type 1 consisted in that a diffusant was in a strongly bound state (in the oxide molecule).

3.   The specimens with deposited metal films were subjected to a thermal diffusion annealing treatment in vacuum (the pressure being 10^{-3} Torr), which eliminated oxidation of the metal film.

Used as sources of the impurity thin films were deposited by thermal evaporation under vacuum. Their thickness was about 400 nm. The diffusant distribution over the depth was measured by the SIMS technique described in [8]. The Pb ion distribution profiles with respect to the depth of the crystal for the diffusion pair KBr-$PbCl_2$ were measured by an optical method with a microspectrophotometer.

3. Experimental results and discussion

The diffusion coefficients D_T obtained from the diffusion profiles are given in table 1. The data listed are indicative of a significant influence of the chemical state of diffusants on the values of diffusion coefficients.

Table 1. Diffusion coefficients for thermal annealing

Diffusion pair	Temperature and type of annealing	D_T, cm^2/s
KBr-$PbCl_2$[*]	773K in air	$(2.5\pm0.6)\times10^{-9}$
KBr-MgO	883K in air	$(2.9\pm1)\times10^{-12}$
KBr-Mg	883K in vacuum	$(3.5\pm1)\times10^{-10}$
KBr-Al_2O_3	883K in air	$(3.5\pm0.7)\times10^{-12}$
LiF-MgF_2	1073K in air	4×10^{-10}
LiF-MgO	1073K in air	1.5×10^{-11}

In particular, for the KBr-Mg specimens annealed in vacuum the diffusion coefficients are by two orders of magnitude higher than their value after annealing in air. It is also obvious that in the case of diffusion from halide films the volume diffusion coefficients of bivalent impurities are more than 1-2 orders of magnitude higher than those obtained in diffusion experiments with oxidized metal films. Thus we may conclude that the diffusion process is sharply retarded if the impurity cation is located on the surface as an oxide compound.

We can assume this to be associated with the fact that when the impurity diffuses into the crystal it does so in a bound state. The molecules of the oxide are quite stable in the temperature interval under study. It is, therefore, very likely that the impurity cations would penetrate into the defective subsurface layers of the crystal in oxygen-bound complexes, thus limiting their mass transport.

Having penetrated into the bulk, the impurity molecules could either decompose in the course of interactions with lattice vibrations or migrate as a single whole within the crystal lattice. In the former case, the bivalent cation would start diffusing at its own characteristic rate. The diffusion coefficients measured under the given experimental conditions were found to be much lower than those for the typical values for bivalent cations in AHCs known from the literature [2]. This circumstance could be accounted for by the fact that in our experiments the impurity continues its diffusion into the bulk of the crystal in a bound state as an oxide molecule, and dissociation of molecular complexes seems very unlikely.

In order to support this supposition, in this work we investigated the composition of the surface layer after a diffusion annealing treatment of a diffusion pair "lithium fluoride crystal – magnesium oxide film", using the x-ray fluorescence method (XRF). This semi-quantitative analysis was performed with an S4 Pioneer spectrometer.

The tests were carried out as follows. A plate measuring $4\times40\times40$ mm^3 rived from crystal lithium fluoride was thoroughly polished. An XRF analysis of the initial specimens demonstrated no oxygen

or magnesium in quantities exceeding the sensitivity of the method, 10^{-3} (Mg) and 10^{-2} (O) wt. %. Following this, a metal magnesium film ~400 nm thick was formed on one of the sides of the plate by the method of thermal evaporation in vacuum. This film was then subjected to thermal oxidation at T=650 K, and the diffusion pair LiF-MgO was thermally annealed in air at T=1073 K for 24 hours. The calculations demonstrated that the diffusion layer depth after this treatment was $20 - 25$ μm. Then both sides of the specimen were analyzed by XRF.

The spectra from the side with a diffusant film exhibited quite strong lines characteristic of magnesium and oxygen. The concentrations of these elements were 0.186 and 0.34 wt % for magnesium and oxygen, respectively. These values have been averaged with respect to the probing depth, being 3 μm for magnesium and 4 μm for oxygen. It should be borne in mind that a certain contribution into the line strength comes from the oxide film partially maintained after diffusion annealing. In order to rule out the effects of this factor and provide an unambiguous answer as to a possibility of diffusion-induced penetration of oxygen into the specimen together with magnesium, a thin layer of $1 - 2$ μm was removed from the specimen by mechanical grinding, which guaranteed a total absence of the oxide film. The removed-layer thickness was measured by an IVK-1 altimeter to a 1 μm accuracy. Then the XRF analysis was repeated on the ground-off side.

The results showed a lower strength of the lines in question as expected. The spectrum, however, still had a strong peak from oxygen. The concentration of the elements for this analysis was as follows: Mg - 0.0824 and O - 0.17 wt %.

The spectra taken from the opposite side of the specimen did not contain any lines typical of magnesium and had a weak line from oxygen, whose strength was lower than that in the impurity diffusion zone and corresponded to a content of oxygen of 0.092 wt %.

It is evident that the weight composition of the impurities Mg and O in the diffusion zone does not correspond to that of the components in magnesium oxide. Hence, the diffusion-induced penetration of one magnesium ion is accompanied by a concurrent diffusion of more than one oxygen ions. This fact is of critical importance.

Thus, the results of XRF support our hypothesis that diffusion of heterovalent cation impurities being part of oxides in the initial state occurs together with oxygen. A two-valent magnesium ion is very likely to be located in the cation site of the lattice. The compensation of the excessive, with respect to the lattice, positive ion charge occurs via two-valent oxygen located in a neighboring anion site. The titanium-oxygen complexes, which are the luminescence centers, were found in crystal lithium fluoride [9]. This shows that our supposition of an impurity being present in the lattice as oxide molecules has a certain physical meaning.

The next stage of investigation consisted in identifying the effects of a high-intensity electron beam heating the crystal on magnesium diffusion in lithium fluoride crystals, which occurred from MgF_2 and MgO films. The coefficients of radiation-thermal diffusion D_{RT} were determined for a fixed annealing temperature T=1073 K. For the radiation-thermal annealing of diffusion pairs, use was made of an ELV-6 accelerator at INP, SB RAS (E= 1.4 MeV, continuous beam current density up to j=3 μA/cm^2). The following results were obtained.

In the case of magnesium diffusion from an oxidized metal film into lithium fluoride crystals, the radiation action gave rise to a marked increase in the diffusion rate. The value of D_{RT}=7.5·10^{-11} cm^2/s measured for this diffusion pair was by far higher than D_T=1.5·10^{-11} cm^2/s obtained under the thermal annealing mode of specimens in the resistance furnace. On the other hand, the high-intensity electron beam used did not result in any change in the rate of the process if diffusion occurred from an MgF_2 film. The latter is attributed to a higher initial diffusion mobility of cations.

Acknowledgements

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