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Healing of discontinuities in the ionic crystals under complex thermo-electric influence

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Abstract. It has been shown that the ionic current in the crystal with a defect in the form of a cleavage crack leads to the healing of the crack. The mechanism of healing is stipulated by the difference in mobility of the ions with different polarity as well as by the electrolysis and recombination crystallization.

1. Introduction

The strength of a real solid material is determined by the presence of in-structural defects, such as cracks and pores. Elimination of these makes it possible to improve the strength considerably. In the modern Materials' Science special attention is focused on the problem of elimination of such in-structural imperfections. In this context, identification of new methods for cracks' healing is important in principle, whereas the research on reconstructive kinetics results subsequently in the extension of the data on the properties of the crystals being investigated.

2. Electric field lines are perpendicular to the surface of the artificially induced cleavage cracks

2.1. Materials and experimental technique

We experimentally investigated a number of LiF single crystals with impurity concentration of Ca^{+2}, Mg^{+2}, Ba^{+2} totally not exceeding 10^{-3} wt. % and NaCl single crystals with impurity concentration of Cr^{+2} corresponding to 10^{-2} wt.%. Samples of 15×10×5 mm size were processed with riving of major blocks along their cleavage planes. Micro-cracks on the clipped surface were induced by indenter PMT-3 [1]. Macro-cracks were induced with blade pressure on the face of the crystal in planes {100} and {110}. The experiments were carried out in the air and in the vacuum (at the pressure ~ 0.01 Pa).

Healing of the micro-cracks' area was controlled by means of comparing the initial state of the defect and its state after the thermo-electrical treatment; in all the other cases – by investigating the structure of dislocations, detected with the chemical etching on the crystal cleavage, crossing the bed of the initial crack.

At the influence of heating and electrical field, the crystal (1, Figure 1) was placed into a closed-type furnace between Ni-Chrome electrodes. The current was supplied to the electrodes with nichrome wires (4). Reliable contacts between the crystal and electrodes were provided by using the fine-dispersed powder (∅ ~ 13 μm) of the examined crystal. This powder was sintered with the crystal and electrode in the process of heating. The speed of crystals' heating in the furnace up to the temperature T0 (673 K ≤ T_0 ≤ 983 K) at the passage of ionic current through specimen did not exceed 200 K/h. The healing was performed at the density of ionic current $J \approx 20 - 1{,}3{\cdot}10^3$ A/m^2. The time was varied within the range of 1 to 6 hours depending on the processing conditions - T_0 and U_0 (U_0 – the direct voltage on the sample). The processing modes were assigned on the basis of experimentally-obtained relationships of crystals' specific conductivity in relation to the temperature of the crystal γ *(T)*. As a criterion for defining the temperature range, we used the values of activation energy in the processes of the impurity and intrinsic conduction, respectively, for LiF – 0.45 and 4.2 eV; for NaCl – 0.49 and 1.7 eV.

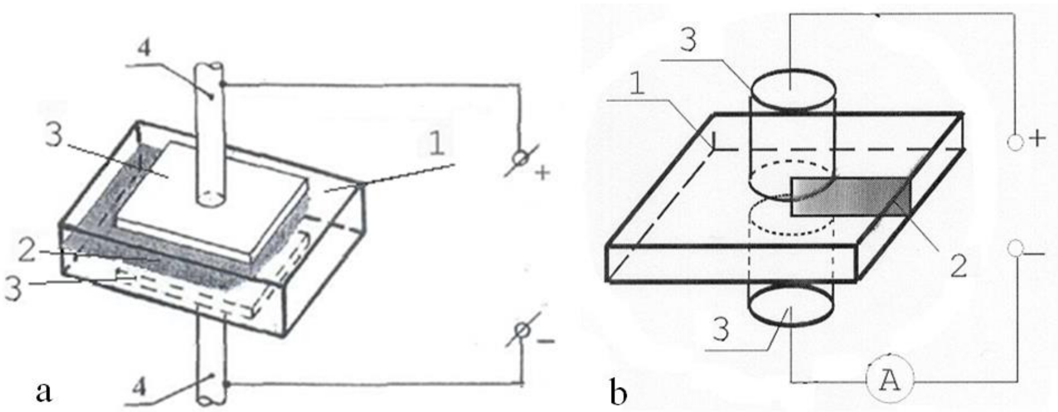

Figure 1. Schemes of experimental setups: electric field lines oriented perpendicular to the plane of the crack (a) and parallel to the plane of the crack (b) 1 - crystal; 2 - crack; 3 - electrodes; 4 – conductors.

