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Selective etching and dissolution of BaF_2 crystals

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The selective etching and dissolution of BaF_2 crystals have been studied in aqueous solutions of inorganic salts, inorganic and organic acids. The effect of additives on selective etch rates is demonstrated. It is observed that chemical exchange reactions determine the selective etching and dissolution of BaF_2 crystals. The form of etch pits corresponds to the real dissolution form of BaF_2 crystals (rhombododecahedron). It has been established that the process of dissolution in HNO_3 and HCl is diffusion controlled. The activation energy is independent of acid concentration and has the same value for both HNO_3 and HCl. The pre-exponential factor is concentration dependent. An empirical equation for dissolution kinetics has been obtained.

1. Introduction

Up to date extensive information is available about selective etching and dissolution of ionic crystals, but no systematic investigation of these processes in BaF_2 crystals has been reported. It is known that nitric and oxalic acids are etchants of BaF_2 crystals [1, 2]. Yet, only the dependence of the form and orientation of etch pits in the (1 1 1) plane on additive concentration and etching temperature has been studied [3].

The results of a systematic investigation into selective etching and dissolution of BaF_2 crystals are reported in this paper. The action of a number of etchings on the (1 1 1) plane at different etching conditions was compared. The form of etch pits was compared with the dissolution form of a BaF_2 sphere. The kinetics of dissolution of BaF_2 crystals in inorganic acids were studied. The kinetics data allow us to draw some conclusions about the mechanism controlling the dissolution process (reaction rate or diffusion) [4].

2. Experimental procedure

The specimens were prepared by cleavage along the (1 1 1) plane of BaF_2 crystals and dissolved in aqueous solutions of different substances. The surface of these specimens was then examined under a metallographic optical microscope and the size of etch pits (along $\langle\bar{1}\,\bar{1}\,2\rangle$) was computed. A Hitachi spectrophotometer ESP-2 was employed to obtain absorption spectra for identifying the complexes in the solutions.

Mechanically polished monocrystalline spheres of BaF_2 (diameter ~ 8 mm) were dissolved in order to study the real form of dissolution. A sphere was placed on a platinum ring (diameter ~ 4 mm) arranged at the centre of the solution. Dissolution was carried out at 60° C for 6.5 h in a permanently stirred solution (200 rpm).

To determine the dissolution kinetics factors, the specimens were dissolved in HNO_3 and HCl aqueous solutions of different concentrations from 0.2 to 10 M at 20 to 100° C. The samples were weighed using a WA-33 balance (Poland) to an accuracy of 10^{-3} g. The etching time was 6 min.

3. Results

3.1. Effect of additives

Different inorganic and organic additives to water were used: (1) a group of inorganic additives with a variable cation and a constant anion (Table I); (2) a group of inorganic additives with a constant cation and a variable anion (Table II); (3) a homologic series of organic acids served as organic additives (Table III).

All experiments were carried out at 50° C for 10 min. The concentration of additives was 0.04 M for the etchants in Tables I and III and 0.22 M for

TABLE I Effect of additive cations on selective etching of (1 1 1) face of BaF_2 crystals

Additive	Additive cation radius, (A) [5]	Difference between additive and crystal cation radii (%)	Solubility in water, (g/100g) [5]	Selective etching capacity	V (10^{-3} km min^{-1})
$FeCl_3$	0.67	50	Highly soluble	Appearance of etch pits and block boundaries	5.40
$CdCl_2$	0.98	28	90.0	As above	1.00
$MgCl_2$	0.65	52	54.6	As above	0.34
NaCl	0.95	42	35.4	Appearance of block boundaries only	0.00
NH_4Cl	1.43	6	29.4	As above	0.00

the etchants in Table II. The tangential growth rate of etch pits (V_t) was measured.

The effect of additive on the etching behaviour of the (1 1 1) surface of BaF_2 crystals is shown in Fig. 1. Following the action of pure water, there is a rough background with many centres of dissolution on the surface (Fig. 1a). In the presence of additive (e.g. $FeCl_3$), clear etch pits appear on the surface (Fig. 1b). The weight of crystal (after etching in $FeCl_3$ solution) dropped by one order of magnitude.

