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On the perfection of cleavage planes of potassium bichromate single crystals

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Abstract

The relative perfection of the 001, 100 and 100 cleavage planes of potassium bichromate single crystals is analysed by calculations of the surface energy of main crystallographic planes. The surface energy was determined for the three cleavage planes as well as for planes corresponding to other theoretically possible orientations. It was found that: (1) among different planes the calculated values of the surface energy of the 001, 100 and 010 cleavage planes of potassium bichromate are the lowest, (2) among the three cleavage planes the 001 perfect cleavage plane has the lowest surface energy, (3) the relative perfection of different cleavage planes can be explained by using the coefficient δ proportional to the ratio of the surface energy of the *hkl* cleavage plane to the energy of dislocations emerging on the plane, and (4) the lower the values of the coefficient δ for a cleavage plane, the better is the cleavage perfection.
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1. Introduction

Cleavage of crystals is a complicated and dynamic process and depends on many factors. Therefore, this subject is relatively reluctantly investigated, although study of the process has fundamental importance in improving our knowledge of the durability of materials and the morphology and smoothness of cleavage faces of single crystals for application as substrates for deposition of films in device fabrication. Novel techniques, like atomic force microscopy (AFM) and scanning tunnelling microscopy (STM), increased interest in the investigation of cleavages (for example, see Refs. [1–3]) but there are few theoretical investigations of cleavages using computer techniques [4].

The cleavage process of crystals leads to the formation of new surfaces by supplying additional external energy. Consequently, unless disturbed by some factor (for example, preferential deposition of impurities along some planes, segregation of impurities along grain boundaries or formation of voids at grain boundaries), cleavage of a crystal is determined by the value of minimum energy per unit area used in creating new surface of given crystallographic plane. Therefore, cleavage planes are the planes of minimum surfaces energy, i.e. planes of minimum cohesion along directions perpendicular to them. It should be noted that crystals, like potassium bichromate, can have many cleavage planes differing in surface energies, but the minimum of surface energy should determine a cleavage plane along a given orientation.

It is well known that different cleavage planes of a given crystal usually exhibit different perfection. For example, potassium bichromate crystals (also known as lopezite in mineralogy) has three cleavage planes: perfect 001, and distinct 100 and 010 [5]. Among these cleavage planes, the perfect 001 is easily obtained while the distinct 100 and 010 planes are obtained with difficulty. Therefore, it is interesting to establish why crystals are cleaved easily along some planes while with difficulty along others. The present paper

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is addressed to theses issues for potassium bichromate single crystals, especially, in view of the fact that until now the concept of cleavage perfection is not precise and depends on the subjective assessment of the investigator. For the study of cleavages, potassium bichromate ($K_2Cr_2O_7$; abbreviated as KBC) was selected for the following reasons:

(1) Their crystallographic structure, in particular anisotropy along the main crystallographic directions, results in differences in cleavage along different crystallographic planes.
(2) The character of bonds in KBC crystals, involving mainly Coulomb and Van der Waals interactions, is somewhat similar to the bonds in potassium acid phthalate crystals studied earlier [6].
(3) Large good-quality KBC single crystals can be grown reliably at precisely defined temperatures and supersaturations from aqueous solutions [7,8].
(4) Large amount of information on the surface morphology of the 001 cleavage plane, obtained by using optical microscope and AFM, has been reported in the literature [9–11].

2. Crystallographic structure of potassium bichromate

Potassium bichromate crystallises in triclinic structure: space group $P\bar{1}$; cell parameters: $a = 0.7445$ nm, $b = 0.7376$ nm, $c = 1.3367$ nm, $\alpha = 97.96°$, $\beta = 96.21°$, $\gamma = 90.75°$; number of formula units per unit cell: $Z = 4$ [12–14]. Fig. 1a shows schematically the molecule of KBC consisting of two K^+ ions and one $Cr_2O_7^{2-}$ molecule composed of the two nearly tetrahedral CrO_4 groups with terminal oxygen atoms O_T and Cr atom in the middle, joined through the shared bridge oxygen atom O_B. The inversion centre builds separate layers A and B parallel to the 001 plane. Fig. 1b shows the [100] projection of the KBC structure with indicated A and B layers.

3. Lattice energy of KBC

Heide et al. [15] carried out the first calculations of the lattice energy of KBC crystals using the GULP program [16]. They applied the following formula for the interaction energy E_{ij} between the atoms:

$$E_{ij} = A\exp(-r_{ij}/\rho) - Cr_{ij}^{-6} + q_iq_j/r_{ij}, \quad (1)$$

where the Van der Waals intermolecular interaction energy with the repulsing factor is given by

$$E_V = A\exp(-r_{ij}/\rho) - Cr_{ij}^{-6}, \quad (2)$$

and the Coulomb interaction energy is of the form:

$$E_C = +q_iq_j/r_{ij}, \quad (3)$$

where A, C and ρ are constants, q_i and q_j are the charges of the atoms and r_{ij} is the distance between the atoms.

Heide et al. [15] calculated the values of parameters like A, C and ρ of the intermolecular potential. Then they determined the charge distribution between the atoms of the bichromate molecule. The value of the lattice energy E obtained by using the GULP programme is −1547 kJ/mol, where the intermolecular energy $E_V = +97$ kJ/mol amounts 5.6% of the sum of the absolute values of E_V and E_C. With the values of the parameters given by Heide et al., we applied our MEC programme for the calculation of surface energy [17] to calculate the lattice energy, and found the same value. These results suggest that KBC crystal is essentially ionic. Since intermolecular interactions energy E_V is positive, it decreases the cohesion of the crystal. This decrease in crystal cohesion results from small distances between the edge atoms of neighbouring bichromate molecules. Since edge atoms also have electric charge, substitution of KBC molecule by a point charge (for instance, in the case of KAP crystal [6]), would not give correct results. However, it is possible to find the centre of the charge distribution of bichromate molecule, which gives the value of the lattice energy identical to that for a structure with precise charge distribution, although in the case of surface energy the discrepancy was significant and was up to 20%. Consequently, instead of substituting molecules by centres of building units, analysis of the profiles of various crystallographic planes of KBC was made using the molecules presented in Fig. 1. In the former case of substitution of molecules by their centres, as is usually applied in the peri-

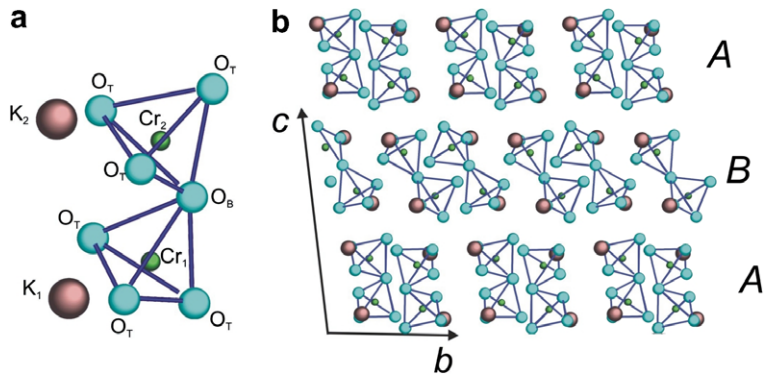

Fig. 1. Structure of KBC crystal composed of A and B slices with indicated dimensions of elementary cell: (a) molecule of KBC and (b) [100] projection. Adapted from Ref. [14].

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