2.2. Experimental results

In all the experiments the segment of the healed crack (2) (Figure 1) was generated directly under the electrodes (3). The increase of the treatment time did not change the effect nature, resulting just in an insignificant increase of the healed zone size.

While healing the micro-cracks induced by the indenter in planes {110}, we observed practically complete disappearance not only of the cracks but also of the dents. The heating of similar defects without the current – under otherwise equal conditions – did not result in the healing of cracks and disappearance of dents (refer to Figure 2). There was just a blunt of the crack tip due to the diffusion that was caused by the gradient of mechanical stressing [2].

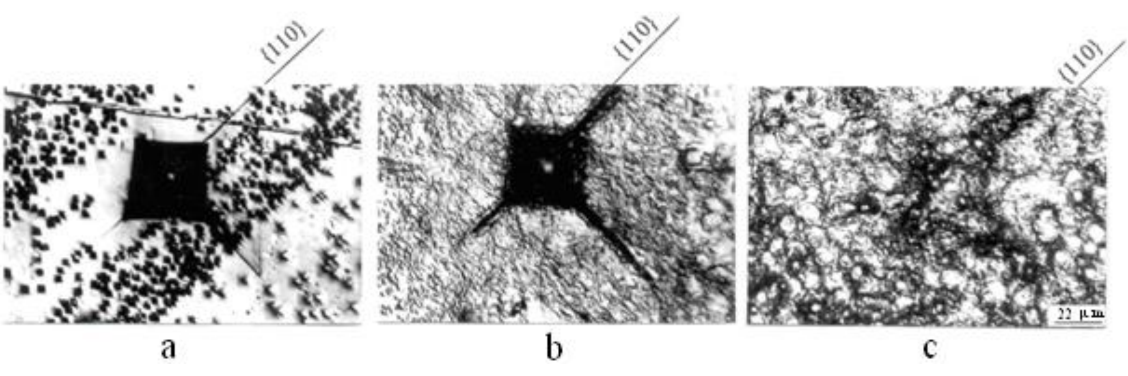

Figure 2. Dents with the cracks induced by indenter PMT-3: a -original sample; b - after heating T = 723 K, t = 4 h; c - after heating and passing the ionic current T = 723 K, t = 4 hours, j = 23 A /m^2.

Micro-structural investigations of the crystals with the healed macro-crack on {110} showed (refer to Figure 3), that in the place of the initial discontinuity there is formed a broken chain of dislocations, the linear density of which is maximal (~ $8 \cdot 10^3$ $см^{-1}$) near the mouth the healed crack; with a gradual decrease towards the crack tip (~ $2 \cdot 10^3$ $см^{-1}$); and in the area of the tip there is formed a zone of a practically defect-free crystal. The density of dislocations along the whole clipped surface was in compliance to the grown-in one (10^4–10^5 $см^{-2}$).

Investigations of the crystals with the healed macro-crack in plane {110} revealed chains of dislocations with the density of ~ $10^4 см^{-1}$ along the whole bed of the healed discontinuity (refer to Figure 3). The density of dislocations on the clipped surface was ~ $10^5 см^{-2}$.

Evaluation of the extent of the recovered material area [3] permits to conclude that it reaches up to ~ 97% of the total healed segment.

After the samples were treated in the range of temperatures of intrinsic conductivity, there were observed formations of micro-pores (in the bed of the initial crack and in its vicinity, mostly – from the side of the negative pole) extending towards <100> in planes {001}. Characteristic dimensions of the micro-pores were 2.5 – 11 microns (refer to Figure 4). When the crystals were heated in the vacuum, formation of the micro-pores was not observed