3.2. Effect of etchant concentration

Fig. 2 shows the dependence of weight loss (Δp) on HNO_3 concentration in the 20 to 80° C interval. With rise of temperature, the maximum observed on these curves becomes displaced.

The dependence of weight loss versus concentration of HCl also exhibits maxima (Fig. 3). In this case, however, the maxima do not change with increase in temperature.

3.3. Change of etch pit form

The form of etch pits changes from triangular to hexagonal or circular with increase in concentration and temperature (Table IV). The sides of the triangular pits are parallel to the ⟨1 1 0⟩ direction and the sides of the hexagonal pits are arranged along the ⟨1 1 2⟩ direction.

3.4. The real dissolution form of the BaF_2 sphere

The real form of dissolution of a BaF_2 sphere in HNO_3 is the rhombododecahedron.

3.5. Dissolution kinetics

As is known, the rate of all thermoactivated processes is described by the Arrhenius equation:

TABLE II Effect of additive anions on selective etching of (1 1 1) face of BaF_2 crystals

Additive	Dissociation constant	Solubility in water of salt products of reaction (g/100g) [5]	Selective etching capacity	V (10^{-3} km min^{-1})
HNO_3	4.37×10	9.000	Appearance of etch pits and block boundaries	2.50
HCl	10^7	31.200	As above	1.60
H_3PO_4	7.5×10^{-3}	0.015	As above	0.60
HF	6.6×10^{-4}	0.160	No etching	0.00
H_2SO_4	10^3	0.002	No etching	0.00

TABLE III Capacity of aqueous solutions of organic acids for selective etching of (1 1 1) face of BaF_2 crystals

Additive (acids)	Molecular weight [5]	Dissociation constant	Selective etching capacity	V (10^{-3} km min^{-1})
Formic	46	1.7×10^{-4}	Appearance of etch pits and block boundaries	0.80
Acetic	60	1.7×10^{-5}	As above	0.60
Propionic	74	2.0×10^{-5}	No etching	0.00
Oxalic	90	5.6×10^{-2}	Appearance of etch pits and block boundaries	1.50
Malonic	104	1.4×10^{-3}	As above	1.40
Glutaric	132	–	No etching	0.00
Lactic	90	1.4×10^{-4}	Appearance of etch pits and block boundaries	0.40
Malic	134	3.5×10^{-4}	As above	0.34
Tartaric	150	6.0×10^{-4}	No etching	0.00
Citric	192	7.4×10^{-4}	No etching	0.00

$$V = V_0 \exp(-E/kT),$$

where V_0 is the pre-exponential factor, E the activation energy of the process, k Boltzmann's constant, and T absolute temperature. The pre-exponential factor and activation energy depend on the conditions of the experiment. The experimental dependence of log Δp versus $1/T$ for dissolution of BaF_2 crystals in HNO_3 and HCl aqueous solutions is shown in Figs. 4 and 5, respectively. This dependence can be approximated by parallel straight lines throughout the temperature interval for all acid concentrations. Thus we suggest that the value of the dissolution activation energy is constant for all concentrations, but the pre-exponential factor depends on the concentrations of the acid: it increases in the interval from 0.2 M to 2 M (lines 1 to 4). The maximum on the curve corresponds to the concentration 2 M (line 4). The pre-exponential factor then decreases with increase in concentration: lines 5 and 6 correspond to 4.5 M and 10 M (Fig. 4).

