ELECTRODE PHENOMENA IN ALKALI-HALIDE CRYSTALS AT HIGH TEMPERATURES

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICS

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ELECTRODE PHENOMENA IN ALKALI-HALIDE CRYSTALS AT HIGH TEMPERATURES

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The existence of a potential barrier at the boundary of a dielectric at the place of its contact with a metal ((^1)) leads to the formation of near-electrode space charges when current passes through the dielectric ((^2)). These space charges give rise to a number of specific phenomena ((^{3–10})).

The accumulation of near-electrode space charges has also been noted in the electrolysis of alkali-halide crystals ((^{11–13})). It is of interest to investigate the optical properties of the near-electrode regions of crystals subjected to electrolysis.

Specimens of single crystals of NaCl, KCl, KBr, and KJ were investigated. The largest faces of the specimens, which had the form of a parallelepiped of dimensions (12 ×15 ×5 mm^3), were polished, and electrodes made of aluminum foil (thickness (10)) were pressed tightly against them by means of the spring of a special holder. Specimens prepared in this way were heated to a constant temperature between 450 and 600° and were subjected to a constant electric field of strength 50–400 V/cm for periods ranging from several minutes to 1 hour. The following were measured: the magnitude of the current passing through; the magnitude of the reverse current, for which purpose after 1–3 min a field of opposite sign was applied for 10 sec; the magnitude of the potential difference on the short-circuited specimen, for which purpose the field was periodically switched off for 10 sec and the potential difference was measured with a Compton electrometer.

Fig. 1. Change of current with time through a specimen at a constant voltage of 15 V and temperature 525°. (a)–current through the specimen; (b)–reverse current; (v)–potential difference on the short-circuited specimen in the absence of an external field.

It turned out that for all the substances investigated, in the indicated intervals

Fig. 2. Absorption spectrum of the near-cathode layer

Figure 2: Fig. 2. Absorption spectrum of the near-cathode layer

of temperature and field strength, the current changes with time as shown in Fig. 1. The processes may be divided into two phases: during the first phase the current at first decreases and then remains constant; the magnitude of the reverse current and the potential difference at the ends of the short-circuited specimen during this time reach their greatest value and then remain constant; during the second phase the current usually increases, and the specimen becomes colored by (F)-centers. The duration of the first phase depends: a) on the quality of the cathode–crystal contact, decreasing to a certain degree···

minimum value with improvement of the contact and b) on the magnitude of the applied voltage, decreasing as the voltage increases.

Before electrolysis and after it, the absorption spectrum of the specimen was studied at room temperature on an SF-4 spectrophotometer, the light passing through the specimen in the same direction in which the field had been applied.

It was found that, in the absorption spectrum of a thin ((<0.05) mm) near-cathode layer, for all the materials studied, after the first phase of electrolysis there arise 2–3 weak absorption bands. The positions of the maxima of these bands coincide with the positions of the maxima of the (V_{2-4}), (V_3)- and (V_7)-bands (Fig. 2). If the crystal had been colored, then, in addition to the known (F)-, (M)-, (U)-bands, the indicated bands are also present in the absorption spectrum of the specimen (Fig. 3).

In Table 1 are given the wavelengths of the maxima observed in the near-cathode layer for the materials studied, as well as of the short-wavelength absorption bands for crystals colored by electrolysis with flat electrodes. Within the limits of measurement error, the positions of the maxima of the observed bands coincide with the positions of the maxima of the bands indicated in the headings of the table columns.

Fig. 2. Absorption spectrum of the near-cathode layer

The facts indicated fit the following picture of the passage of current through a dielectric. Under the action of an external field, space charges accumulate in the near-electrode regions of the specimen owing to electrons and holes formed in the corresponding zones by thermal ionization of impurity centers.

Table 1

Material	Localization site of absorption centers	(U)	(V_3)	(V_2)	(V_4)	(V_7) (?)
KBr	Near-cathode layer	(228±2)	(223±3)	(267±3)		(300) (?)
KBr	Volume colored with flat electrodes of the specimen	(228±2)	(223±3)	(267±3)		(300) (?)
KCl	Near-cathode layer	(214±2)	(210±2)	(227±3)	(245±6)	
KCl	Volume colored with flat electrodes of the specimen	(214±2)	(210±2)	(228±3)	(246±6)	
KJ	Near-cathode layer		(278±3)	(310)		
KJ	Volume colored with flat electrodes of the specimen		(280±3)	(310)		
NaCl	Near-cathode layer		(210±2)	(230±3)		(270±10)

Fig. 3. Absorption spectrum of a crystal colored with plane electrodes

Figure 3: Fig. 3. Absorption spectrum of a crystal colored with plane electrodes

Material	Localization site of absorption centers	(U)	(V_3)	(V_2)	(V_4)	(V_7) (?)
NaCl	Volume colored with flat electrodes of the specimen		(210±2)	(230±4)		(290±10)

In the indicated temperature range, for alkali-halide crystals the space charge at the cathode probably creates a stronger field, which forces the alkali-metal ions to overcome the boundary barrier and to "evaporate" onto the cathode, becoming neutralized on it. The formed

In this case, cation vacancies in the crystal will partially neutralize the space charge, recombining with holes and thereby forming (V)-centers. The current lines are closed by the holes entering from the anode. Their entry is facilitated by the electronic space charge at this electrode. The alkali metal, being liberated at the cathode, lowers the potential barrier for the entry of electrons into the crystal. The electrons entering the crystal create a layer of increased conductivity, which is essentially a blocking electrode, so that at the boundary between the colored and uncolored parts of the crystal processes take place analogous to the processes at an electrode; therefore, a small concentration of (V)-centers is also formed in the bulk.

Fig. 3. Absorption spectrum of a crystal colored with plane electrodes

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Note: Figure translations are in progress. See original paper for figures.