Physicochem. Probl. Miner. Process. 52(1), 2016, 451−458

www.minproc.pwr.wroc.pl/journal

Physicochemical Problems of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received May 15, 2015; reviewed; accepted October 1, 2015

STRUCTURE AND SURFACE ENERGY OF BOTH FLUORITE HALVES AFTER CLEAVING ALONG SELECTED CRYSTALLOGRAPHIC PLANES

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Abstract: The density functional theory, supported with a commercial software, was used to compute the geometry and surface energy of fluorite cleaved along the (111), (110) and (100) planes. In the case of cleaving a piece of fluorite along the (111) plane the two newly created surfaces are identical consisting of fluorite ions with the surface energy equal to 0.384 J/m^2. Cleaving fluorite along the (110) plane also provides identical halves and, both contain one Ca ion next to two F ions, with the surface energy equal to 0.723 J/m^2. When cleaving takes place along the (100) plane, it creates two corresponding halves with different surface structures. One half, having only surface Ca ions (100^{Ca}) has the surface energy equal to 0.866 J/m^2, while the surface energy of the second half, having only F surface ions (100^{F}), is 0.458 J/m^2. Different structures and energies of the corresponding fluorite surfaces, that is (100^{Ca}) and (100^{F}) planes, should have an impact on their chemical properties, including hydrophobicity expressed by contact angle. The calculations performed in the paper also showed that reorganization of fluorite surfaces after cleaving was insignificant for all of the investigated planes.

Keywords: fluorite, fluoride, surface energy, interfacial energy, cleaving, reorganization, surface ions

Introduction

Fluorite is an important industrial mineral which is commonly used for production of aluminum, hydrofluoric acid, glasses, enamels, optical windows, spectroscopic mirrors etc. (Janczuk et al., 1993; Wu and Forsling, 1995; Reichling et al., 1996; Schick et al., 2004). Recovery of fluorite from mineral resources is achieved mostly by flotation (Fulton and Miller, 2006).

Fluorite contains calcium Ca^{2+} and fluoride F^- ions having radii of 0.112 and 0.133 nm, respectively (Shannon and Prewitt, 1969). The electronegativity of fluorine is 3.98 being the greatest on the Pauling scale, while the electronegativity of calcium is 1.00 (Pauling, 1960). The difference in electronegativity is equal to 2.98 indicating a highly ionic character of crystalline CaF_2.

http://dx.doi.org/10.5277/ppmp160137

Fluorite is a naturally hydrophobic mineral (Bakakin, 1960; Barskij, 1984; Janczuk et al., 1993; Drzymala 1994a, 1994b; Zawala et al., 2007, 2008; Gao et al., 2011; Zhang et al., 2014). According to these papers the hydrophobicity, characterized by the so-called contact angle, depends on many parameters, including fluorite color, origin, pH of aqueous solution and crystallographic plane. The maximum difference of about 100° in hydrophobicity of various treated and untreated fluorite specimens was observed by Janczuk et al. (1993), who reported that this mineral formed with water contact angles from 0^o to 100.6^o. These values agree well with theoretical considerations according to which the maximum hydrophobicity of fluorite is 104^o, when only dispersive forces operate in the fluorite-water drop system (Drzymala, 1994a), while for pure (110) and (100) fluorite planes the non-equilibrium contact angle is zero (Zhang et al., 2014). However, upon equilibration with water, the (100) and (110) planes become hydrophobic (Zhang et al., 2012, 2014).

There is one more aspect of fluorite hydrophobicity. When a piece of fluorite is split into halves, the newly created two surfaces are not necessarily identical in arrangement of surface ions. It can be seen, for instance, in the paper of Tasker (1979), who plotted schematic representation of stacking sequence in the fluorite structure for different planes, including not identical (100) planes. In other studies the surface structure differences of the fluorite (100) plane were not recognized (Maldonado et al., 2013), while Zhang et al. (2014) once showed Ca ions on the top of the (100) plane and next F ions forming the (100) surface. Therefore, the aim of this paper is to examine the structure of fluorite after cleaving along certain planes and to calculate their surface energies taking into account surface ions reorganization. The surface structures of the two newly created surfaces formed by cleaving a lump of crystal fluorite along the (111), (110) and (100) planes and their surface energies are considered in this paper.