The dependence of log Δp on $1/T$ for dissolution of BaF_2 crystals in HCl has a similar form (Fig. 5). Activation energy is again constant

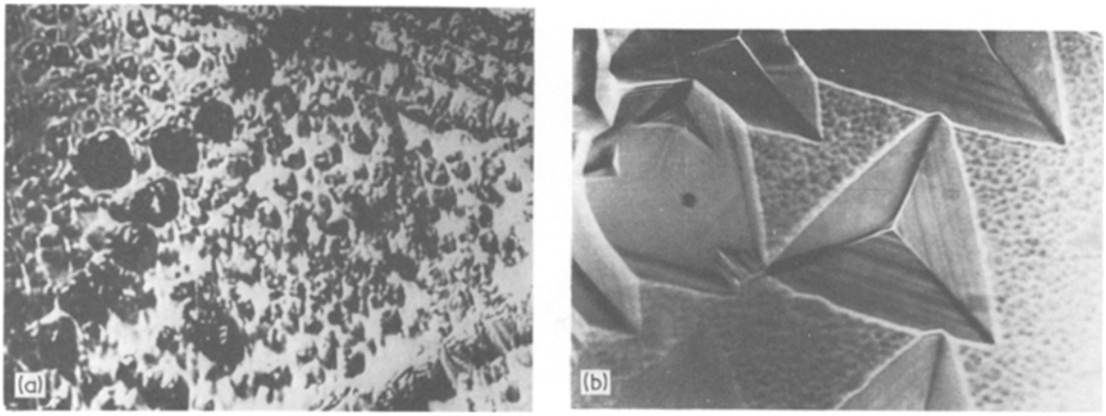

Figure 1 Effect of additive on selective etching of face (1 1 1) of BaF_2: (a) dissolution in water (50° C, 10 min), (b) dissolution in water and $FeCl_3$ (traces, 50° C, 10 min).

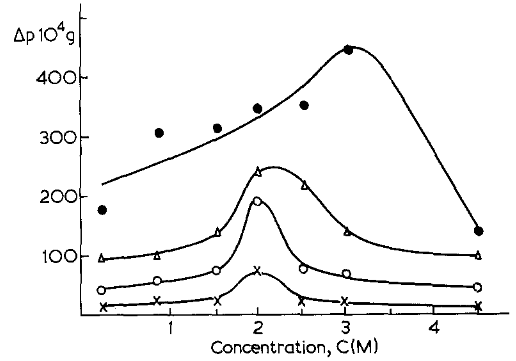

Figure 2 Effect of concentration of etchant (HNO_3) on weight loss.

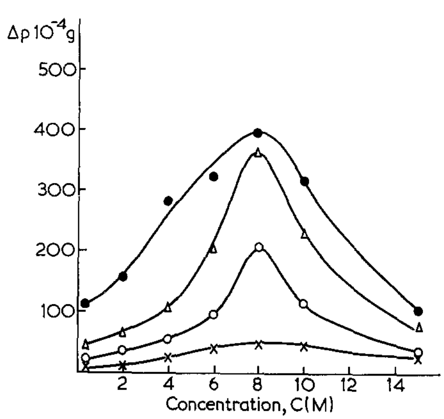

Figure 3 Effect of concentration of etchant (HCl) on weight loss.

throughout the temperature interval. The pre-exponential factor increases with increase in acid concentration from 0.2 M (line 1) to 8 M (line 2). However, we can estimate only the upper and the lower limits of the pre-exponential factor of the variation interval, because of scatter in the experimental data.

The dissolution activation energy values for HNO_3 and HCl are identical (0.39 eV). The pre-exponential factor for these two acids is also similar: 0.3 to 4×10^4 g for HNO_3 and 1.5 to 10×10^4 g for HCl.

4. Discussion

The experimental data permit one to suggest a controlling mechanism of the processes of selective etching and dissolution of BaF_2 crystals. It is known that the capacity of an additive to influence selective crystal etching is associated with the proximity of the ionic radii of the cations of the additive and the crystal [6]. According to another opinion, however, this factor is not important [7]. In our experiments we used additives with different radii and observed that the proximity of cation radii is not an important criterion for the choice of additive. The main factor controlling the selective etching of BaF_2 crystals is the solubility in water of inorganic salt additives and reaction products. In the case of dissolution of BaF_2 in inorganic acids, V_t increases with increase in the solubility of inorganic salt additives and reaction products in inorganic acids. If the products of reaction dissolve poorly, they precipitate on the surface of the crystal and hinder etching. In the case of organic acids, V_t increases with decrease in the molecular weight of the acid (within the limit of the homologic series). It is known that the power of acids depends upon their dissociation constant, the latter decreasing with increase in molecular weight of the acid. Thus, V_t increases with increase of the additive's dissociation constant (Table III). This rule holds within the limits of the homologic series.

