Theoretical and Experimental Analysis of SiO$_2$ - a Proof of Hartman Perdok Method

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In the present paper is done a comparison between simulation of the growth form of quartz crystal using attachment energies and SEM and AFM analysis. This comparison is done to make a complete analysis of quartz crystal. This analysis from theory to experiment and to applications for α-SiO$_2$ presents a complete study of how are the results from simulations of growth forms of quartz crystals and which are the proofs given by SEM and AFM analysis that the obtained crystals are like in the simulations.

Keywords: quartz crystal, SEM, AFM, α-SiO$_2$

In the present paper is done a comparison between simulation of the growth form of quartz crystal using attachment energies including the Coulomb interaction energies, van der Waals attraction and Born repulsion and experimental results for obtaining quartz crystals with SEM and AFM analysis to make a complete analysis from theory to experiment and to applications for α-SiO$_2$.

The crystal structure determines the surface related energies, *e.g.*, specific surface energy, attachment energy and slice energy. the growth rates of *F* faces are directly proportional to attachment energies [1]. Calculations of attachment energies enable to construct the theoretical growth forms. Hartman [2,3] derived these forms for quartz by calculating the Coulomb interaction energies in an electrostatic point charge model. In the present paper we use the Space Group P3$_2$2$_1$ with the hexagonal unit cell constants of: *a* = *b* = 0.4921 nm and *c* = 0.5163 nm [4, 5].

In the present paper is presented a method of crystals analysis based on the point charge model which is fully validated in the present paper by the proofs of obtained crystals and SEM and AFM analysis. This method is robust and is fitting for the purposes of prediction of growing and equilibrium form of the crystals. The significance, novelty and wider societal impact of the work reported in this article is height because can be applied to fields of healthcare and pharmaceuticals, environmental and forensic analysis, agricultural science and food products too.

Computations of Energies

The surface related energies are calculated in a point charge model. These calculations take only into consideration the Coulomb interactions. Recently, the contributions by the van der Waals interaction energies and Born energies can also be computed. Since the partly covalent character of the ionic bond can be compensated by decreasing the effective point charge, the energy calculations in the point charge model must now be more reliable.

The attachment energy, E_a is the energy released per mole, when a new slice of a thickness d_{hkl} crystallizes on an already existing crystal face (*hkl*) [6, 7].

Matsui approximates in his model the potential energy as an approximation of the sum of pair wise interactions between atoms [8]:

$$Eatt(r_{ij}) = -\frac{q_i q_j}{r_{ij}} - \frac{C_i C_j}{r_{ij}^6} + f(B_i + B_j) x \exp\left[\frac{(A_i + A_j - r_{ij})}{(B_i + B_j)}\right] \quad (1)$$

where the terms represent Coulomb , van der Waals and Born repulsions, respectively. Here r_{ij} is the interatomic distance between atoms *i* and *j*, $f = 4.184$ kJ A^{-1}mol^{-1}, and q_i, are the net charges A_i, B_i and C_i are repulsive radii , softness parameters and van der Waals coefficients of the ion *i*.

All the results in computation depends on charges of Si and O.

The Charges used in simulations for the energy are for Si : q$_{Si}$ = +4 |e| and for O:q$_O$ = -2 |e|.

When we compute corrections for the attachment energies we take into account the contributions Si-Si , Si-O and O-O for the total total attachment energies in the case of van der Waals attractions and Born repulsions .We can say in all the cases that the contribution of O-O is bigger almost 20 times the Si-Si contribution to the total attachment energy in the case of van der Waals attractions, and the contribution of Si-O to this energy has an intermediate value. But for Born repulsion O-O contribution to the attachment energy is almost 1000 times bigger then Si-Si and 50.000 higher then Si-O.

The attachment energies including only Coulomb interactions are listed in table 1. Hartman made calculations for attachment energies, but he used in his calculation only Coulomb interactions and the orientation for the unit cell that he used was 60° than usual [1,2]. He has the next values: for prism m 248.06 kcal/mol, for the rhombohedra r: 303.27kcal/mol and for rhombohedra z : 275.88 kcal/mol.

We can see from table 1 in column 3 the correction for the energy using Born repulsion are always positive and corrections for the attachment energy using van der Waals attraction (column 4 in table 2) are always negative . We can obtained the attachment energy corrected with those two values using Born and van der Waals energies and we can obtained the value listed in column 5 of table 1.

