The monoclinic I2 structure of bassanite, calcium sulphate hemihydrate ($CaSO_4 \cdot 0.5H_2O$)

Article *in* European Journal of Mineralogy · September 2001

DOI: 10.1127/0935-1221/2001/0013/0985

4 authors:

Paolo Ballirano
Sapienza University of Rome
189 PUBLICATIONS **2,357** CITATIONS
SEE PROFILE

Adriana Maras
Sapienza University of Rome
88 PUBLICATIONS **940** CITATIONS
SEE PROFILE

Simone Meloni
University of Ferrara
91 PUBLICATIONS **2,583** CITATIONS
SEE PROFILE

Ruggero Caminiti
Sapienza University of Rome
307 PUBLICATIONS **8,560** CITATIONS
SEE PROFILE

Eur. J. Mineral.
2001, **13**, 985–993

The monoclinic *I*2 structure of bassanite, calcium sulphate hemihydrate ($CaSO_4 \cdot 0.5H_2O$)

PAOLO BALLIRANO[1], ADRIANA MARAS[1], SIMONE MELONI[2] and RUGGERO CAMINITI[2]

[1] Dipartimento di Scienze della Terra, Università di Roma “La Sapienza”,
P.le A. Moro 5, I-00185 Roma, Italy
e-mail: paolo.ballirano@uniroma1.it
[2] Dipartimento di Chimica, Istituto Nazionale per la Fisica della Materia,
Università di Roma “La Sapienza”, P.le A. Moro 5, I-00185 Roma, Italy

Abstract: A structural analysis of $CaSO_4 \cdot 0.5H_2O$, a dehydration product of gypsum, has been carried out through the Rietveld method on X-ray powder diffraction data. A dehydrated powder of synthetic gypsum has been charged inside a non-hermetically sealed capillary in order to allow a slow rehydration. The starting material has been identified as γ-anhydrite, space group $P6_222$, cell parameters $a = 6.9691(2)$ Å, $c = 6.3033(2)$ Å. The final product of the rehydration of γ-anhydrite is $CaSO_4 \cdot 0.5H_2O$, space group *I*2 (unique axis *b*), cell parameters $a = 12.0350(5)$ Å, $b = 6.9294(3)$ Å, $c = 12.6705(4)$ Å, $\beta = 90.266(3)°$. The structure of the hemihydrate is strongly pseudo-trigonal, space group $P3_121$. The symmetry lowering arises from water molecules ordering inside the channels.

Key-words: γ-anhydrite, $CaSO_4 \cdot 0.5H_2O$, bassanite, gypsum, X-ray powder diffraction, Rietveld method.

Introduction

The dehydration process of gypsum, $CaSO_4 \cdot 2H_2O$, has been investigated for many years. Thermogravimetric and IR spectroscopy studies (Putnis *et al.*, 1990) indicated an apparently continuous water-loss mechanism characterised by an activation energy of 90.3 kJ mol^{-1}. According to these authors the reaction proceeds from gypsum to hemihydrate ($CaSO_4 \cdot 0.5H_2O$, corresponding to the natural phase bassanite) to γ-$CaSO_4$ (soluble anhydrite) without the occurrence of any further intermediate-water-content form. These data were consistent with the opinion of Ball (1977) that the apparent deviations from stoichiometric bassanite were caused by physical sorption of water. The absence of subhydrates different from the hemihydrate was also indicated, from proton magnetic resonance data, by Saito (1961). In contrast, other authors (*e.g.* Frik & Kuzel, 1982; Bushuev & Borisov, 1982; Abriel, 1983; Kuzel, 1987; Kuzel & Hauner, 1987; Abriel *et al.*, 1988) have synthesised and described different forms of subhydrates ($CaSO_4 \cdot nH_2O$, $0.48 \le n \le 0.81$) whose occurrence has been attributed to different condition of synthesis and in particular to the H_2O partial pressure.

The structural investigations of subhydrates and γ-anhydrite proceeded almost at the same rate as the similarities among the various structures were rapidly hypothesised and proved. For an early collection of relevant references see Deer *et al.* (1962).

The first structural model for the hemihydrate was proposed by Gallitelli (1933). From Weissenberg photographs he determined cell parameters ($a = 11.94$ Å, $b = 6.83$ Å, $c = 12.70$ Å, β *ca.* 90°) and space group (*C*2) demonstrating that the monoclinic, pseudo-trigonal structure was characterised by channels containing the water molecules. Since then various subhydrates have been described

0935-1221/01/0013/0985 $ 2.25

DOI: 10.1127/0935-1221/2001/0013/0985

which are characterised by cell parameters derived from a common trigonal cell with a_{trig} *ca.* 6.9 Å, c_{trig} *ca.* 6.3 Å. The structure of γ-$CaSO_4$ was deduced by Flörke (1952) from single-crystal X-ray data. He proposed two possible models, the preferred one in space group $P6_222$, is the hexagonal analogue of the hemihydrate structure proposed by Gallitelli (1933), however, with halved *c* parameter (*a* = 6.99 Å, *c* = 6.34 Å).