Now let us consider the other chemical aspects of selective etching of BaF_2 crystals. It is known that a solvent dissolves a crystal, but an additive is adsorbed on the walls of etch pits and hinders dissolution [6]. If an additive forms chemical complexes, no weight loss of the crystal is observed. In our case, however (additive $FeCl_3$,

TABLE IV Effect of concentration of aqueous solution of HNO_3 and temperature on etch pit form

Concentration (M)	Temperature (°C)	Time (min)	Pit form
0.22	20	5	Triangular
0.50	20	5	Triangular
0.75	20	5	Triangular
1.00	20	5	Triangular
2.00	20	5	Hexagonal
0.22	50	5	Hexagonal
0.22	100	1	Circular

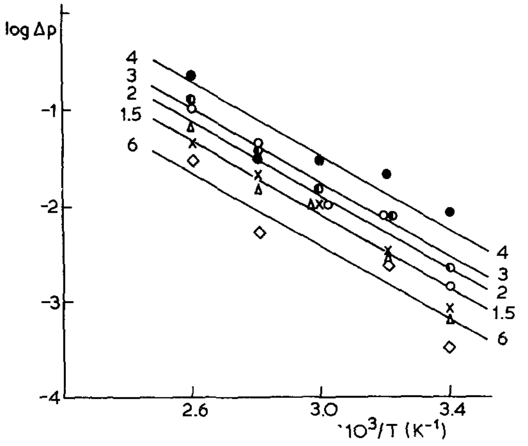

Figure 4 Plots of log Δp versus $1/T$ for aqueous solutions of HNO_3 of different concentrations: 1, 0.2 M; 2, 0.8 M; 3, 1.5 M; 4, 2 M; 5, 4.5 M; 6, 10 M.

solvent H_2O), we observed the formation of etch pits (Fig. 1b) and a significant weight loss of crystal (by one order of magnitude). This means that the additive accelerates dissolution of BaF_2 crystals. We tried to reveal the formation of chemical complexes by investigating the ultraviolet absorption spectra of HNO_3 solutions of different concentrations. No characteristic peaks corresponding to the complexes were observed. However, the formation of some complexes is possible. Thus, chemical exchange reactions take place in solutions of the type:

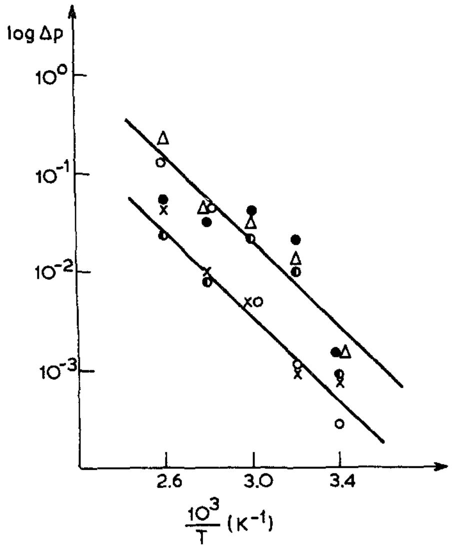

Figure 5 Plots of log Δp versus $1/T$ for aqueous HCl solutions of different concentrations; × and ○, 0.2 M(1) and 1 M(1); ◐, 2 M; ●, 8 M(2); △, 10 M.