This is the pair potential approximation, which assumes that the potentials depends only on inter atomic distance and has no angular dependence. In systems where this is not true, three - body forces can be used to represent quadrupolar effects partially. We consider Born models of solids which consists only the pair wise additive interactions describes above.

# Authors with equal contribution to this work.

Growth Form of SiO₂ Simulations

Using calculations for attachment energies and taking into account that the rate of growth form of the face (hkil) is direct proportional to the attachment energy, we can construct the growth form of quartz crystal .

Using the values of the column 2 and 5 from the table 2 we can obtained the growth form of quartz as is shown in figure 1a and 1b .

In figure 1 a we can see a growth form of quartz when we took into account only coulomb interaction and formal charges. We can see here very well the major rhombohedra r{10-11} , the minor rhombohedra z{10-11} and the prism m{10-10}. All those forms were predicted by PBC theory and were obtained in the Hartman Theory analysis as F(Flat) forms. Figure 1b shows the image of the growth form of a crystal when we take into account van der Waals attractions and Born repulsions as corrections for the attachment energy.

All those growth forms are simulated at the same volume V=109 Å [3].

In those cases where the volume obtained in simulations are not the same as 109 we applied a correction for the volume and in this situation the growth form of the quartz for all the figures 1 a and b in have the same volume.

Table 1
ENERGIES IN THE QUARTZ CRYSTAL

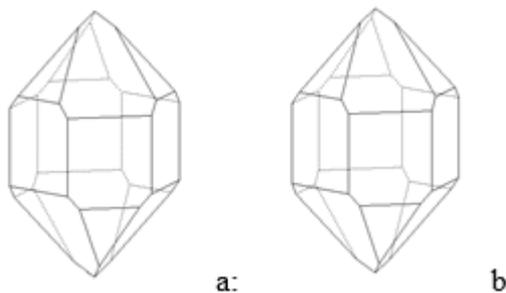| hkil	Eat	corrections		Eatcor
		Born	van der Waals	
(1010)	-1043	+97.3	-88.2	-1033
(1011)	-1279	+101.2	-98.6	-1274
(0111)	-1162	+88.4	-97.7	-1171

Fig. 1. Growth form of α-SiO₂ , a) Coulomb interactions only, b) Including Born and van der Waals

Experimental part
Materials and methods
Raw materials

The reagents (analytical grade): $NaNO_3$, $Al(NO_3)_3 \cdot 9H_2O$, $(C_2H_5O)_4Si$, $(C_2H_5O)_4Si$
were provided by Merck and Sigma-Aldrich (Germany).

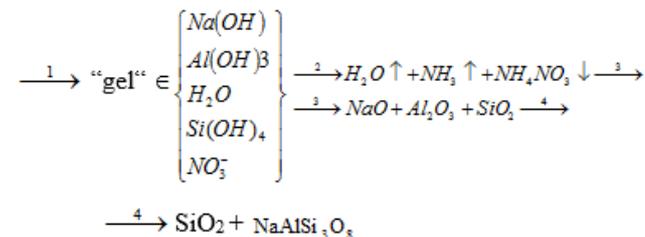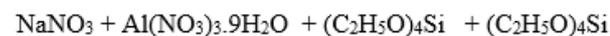Preparation of compositions & materials

This method depends on one or more of the constituents forming a gel structure, the remaining non-gel forming constituents presumably being held within the framework of the gel. The product of drying and then firing the gel at temperatures below 1000°C is a fine grained powder that shows no bi-refringent material under the microscope and gives no X-ray diffraction pattern. This dried, decomposed and fired material is known as *GEL* [16-18]. This method is not recommended for the preparation of compositions with volatile constituents because of processes at high-temperature [18].

It is better to analyze *gels* to test their homogeneity rather than to determine their absolute composition. The method of *gel* preparation employs only weightings of pure chemicals, the bulk chemical compositions depends only on the accuracy of weighing and purity of the chemicals and reagents used in the preparation. It known what was added and if the *gels* are shown to be homogeneous then they must be on composition [18].

Two sources of SiO_2 are available. One is Tetraehyl Orthosilicate (T.E.O.S.) and other is an ammonia-stabilized colloidal solution (LUDOX). In the experiment was used TEOS.