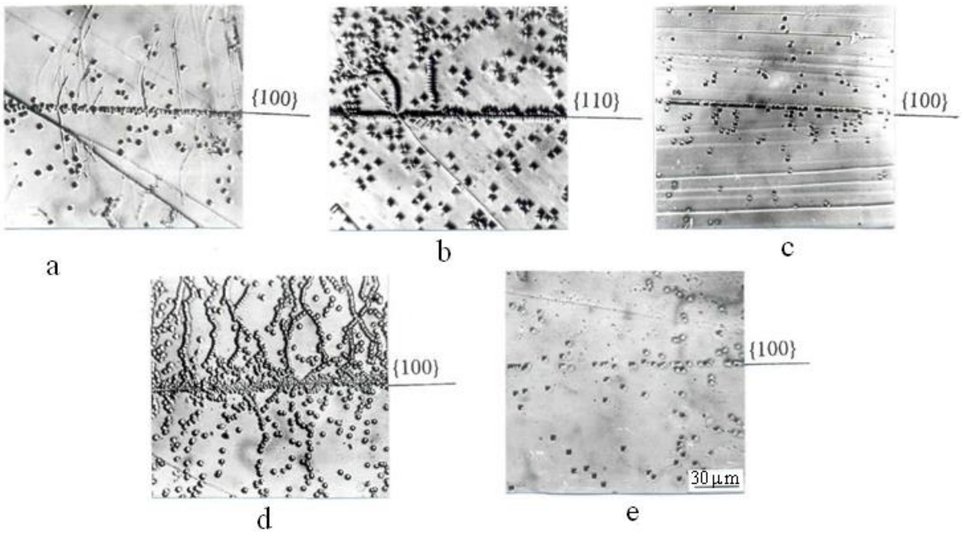

Figure 3. Dislocation structure of segments of the crack healed in the air: a - NaCl; b, c - LiF; and in the vacuum (0,01 Pa): d - NaCl; e – LiF.

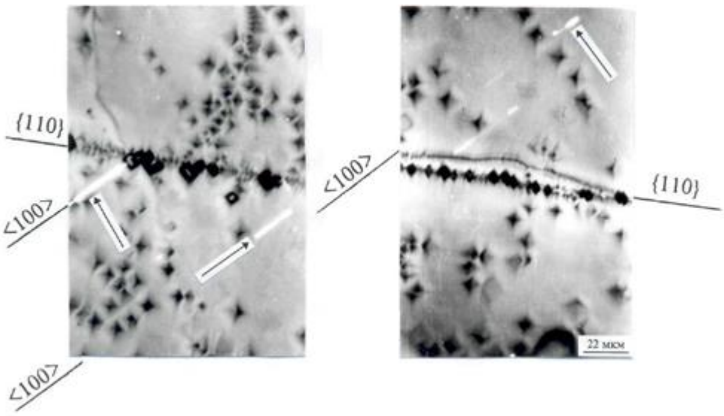

Figure 4. Sub-surface pores in the bed of the initial crack, plane {110} and its vicinity, LiF, the air.

2.3. Discussion on the results obtained

The suggested influence of heating and electrical field on the crystal makes it possible to restore the continuity of the alkali-halide crystals (AHCs) deformed on {100} and {110}. Healing is possible not only by shifting the substance mass, effected by the ionic current, but also by the difference in the mobility of ions of different polarity [4], resulting in unequal increase of the mass on the opposite sides of the crack being healed. The opposite inner surfaces of the crack react differently to the electrical field treatment.

In the crystal portion, located on the positive electrode, mostly higher-mobile ions of Li^+ and impurities ions [5, 4] move over towards the external electrical field. The ions of F^- are practically fixed. At that, the crack surface is charged with a positive charge without destructing the crystal lattice. Being the energy barrier for the ions of Li^+ and impurities' ions, the surface prevents from their emission. As contrasted to this, the negatively charged crack surface is depleted by the positive charge, diffusing to the negative electrode. Inter-ionic Coulomb forces and external electrical field help to the release of the ions of F^- [6], providing for the emission anionic current. It is to be pointed out that the structural changes of the clipped surface under consideration promote the decrease of F^- ions' sublimation energy, due to depletion of the surface by the positively-charged ions.

Bombarding the positively-charged surface, the originated anionic emission current results in deformation shifts. The F^- ions' energy, under the observed electrical field densities, can reach up to ~ 70 eV. The breakthrough takes place, primarily, in the points of electrical field concentration (i.e. on the cleavage steps). During the bombarding of the positively-charged crack surface by the F^- ions, there occurs mechano-emission of the ions of Li^+ [7] in the zones of plastic slips. As a result of the recombination crystallization, on the positively-charged surface there occurs the increase of the crystal mass along the whole surface of the crack. The crack cavity is filled with the crystal material till its complete disappearance.

The observed chains of dislocations in the bed of the initial crack can be identified with sub-boundaries of grains, because the procedure of crack introduction or joining of two crystals (in case of healing the cavity, limited by two halves of a crystal, placed on each other) makes the turning and shifting of the joined halves inevitable [8 – 11]. Evaluation of disorientation provides for the values of the angles, not exceeding 10′ for different samples.

The healing is not followed by the voltage gradients, as confirmed by the absence of clearings in the crystals while the crystals were examined in the polarized light. Besides, the high level of materials' structure restoration is also specified by the evolution of dislocation beams of the indenter hit. The passing of dislocations from the indenter hit through the healed segment and through the pure crystal is practically identical.