$$2\,BaF_2 + 2\,FeCl_3 \rightleftarrows 3\,BaCl_2 + 2\,FeF_3$$

$$BaF_2 + 2\,HNO_3 \rightleftarrows Ba(NO_3)_2 + 2\,HF.$$

Etch pit morphology and the morphology of the dissolution form, are of special interest. We introduced the concept of an ideal crystal dissolution form and constructed such forms [8]. Rhombododecahedron is the ideal dissolution form of BaF_2 crystals, and this form was present in our experiments. In addition, we observed a conformity between the form of dissolution (rhombododecahedron) and the form of etch pits. The sides of triangular etch pits are parallel to the ⟨1 1 0⟩ direction (they are traces of the intersection of the surface with the three faces of dissolution of the rhombododecahedron). The sides of hexagonal etch pits are parallel to the ⟨1 1 2⟩ direction (an intersection of the surface with the faces of the rhombododecahedron, which form 90° with the surface). Thus hexagonal pits are deeper than triangular pits.

The process of dissolution may be diffusion controlled or reaction-rate controlled. It depends upon the conditions of the experiment [4, 9]. As a rule, the process controlled by reaction rate requires an activation energy in the 1 to 3 eV range [10]. The activation energy of dissolution is limited by diffusion changes in the 0.1 to 0.5 eV interval [4, 11]. In our case the activation energy value is 0.39 eV. We therefore conclude that the process of dissolution of BaF_2 crystals in HNO_3 and HCl solutions is diffusion controlled.

Acid concentration influences the value of the pre-exponential factor (Fig. 6). As is known from the chemical kinetics theory, the pre-exponential factor characterizes the total number of collisions between reacting molecules. The non-uniform behaviour of the pre-exponential factor with increasing acid concentration means that a critical

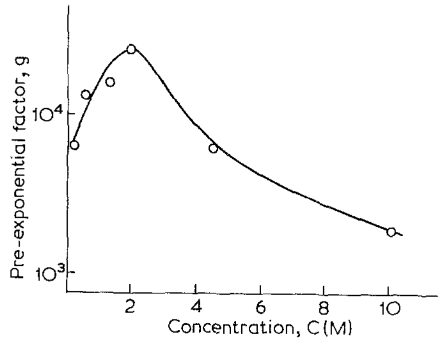

Figure 6 Dependence of pre-exponential factor on HNO_3 concentration.

concentration exists above which the total number of collisions decreases. One can suppose that the reaction products screen the crystal surface and hinder the adsorption of acid molecules on the surface. From this point of view it is clear why the concentration–weight loss plots (Figs. 2 and 3) have maxima.

Thus, it is possible to write the kinetics equations of BaF_2 crystal dissolution as:

$$\Delta\rho \sim (0.3 \div 4)\, 10^4\, e^{-0.39/kT}$$

(for dissolution in HNO_3)

$$\Delta\rho \sim (1.5 \div 10)\, 10^4\, e^{-0.39/kT}$$

(for dissolution in HCl).

5. Conclusions

(1) Chemical exchange reactions determine selective etching and dissolution of BaF_2 crystals in aqueous solutions of different salts and acids.

(2) The dependence of crystal weight loss versus concentration of HNO_3 and HCl solutions has a maximum. The decrease in crystal weight loss after passing this maximum is explained by the inhibition of dissolution by the products of reaction on the crystal surface.

(3) A rhombododecahedron is the real form of dissolution of a BaF_2 sphere in HNO_3. The form of etch pits changes from triangular to hexagonal or circular with increasing concentration or etching temperature. The sides of the etch pits correspond to the sides of the rhombododecahedron of dissolution.

(4) The process of BaF_2 crystal dissolution in HNO_3 and HCl is controlled by diffusion throughout the temperature interval 20 to 100° C. The activation energy is independent of HNO_3 and HCl concentration and has the same constant value for both. The pre-exponential factor is concentration dependent. There is a maximum on the pre-exponential factor versus concentration curve: the total number of collisions between the molecules of the reagent decreases after reaching a certain critical concentration because of screening by the reaction products on the crystal's surface.

(5) An empirical equation has been obtained for BaF_2 crystal dissolution kinetics in aqueous solutions of HNO_3 and HCl.

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