Hartman Perdok Method Applied to $A_2BSi_2O_7$ and AB_2O_6 Types of Microcrystals and the Concept of Fractional Charges

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Using the concept of Fractional Charges were calculate the attachment energies and was simulated the growth form of quartz crystals in the past. In this paper , by using the concept of normal and fractional charges in the system for $A_2BSi_2O_7$ and AB_2O_6 types of crystals, will be computed the attachment energies and it will be done the conclusions of influences of fractional charges in the system for energies calculations the first step in Hartman Perdok Method applied to microcrystals.

Keywords: energy, surface structure, mathematical methods in chemistry, attachment energy, coulomb interactions

The interatomic interactions are described by using two or three body potentials, that were determined in the past empirically , and even like these they describe a set of experimental quantities [1].

Computer modeling based on inter atomic interactions has been used to investigate the microstructures of advanced materials and melts, and their macroscopic, thermodynamic and physical properties. Numerical computations are useful and powerful the cases that may be inaccessible to direct experimental study. Equilibrium and dynamic properties of advanced materials at a specified temperature and pressure can be calculated by using either lattice dynamics or molecular dynamics methods. For accurate simulations of advanced materials, the behavior at height temperature where anharmonicity of atomic vibration is important and quantum effects are small. For these reason the molecular dynamic method is useful, while corrections to quasi-harmonic lattice dynamic method of calculations are needed to take full account of intrinsic anharmonic effects. A very important component of numerical computations is the using of interatomic potentials, derived from the first principle of quantum mechanics or fitting the observed properties [2].

Experimental part

Materials and methods

The present study is done using an electrostatic point charge model. The attachment energies were calculated in the past for the F-faces using only Coulomb interactions and now we took into account the van der Waals attractions and Born repulsion for $A_2BSi_2O_7$ and AB_2O_6 types of crystals.

In the present study are presented the energies for different charges in the system. It is assumed in the present paper that the charges in system can be normal, and reduced charges as is presented in table 1 for $A_2BSi_2O_7$ and for AB_2O_6 .

Hartman Perdok method

The surface related energies are calculated in a point charge model. The equations used in calculations tooke into consideration only the Coulomb interactions. The contributions by the van der Waals interaction energies and Born energies can also be computed. Since decreasing the effective point charge can compensate the partly covalent character of the ionic bond, the energy calculations in a point charge model with lower effective charges can be more reliable.

Model I Normal charges	Model II Reduced Charges 2	Model II Reduced Charges 3
$A_2BSi_2O_7$		
$q_O = -2\ |e|$	$q_O = -0.945\ |e|$	$q_O = -1.2\ |e|$
$q_{Si} = +4|e|$	$q_{Si} = +1.89|e|$	$q_{Si} = +2.4|e|$
$q_A = +2\ |e|$	$q_A = +0.945\ |e|$	$q_A = +1.2\ |e|$
$q_B = +3|e|$	$q_B = +1.417|e|$	$q_B = +1.8|e|$
AB_2O_6		
$q_O = -2\ |e|$	$q_O = -0.945\ |e|$	$q_O = -1.2\ |e|$
$q_A = +2|e|$	$q_A = +0.945|e|$	$q_A = +1.2|e|$
$q_B = +5|e|$	$q_B = +2.365|e|$	$q_B = +3|e|$

Table 1
CHARGES IN THE SYSTEM

An approximation of the potential energy is:

$$E_a^{cor} = +E_a + E_{vdw} + E_B \qquad (1)$$

where E_a is the attachment energy, E_a the energy released per mole, when a new slice of a thickness d_{hkl} crystallizes on an already existing crystal face (hkl).

Where the terms in the sum are [1,2]

$$E_a^{cor} = -\frac{q_i q_j}{r_{ij}^2} - \frac{C_i C_j}{r_{ij}^6} + f(B_i + B_j) e^{\left[\frac{(A_i + A_j - r_{ij})}{(B_i + B_j)}\right]} \qquad (2)$$

The potential energy is formulated as an approximation of the sum of pair wise interactions between atoms[6]

$$E_B = f(B_i + B_j) e^{\left[\frac{(A_i + A_j - r_{ij})}{(B_i + B_j)}\right]} \qquad (3)$$

where $f = 4.184$ kJ mol^{-1}, A_i and B_i are the repulsive radii and softness parameters of the ion i, r_{ij} is the interatomic distance between atoms i and j, respectively.

The van der Waals energy is: $E_{wdW} = -\frac{C_{ij}}{r_{ij}^6} \qquad (4)$

The errors in molar volums are 1.3% [2, 7]

Results and discussions

The attachment energies including only Coulomb interactions are listed in table 1a. The Coulomb part of attachment energies, E_a, calculated in the point charge model with normal situation are listed in table in the second column.

When we compute the van der Waals attractions and Born repulsions as corrections for the attachment energies by means of the Gilbert equation (eq.2), we take into account the contributions of A-O and O-O. and B-O.