It should be noticed that perfect octahedral cleavage of fluorite occurs along four (111) planes and parting (poor) is observed on the (110) planes (Anthony et al., 2015). According to Vitov and Konstantitov (2001) splitting fluorite provides not only (111) but also (100) and (110) planes. Indistinct parting or cleavage on (110) was also mentioned by Palache et al. (1951). According to Minerals.net (2015) octahedral (111) cleavage fragments are flat with triangular shaped pieces, while cubic (100) and (110) cleavage fragments are flat with three dimensional rectangles.

Calculations

The calculations of fluorite primitive cell parameters and relaxation of the surface ions after cleaving were performed using the density functional theory (DFT) as well as the Perdew−Burke−Ernzerhof (PBE) functional (Perdew et al., 1996) and the CRYSTAL09 software package (Dovesi et al., 2009). The calculations are based on the pob_TZVP_2012 functions, which describe molecular orbital of Ca and F atoms as linear combinations (Peintinger et al., 2012). The Brillouin zone integrations were

performed on a special *k*-point mesh generated by the Monkhorst−Pack scheme (9×9×9) in the bulk (Monkhorst et al., 1973). The sampling of the Brillouin zone for the surfaces was performed with an 8×8×1 Monkhorst−Pack *k*-point mesh (Maldonado et al., 2013).

The Amsterdam Density Functional (ADF) computational chemistry package was used for determination of the surface energy ($\gamma^{(hkl)}$) of fluorite planes after cleavage (Velde et al., 2001). The calculations were performed using the periodic density functional theory (DFT) employing the generalized gradient approximation (GGA) with the Perdew−Burke−Ernzerhof (PBE) functional for CaF_2 and two-dimensional translational symmetry. The following equation (Maldonado et al., 2013) was used

$$\gamma^{(hkl)} = \frac{1}{2}\frac{\left[E_n^{(hkl)} - n\cdot\left\{\frac{1}{p}\left(E_n^{(hkl)} - E_{n-p}^{(hkl)}\right)\right\}\right]}{A^{(hkl)}},$$

where $E_n^{(hkl)}$ is the total energy of the *n*-layer slab with the Miller index (*hkl*) and factor 1/2 accounts for the presence of two surfaces at either side of the slab. Symbol *p* stands for number of rows of atoms in a terrace of any stepped surface and $A^{(hkl)}$ is the unit cell surface area.

Results and discussion

Basic fluorite structure parameters include the length of translation vectors (*a*, *b*, *c*), interaxial angles (α, β, γ) and distance between calcium and fluoride ions. These parameters determine the primitive cell of fluorite (Strunz, 1970). In the bulk structure of fluorite the distance between the layer of fluoride ions (F^-) and the next layer of calcium ions (Ca^{2+}) in the case of the (111) plane is 0.0788 nm, while the distance of third layer of fluoride ions from the first layer is 0.1577 nm (Schreyer et al., 2014). In the case of the (110) plane the distance between each layer containing both Ca and F ions is 0.1932 nm (Schreyer et al., 2014). The (100) plane is formed by separate layers of F and Ca ions, which are 0.1366 nm apart (Schreyer et al., 2014). Our calculations provided parameters of the primitive cell of fluorite which well agree with the literature experimental data (Table 1).

Table 1. Experimental and calculated parameters of fluorite cell

	α, β, γ [°]	*a*,*b*,*c* [nm]	Length of Ca–F bond [nm]
Experimental (Schreyer et al., 2014)	90	0.5463	0.2365
Calculated (this paper)	90	0.5475	0.2371

Splitting a piece of fluorite provides new surfaces. There is also reorganization of surface ions forming the surface in relation to the bulk structure (Leeuw et al., 2000). Our calculation indicated that the relaxation of the surface ions of fluorite is not

significant because the change of the Ca-F bond length, when the surface is formed, is less than 3.5%. The results of calculations of the relaxation of surface ions for (111), (110) and (100) planes of fluorite are shown in Table 2. To indicate the ions forming the surface, the *hkl* symbol of the considered plane was supplemented with the chemical name of the ion or ions. Therefore, for instance the (111) plane consisting of only F ions was denoted as (111^{F}). Details regarding the surface structures created by splitting fluorite along different planes will be discussed further in this work.