Hydrothermal Experiment

$$NaNO_3 + Al(NO_3)_3 \cdot 9H_2O + (C_2H_5O)_4Si + (C_2H_5O)_4Si$$

$$\xrightarrow{1} \text{"gel"} \in \begin{cases} Na(OH) \\ Al(OH)3 \\ H_2O \\ Si(OH)_4 \\ NO_3^- \end{cases} \xrightarrow{2} H_2O \uparrow + NH_3 \uparrow + NH_4NO_3 \downarrow \xrightarrow{3}$$

$$\xrightarrow{3} NaO + Al_2O_3 + SiO_2 \xrightarrow{4}$$

$$\xrightarrow{4} SiO_2 + NaAlSi_3O_8$$

where:
- is gelling process by adding excess of NH_4OH (15 mL of solution 25%)
- is drying process to 110 °C
- is heating process to 800 °C in Ar/H₂ atmosphere
- is HPT(height pressure and temperature) experiment at a pressure of p=3 kbar, temperature of t=700°C and for different period for example T = 7 days .

Preparation and welding of gold capsule used in the hydrothermal experiment

The gold tubes with $\Phi_{internal}$=2.5 mm and $\Phi_{external}$=2.9 mm are cut at a length h=2.5 mm .They are weight before the experiment (5 tubes of that dimensions have 4.14 g).The gold tubes are pressed and squeezed and after this begin the welding procedure of the free end of the gold tube. For welding the used electrode is from Tungsten or Carbon. The intensity of electric current is I =12A . The welding takes place in an Ar flow to avoid oxidation (is not obvious for gold but is recommended). After the welding the free end of the tube is close. To check this we use a stereo loupe which magnified a few times to see if the result are good or not. The material (the gel) is put inside of these gold capsules and weight the quantities o materials and the quantities of water and we can write that we know that liquid solid ration is then mL/mS is already known. We close the other free end of the gold capsule with material inside. This time the welding takes place in a place where below the gold capsule we use a glass with ice. The gold capsule with material inside (gel with water in a well known liquid-solid ratio) is put inside of a TUTTLE vessel. The volume which is not use from the vessel is filled with a steel rod. The vessel in mounted inside of a safety cabinet. We connect the water cooling system at the bottom part of the vessel, the thermocouple (Type K till 1200 °C), pressure and close the valves and leave the system 12 h to check for leakage. If everything is OK we can switch on the heating in the furnace. After 1 h we can put down the furnace, on top of the vessel and using these we can increase the temperature. In the same time we
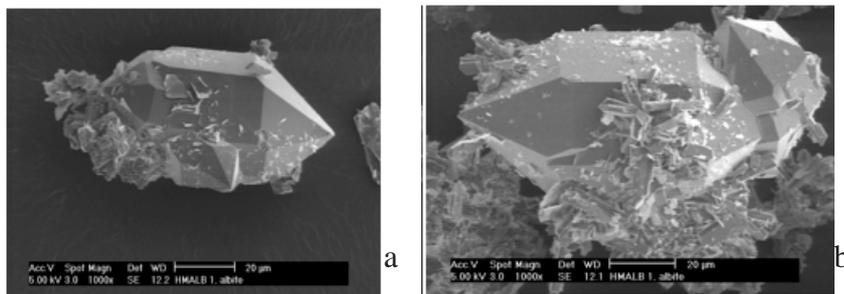
Fig. 2. a) and b) SEM images of SiO$_2$ crystals obtained in a hydrothermal experiment
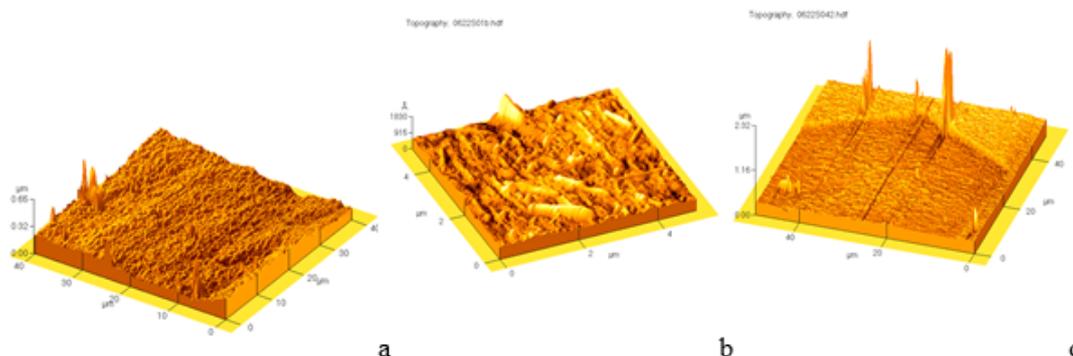