In table 2 and 3 the Born repulsion, E_B, and the van der Waals attraction (E_{vdW}) are also listed in the 3 and 4– th column, respectively. The attachment energy (E_a^{cor}) corrected for the Born repulsion and the van der Waals interaction are listed in 5 – th column.

Interatomic potentials by using molecular dynamic computations by using a point charge model were used for energies simulations in different cases of charges used in the system.

In table 1 is presented for different types of materials $A_2BSi_2O_7$ and AB_2O_6 different types of charges in the system: Model I - normal charges; Model II - Reduced charges 2: Model III - Reduced charges 3. We can see here that in Model II where are presented the reduced charges 2 is the model introduced by Matsui and generalized here for $A_2BSi_2O_7$ and AB_2O_6 types of crystals. In Model II the charges are 47.25% from the charges in the Model I. In Model III is presented the reduced charges 3, a model introduced by Beest & Stanten and generalized here for $A_2BSi_2O_7$ and AB_2O_6 types of crystals. In Model III the charges are 60% from the normal charges.

In table 2 and 3 are presented attachment energies in Model I, II and III and corrections for Born repulsions and van der Waals attractions for $A_2BSi_2O_7$ and for AB_2O_6 types of crystals. We can see here that Born repulsion E_B are

hkl	Only Coulomb interactions	Gilbert corrections		
	E_a [kJmol^{-1}]	E_B [kJmol^{-1}]	E_{vdW} [kJmol^{-1}]	E_a^{cor} [kJmol^{-1}]
Model I - normal charges				
001	-1187	+160.957	-24.013	-1050.056
100	-1982	+268.759	-40.095	-1753.336
101	-1596	+265.3698	-32.287	-1411.87
111	-1957	+265.3698	-39.590	-1740.221
120	-2448	+331.948	-49.523	-2165.575
130	-3313.2	+446.8	-67.02	-2923.42
Model II - Reduced charges 2				
001	-279.78	+37.938	-5.659	-247.500
100	-298.3	+40.449	-6.034	-263.885
101	-532.6	+72.220	-10.774	-471.154
111	-294.5	+39.932	-5.9757	-260.521
120	-884.70	+119.965	-17.897	-782.632
130	-496.98	+67.390	-10.053	-439.643
Model III - Reduced charges 3				
001	-946.893	+128.3986	-19.15565	-837.65
100	-1581.081	+214.394	-31.98458	-1398.671
101	-1273.1611	+211.690	-25.75598	-1087.127
111	-1561.1380	+211.690	-31.58173	-1381.029
120	-1952.7175	+264.801	-39.50548	-1737.421
130	-2643.0059	+356.421	-53.46319	-2340.048

Table 2
ATTACHMENT ENERGIES FOR $A_2BSi_2O_7$

	Only Coulomb interactions	Gilbert corrections		
Model I - normal charges				
hkl	E_a [kJmol^{-1}]	E_B [kJmol^{-1}]	E_{vdW} [kJmol^{-1}]	E_a^{cor} [kJmol^{-1}]
001	-1033.6304	+637.0452	-95.0466	-491.6318
110	-616.132	+379.7610	-56.6559	-293.0269
103	-1011.56	+623.4428	-93.0172	-481.1344
101	-936.1528	+576.9679	-86.0832	-445.2649
Model II - Reduced charges 2				
001	-243.630	+150.15	-22.402	-115.882
110	-145.222	+89.509	-13.353	-69.066
103	-238.4246	+146.945	-21.924	-113.403
101	-220.6512	+20.277	-135.9913	-356.6425
Model III - Reduced charges 3				
001	-824.55516	2.78798	-2.52804	-824.2952
110	-491.5053	+1.6619	-1.50693	-491.3503
103	-806.9490	+2.7284	-2.47407	-806.6946
101	-746.7946	+2.5250	-2.28964	-746.5592

Table 3
ATTACHMENT ENERGIES FOR
AB_2O_6

13.55% from the values obtained for attachment energies Ea. The contributions of van der Waals attractions are only 2.02% to Ea. From table 2 and 3 we conclude that corrections for attachment energies E_a^{cor} is 88.46% from the attachment energies when we take into account only Coulomb interactions.

In table 2 and 3 are presented the energies for Model II., even the charges from Model II are 47.25% from the charges in the Model I, the attachment energies are 23.57% from the energies in the case of Model I. In table 2 and 3 are presented the energies for Model III too , even the charges from Model III are 60.0 % from the charges in the Model I, the attachment energies are 79.772% from the energies in the case of Model I.

Conclusions

This work is an extension on the work done by Beest & Stanten from 1990 [2] and Matsui from 1996 [1]. Some results are presented for quartz in a work done before [9] and the simulations for materials as $A_2BSi_2O_7$ and AB_2O_6 using different types of charges in the system was done in the present paper with important conclusions concerning energies.

In this paper, by using the concept of normal and fractional charges in the system for $A_2BSi_2O_7$ and AB_2O_6 types of crystals, were computed the attachment energies, van der Waals atractions and Born repulsions and conclusions are very clear that exist an influence of fractional charges in the system for energies calculations in Hartman Perdok Method which applied to microcrystals.

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