Table 2. Calculated relaxation of ions forming different surfaces of fluorite

Plane	Ca-F bond length between atoms of the first and second layers [nm]	Ca-F bond length change based on bond lengths before and after relaxation [%]
(111^{F})	0.2346	1.04
(110^{CaF2})	0.2413	1.78
(100^{Ca})	0.2304	2.82
(100^{F})	0.2285	3.51

Knowing the arrangement of ions in the bulk structure of fluorite and extend of the relaxation of fluoride and calcium ions present on the surface of the considered planes, we can plot the fluorite surface structures for the (100), (110) and (111) planes. Figures 1a-c show the inner fluorite structure as well as the surface structures of both halves created by cleaving and relaxation. It can be seen that cleaving fluorite along the (111) plane provides identical halves (Fig. 1a) with fluoride ions forming the surface (111^{F}). Similar situation occurs for the (110) plane (Fig. 1b). In this case both halves contain fluoride and calcium ions (110^{CaF2}) in the same proportion 2:1 as in the CaF_2 molecule. However, the situation is different in the case of the fluorite (100) plane (Fig. 1c). Splitting along the (100) plane leads to two entirely different surfaces. One of them consists of Ca (100^{Ca}), while the second one with fluoride (100^{F}) ions.

Since the halves produced by splitting along the (100) plane of fluorite are very different, their properties, especially the surface energies, are expected to be different. Initially the calculations of the surface energies were performed for the (111) and (110) planes to check the accuracy of determination. Table 3 shows that the calculated energies of the (111) and (110) planes of fluorite are similar to those reported by Maldonado et al. (2013). In the case of the (100) plane the surface energy of the half covered with the Ca ions (100^{Ca}) is equal to 0.866 J/m^2, while the surface energy of the second half with the fluoride atoms (100^{F}) is 0.458 J/m^2. Thus, there is a significant difference in the surface energies of the created halves. As a result, it should be expected that the hydrophobicity of both halves can be different. Perhaps, the difference in the contact angles of the fluorite (100) plane observed by Zhang et al. (2014) (0^{o}) and by Gao et al. (2012) (32.4^{o}) was caused by measuring contact angle for not the same but corresponding halves.