Formation of the pores is explained by a discharge which (within the specified range of temperatures) originates in the gas filling the space of discontinuity. The air ions penetrate into the crystal and diffuse to the electrodes under the influence of the electrical field.

3. Electrical field lines are parallel to the surface of the artificially induced crack

3.1. Materials and experimental technique

We experimentally investigated a number of LiF single crystals with impurity concentration of Ca^{+2}, Mg^{+2}, Ba^{+2} in the range 10^{-3}–10^{-5} wt. % and NaCl single crystals with impurity concentration of Fe^{+2} in the range of 10^{-2} – 10^{-5} wt.% . The samples of 20×10×5 mm size were processed with riving of major blocks along their cleavage planes {100}.

The experiment was performed on the set-up, the scheme of which is shown in Figure 1. The crystal was placed between cylindrical electrodes, made of nichrome. Reliable electrical contact between the crystal and electrodes was provided by the method similar to the one described in Item 2.1 (refer to the above). A macro-crack was artificially introduced into a crystal in the plane of primary cleavage. The sample was positioned in such a way that the crack tip was between the electrodes. The

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gap between the sides of the crack varied from 1 to 5 microns. Direct voltage, U_0 = 400 V, was supplied to the electrodes. The density of the external electrical field, *E0,* was equal to $8{\cdot}10^4$ В/м.

The set-up was placed into the furnace. The experiments were carried out in the range of temperatures 293 – 893 K. The heating speed was 200 K/hour. After the heating, the electrical field was shut off, and the sample subsequently cooled down with the furnace up to the ambient temperature.

Dislocation structure of the processed LiF and NaCl crystals was identified by means of chemical etching in the saturated solution of iron acid and in the ice-cold acetic acid respectively [12].

3.2. Experimental results
Within the temperature range of impurity conductivity (T < 823 K) there were no visible changes observed on the surfaces limiting the crack cavity along plane (001). Within the temperature range of intrinsic conductivity (T > 823 K) the crack, positioned between the electrodes, was healed (refer to Figure 5). The area of the segment of recovered continuity grew up with the increase of time of heating and electrical field influence on the crystal. At the duration of influence $t \approx 3.5$ hours, that is, corresponding to the heating up to the temperature T = 893 K, the area of the restored portion of the crack, located between the electrodes, practically reached the value of 100%.

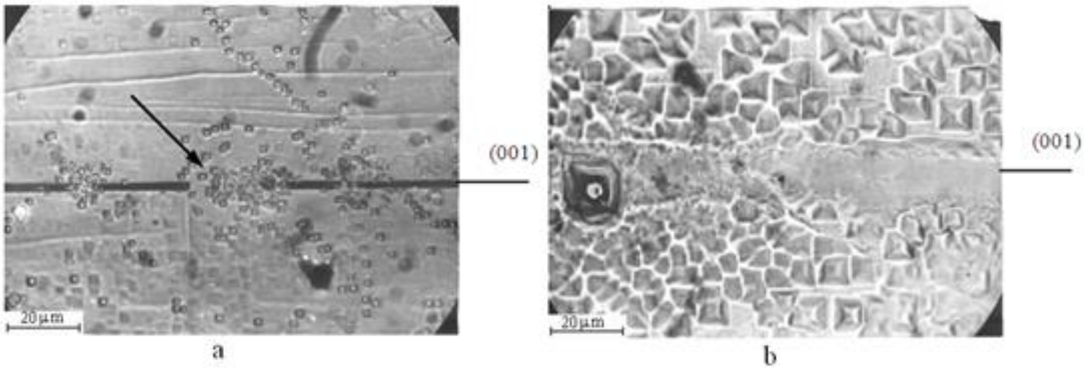

Figure 5. The healed segments of the crack: a – LiF (marked by the arrow), b – NaCl.

3.3. Discussion on the results obtained.
As such, while supplying the ionic current along the crack surfaces, these surface were influenced by the surface currents. The ionic current in the near-surface areas, limiting the crack cavity, is of higher value than the value of the current in the crystal volume, with all the conditions otherwise equal. This stipulates the unequal heating of the given surfaces and volume of the sample and, subsequently, is the reason of different thermal expansion in the surface layers, comparing to the parts of the crystal, distant from them. The process is of a growing nature: in course of time the power of the surface current increases, subsequently resulting in more intensive diffusion of the positively-charged ions to the surfaces limiting the crack cavity. The increased concentration of the positively-charged ions in the given areas is the reason of bringing the crack sides together till their complete joining. That is, the restoration of continuity takes place.

Acknowledgments
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