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STUDY OF THE CRYSTAL STRUCTURE OF α-$CaSO_4 \cdot 0.5H_20$

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Abstract

The study of the crystal structure of α-$CaSO_4$*$0.5H_20$, obtained under hydrothermal conditions in the presence of a small amount of succinic acid, indicated that the crystals exhibit trigonal symmetry at room temperature. The unit cell parameters are the following: a_o = 6.83 Å, c_o = 12.71 Å, α = ß = 90°, γ = 120°, Z = 6.

Introduction

The crystal structure of the hemihydrate is complicated. According to morphological studies, $CaSO_4$*$0.5H_20$ has rhombic structure, but according to optical measurements the structure is pseudorhombic.(1) However, Gallitelli has found that the hemihydrate has monoclinic symmetry.(2) Flörke(3) has proven, that at the temperatures above 45°C the hemihydrate shows the symmetry assigned to scalene class (i.e., 3 2/ m = D_{2d}), containing simultaneously elements of trigonal system (i.e., 3-three-fold inversion axis) and of monoclinic system (i.e., a two-fold symmetry axis and a perpendicular symmetry plane). Above 45°C the hemihydrate constitutes a non-uniform system of lower symmetry. Its crystal structure resembles a combination of three overlapping rhombic lattices, rotated for 120° one relative to another. Only at much higher temperature, lattices with three-fold symmetry occur. According to Flörke, the parameters of the trigonal unit cell are the following: a_o = 6.86 A, c_o = 12.70 A, α = ß = 90°, γ = 120°, Z = 6, whilst the parameters for the monoclinic unite cell found by Gallitelli are: a_o = 11.49 A, b_o = 6.83 A, c_o = 12.70 A, ß = 90°36', Z = 6.

The discrepancies between the crystalline lattice parameters determined by Gallitelli, Flörke and other researchers result from experimental difficulties, as well as from instability of the crystalline lattice of hemihydrate, which undergoes deformations upon change of temperature and the content of water.(4)

Experimental Part

The crystals of α-$CaSO_4 \cdot 0.5H_20$ used for the study were obtained by a hydrothermal method in the presence of a small amount of succinic acid (0.02%). The shape of the crystals is shown in Fig. 1. The crystals were identified by recording of their powder pattern on DRON-1.5 X-ray diffractometer using a CuK_α X-ray source, and comparison of the results with the reference data from an ASTM catalog (i.e., F.H. Gillery, ASTM Card 6-0046).

FIG. 1
The Photograph of Monocrystal of α-$CaSO_4 \cdot 0.5H_2O$, Magnification 150.

For morphological studies, transparent rod-shaped crystals were selected. The crystal size measured by means of a microscope was on average 1 x 0.5 x 0.5 mm. On the basis of a microscopic studies and measurements of dihedral angles with a bicircular reflexive goniometer, it has been found that the crystals of hemihydrate show the symmetry of a trigonal system. On the crystals there are visible walls of a hexagonal pillar and also walls of a trigonal trapezoid. The data obtained from goniometric measurements are collected in Table 1.

Table 1
Polar Coordinates of the Walls of Monocrystals of α-$CaSO_4 \cdot 0.5H_2O$.

Wall number	Angles	
	ϕ	ρ
Walls of hexagonal pillar		
1	345°35'	84°48'
2	282°38'	86°46'
3	224°08'	90°14'
4	164°31'	91°06'
5	104°42'	89°56'
6	45°46'	86°37'
Wall of trigonal trapezoid		
1	288°15'	30°12'
2	37°40'	31°18'
3	163°44'	34°42'

For the purpose of determination of unit cell parameters and confirmation of the trigonal symmetry, the rocking crystal method, Weissenberg method, and De Jong-Bouman method were applied.[5]

The roentgenograms of rocking crystal were recorded in a Weissenberg camera using CuK_α rays. The axis of rocking was overlapped with the three-fold symmetry axis, and the angle of rocking equaled 40°. By measurement of the distances between symmetrical contour lines, the parameter c_0 of the unit cell was determined, which equaled to 12.71 Å. As the monocrystals studied were small, the remaining parameters of the unit cell were calculated from the Weissenberg roentgenogram of zero contour recorded to the rotation axis c. So the calculated lattice constant a_0 equals 6.83 Å and the angle between x_2-x_3 axes equals 60°. By means of a De Jong-Bouman camera, the zero contour line for a hemihydrate crystal relative to the rotation axis c was recorded. The reflexes on the diffractogram are consistent with the symmetry of a trigonal system.

By modeling of the structure of $CaSO_4 \cdot 0.5H_20$ the following distribution of the structural components within the unit cell was determined:

$6Ca^{2+}$ are positioned on the cell walls	6:2=3
$4Ca^{2+}$ are localized on the edges, so they belong to 4 unit cells	4:4=1
$2Ca^{2+}$ are inside the cell	2:1=2
Total	6

$8SO_4^{2-}$ are localized on the cell walls	8:2=4
$2SO_4^{2-}$ are inside the cell	2:1=2
Total	6

Twelve molecules of water localized on the edges of unit cell indicate that there are three water molecules per one cell (12:4=3). Hence, the calculations shown indicate that the unit cell of hemihydrate is composed of six molecules of $CaSO_4 \cdot 0.5H_20$.

Conclusions

On the basis of the studies presented, it can be concluded that small quantities of succinic acid fix trigonal symmetry of the crystals of $CaSO_4 \cdot 0.5H_20$ even at room temperature.

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