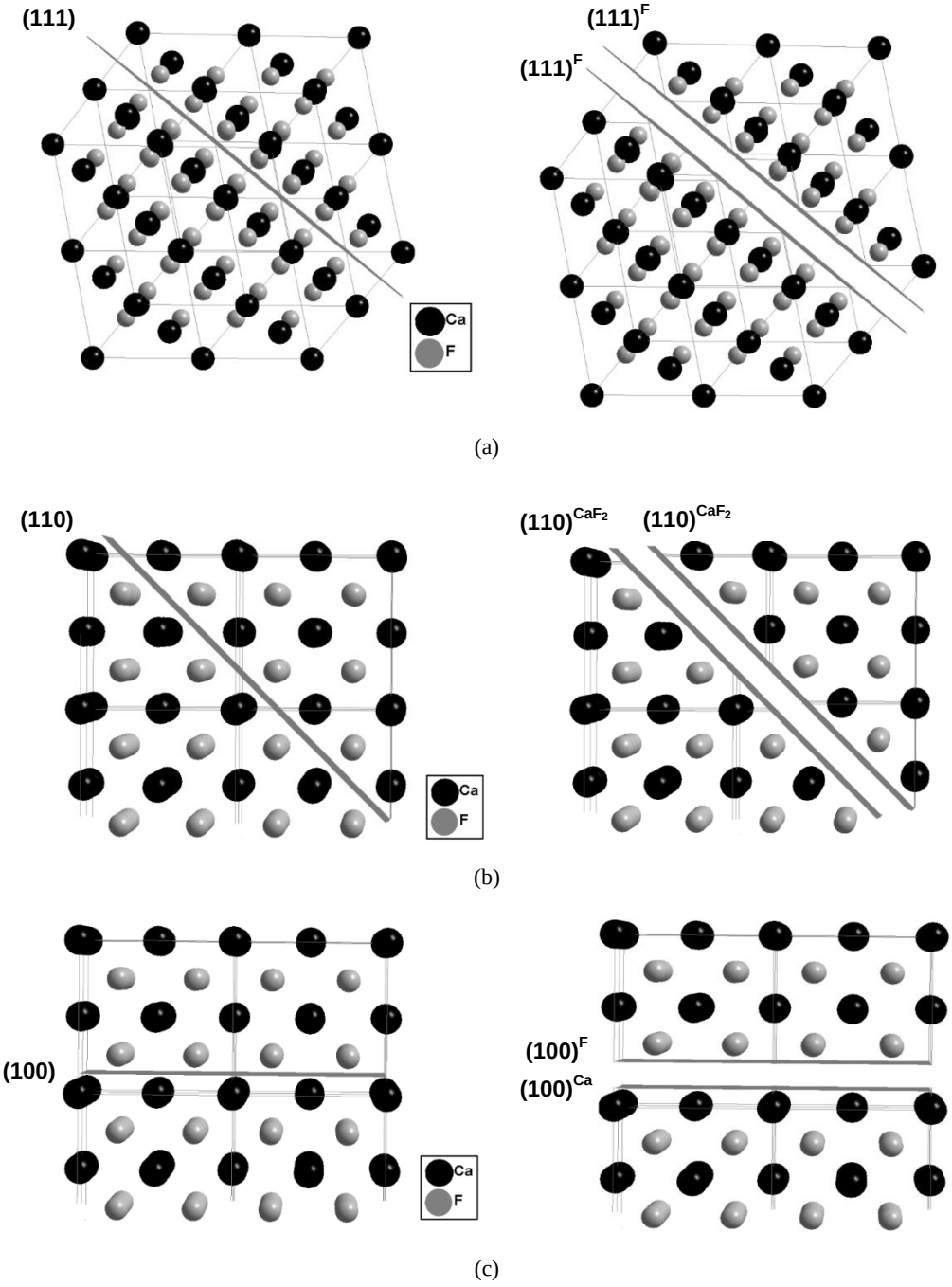

Fig. 1. Primitive cells (left) and surface structures (right) of fluorite split into halves along a) (111), b) (110), and c) (100) planes

Table 3. Calculated surface energies of different planes of fluorite

Cleavage planes	surface energy, J/m^2 (this work)	surface energy, J/m^2 (Maldonado et al., 2013)*
(111^{F})	0.384	0.392
(110^{CaF_2})	0.723	0.613
(100^{Ca})	0.866	0.840
(100^{F})	0.458	n/a

*recalculated from the eV/f.u. units

Theoretically, it is possible to split a piece of fluorite along the (100) plane to create halves having both fluoride and calcium ions on their surfaces. However, this is very unlikely because it would create electrical charge and holes (about 50% of the surface) on both halves. In addition to that, the removal of atoms would require breaking chemical bonds. Impossibility to form one half with (111^{F}) surface plane and the second with (111^{Ca}) surface plane was discussed by Tasker (1979), who pointed out that such cleaving would create a great dipole moment leading to a significant surface ions reorganization.

According to Tasker (1979) splitting fluorite along the (100) plane provides two different surfaces, both having dipole moments, and thus requiring serious relaxation, while our calculations for these surfaces point to a small reorganization. This discrepancy requires further considerations.

A comparison of the surface energies of different fluorite surfaces indicates that planes containing either only calcium or calcium and fluorine have the surface energy value in the vicinity of 0.8 J/m^2, while planes containing only fluoride ions have the surface energy equal to about 0.4 J/m^2.

Conclusions

The paper shows that splitting a piece of fluorite along a selected plane provides halves which, after a slight reorganization in comparison to the bulk structure, can be either identical or different. The same structure of the corresponding halves was found for the (111) and (110) planes. In the case of the (100) plane, splitting provides halves of different structures. The first one with only fluoride ions (100^{F}) forming the the surface has the surface energy equal to 0.458 J/m^2, while the second one with only calcium atom forming the surface (100^{Ca}) has the surface energy equal to 0.866 J/m^2. Thus, there is a significant difference in the surface energy and it should be expected that the hydrophobicity of both halves are different.

Acknowledgements

The paper was partially financed by the Polish Governmental Statutory Works Program S50167. Calculations were carried out at the Wroclaw Centre for Networking and Supercomputing within grant No. 012. Figures was rendered by Diamond - Crystal and Molecular Structure Visualization Crystal

Impact - Dr. H. Putz & Dr. K. Brandenburg GbR, Kreuzherrenstr. 102, 53227 Bonn, Germany http://www.crystalimpact.com/diamond

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