Fig. 3. a) AFM images of quartz crystals obtained in a hydrothermal experiment;
b) AFM images of quartz crystals obtained in a hydrothermal experiment. Image presents inclusions;
c) AFM images of quartz crystals obtained in a hydrothermal experiment with irregularities

have pressure in the vessel (furnace). The temperature in the vessel increase and for this reason pressure increase too and we have to decrease the pressure manually to avoid excess pressure in the system. Hydrothermal experiment can be made for different pressure, temperature times and different liquid -solid ratio ml/mS calculated already. The experiment ends by taking up the furnace and cooling the system with air and after that released the pressure again. After opening the vessel and then the gold capsule we start the experimental part of recognition of the material obtained in the experiment. First the material is took out using water .First we can have an optical observation on a normal optical microscope to see there are crystals inside of he material or not. When we looked at the microscope using polarized light we can see very well the anisotropic crystals. We can still recognize the morphology of the crystals by using 1 polarized filter.

SEM analysis of SiO$_2$
After the hydrothermal experiment we made a SEM analysis of the obtained sample. We can observe that in the sample we got quartz crystals with F faces as those simulated in the theoretical model .

In the sample of we can see SiO$_2$ and NaAlSi$_3$O$_8$ crystals after the hydrothermal experiment. Most of them are twins. In figure 2a we can see twin quartz crystals; and in figure 2b we can see together with the quartz crystals NaAlSi$_3$O$_8$ crystals which have the forms like polygonal bars.

AFM analysis of SiO$_2$
We did AFM analysis of the obtained quartz crystals and we observed that the surface of the obtained crystals are not perfectly flat.

In figure 3a we can observe the surface which is flat but has irregularities in heights.

In figure 3b we can observe on the quartz surface some small inclusions.

In figure 3c are shown some small striations on the flat faces of obtained quartz crystals from the hydrothermal experiments.

In his paper from 1978 Hartman continued his work with a review of the role of super saturation and adsorption of impurities in habit change [12]. The presence of high index faces is attributed to a slow growth of steps of which the interaction energy becomes repulsive when they move closer. Here is stated again that F forms are $m\{10\bar{1}0\}, r\{10\bar{1}1\}, z\{\bar{1}011\}$ .The absence of the basal plane and of S faces between the basal plane and the rhombohedra r and z is attributed to the fact that these faces haves a K character. The absence of S faces between the prism faces is due to the fact that two neighboring faces do not contains the same PBC.

Simulations of the interatomic interactions investigate micro structures of crystals and melts, and their macroscopic, thermodynamic and physical properties. Numerical computations are particularly useful and powerful for problems that may be inaccessible to direct experimental study, such as extremes of temperature and pressure . Work of quartz crystals have been done by Burnham(1990) and Catlow and Price (1990) , Cohen (1992), Stixrude and Cohen (1995), Dovesi et.al(1992), Winkler and Dove (1992), Parker et al. (1993), Catti et al.(1994), Matsui and Price (1991, 1992) [5].

Conclusions
From the studies of structure we find that {10-10}, {10-11}, {-1011}, {01-10} and 01-11} are F faces .Quartz is very good example that has faces which are parallel to at least 2 PBCs and are not always F faces.

From the SEM analysis we observe that the simulated growth forms of quartz is in a good agreement with the crystals obtained from the hydrothermal experiment.

The microstructure of quartz crystals observed in an AFM analysis gave us information that quartz crystals grow with striations and small inclusions on the Flat faces.

In the present paper is presented a method of crystals analysis which is fully validated by experimental results. This method is robust and is fitting for the purposes of prediction of growing and equilibrium form of the crystals in the next future. The significance, novelty and

wider societal impact of the work reported in this article is height because can be applied to fields of healthcare and pharmaceuticals, environmental and forensic analysis, agricultural science and food products too.

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