A few structural determinations have been carried out since then on subhydrates and γ-anhydrite. Bushuev (1982), from single crystal data, was able to solve and refine the structure of $CaSO_4 \cdot 0.67H_2O$ in space group *I*2 (unique axis *c),* cell parameters *a* = 12.028 Å, *b* = 12.674 Å, *c* = 6.927 Å, γ = 90.21°. Subsequently Abriel (1983) refined the structure of $CaSO_4 \cdot 0.81H_2O$ in $P3_121$ (cell parameters: *a* = 6.968(9) Å, *c* = 6.410(4) Å). Flörke's structural model of γ-anhydrite was proved to be correct by Lager *et al.* (1984). The reported cell parameters (*a* = 6.9694(8) Å, *c* = 6.3033(4) Å) were similar to those by Bushuev & Borisov (1982) for $CaSO_4 \cdot 0.5H_2O$ if the *c* dimension was halved (*a* = 6.977 Å, *c* = 6.308 Å). Following Lager *et al.* (1984), this fact seems to indicate that the phase described by Bushuev & Borisov (1982) was probably not $CaSO_4 \cdot 0.5H_2O$ but γ-$CaSO_4$. Moreover, Lager *et al.* (1984) attempted to refine the structure of $CaSO_4 \cdot 0.5D_2O$ from neutron powder diffraction data. They used a model derived from the hexagonal structure of γ-$CaSO_4$ but obtained a poor agreement with the experimental data. These authors indicated that, because of the occurrence of short O_W–O_W contacts of about 2 Å, the maximum water content of subhydrates is of 0.5 molecule which is in disagreement with the results of Bushuev (1982) and Abriel (1983). Lager *et al.* (1984) reported a good fitting of the neutron data using the structural parameters of Bushuev (1982) and assuming 50 % occupancy of the water molecules. Recently Abriel & Nesper (1993) have reported the substructure of $CaSO_4 \cdot 0.5H_2O$. These authors pointed out that this modification, presenting pseudo-merohedral twinning, is characterised by a monoclinic, pseudo-trigonal superstructure arising from ordering of the water molecules due to the presence of hydrogen bonds. Ordering was also supported by potential profile calculations. These authors, however, were not able to successfully refine the *I*2 structure from their X-ray data, because of the pseudo-merohedral twinning.

The aim of this paper, which is part of a larger research project on the kinetics of the dehydration of gypsum, is a structural study on the various dehydration products, in particular on $CaSO_4 \cdot 0.5H_2O$, in order to clarify the pending structural problems. Because of the reported occurrence of twinned crystals and the strong tendency of γ-$CaSO_4$ to rehydrate, X-ray powder diffraction and the capillary technique appear to be ideally suited for structural investigations of such phases.

Experimental procedure

The powder of analytical-grade gypsum $CaSO_4 \cdot 2H_2O$ (Analar, product 10071) was heated for one week at 150°C in a furnace containing several beakers filled with silica gel and, without removal of the sample from the furnace the powder was packed inside a 0.5 mm ∅ borosilicate-glass capillary (W. Müller, D-1000 Berlin, Germany). The open capillary was again kept at 150°C for one week and subsequently non-hermetically sealed. The X-ray powder diffraction data were collected on an automated Siemens D5005, equipped with an incident beam X-ray mirror, a goniometer head as a sample holder, and two sets of Soller slits (divergence of 2.3°) on both incident and reflected beams. Data were collected in 2θ scan mode. Analyses were reiterated, in order to detect the end of the rehydration process, until no further modifications of the spectra were observed. The data set comprises 13 diffraction patterns (Fig. 1). Experimental details are reported in Table 1. A diffraction pattern was also collected on the starting material as a check for sample purity. The data evaluation included structure refinements that were carried out by the Rietveld method using the PC version (release 9-2000) of the GSAS crystallographic package (Larson & Von Dreele, 1985). The scattering

Table 1. Experimental details of the X-ray powder diffraction data collection.

Instrument	Siemens D5005
X-ray tube	Cu at 40 kV and 40 mA
Incident beam optics	Multilayer X-ray mirror
Sample mount	Rotating capillary (30 r.min^{-1})
Soller slits	2 (2.3° divergence)
Divergence and antidivergence slits	1 mm
Detector slit	0.1 mm (0.05°)
Detector	Scintillator
2θ range	13-150°
Step size	0.02° (6851 points)
Counting time	30 s

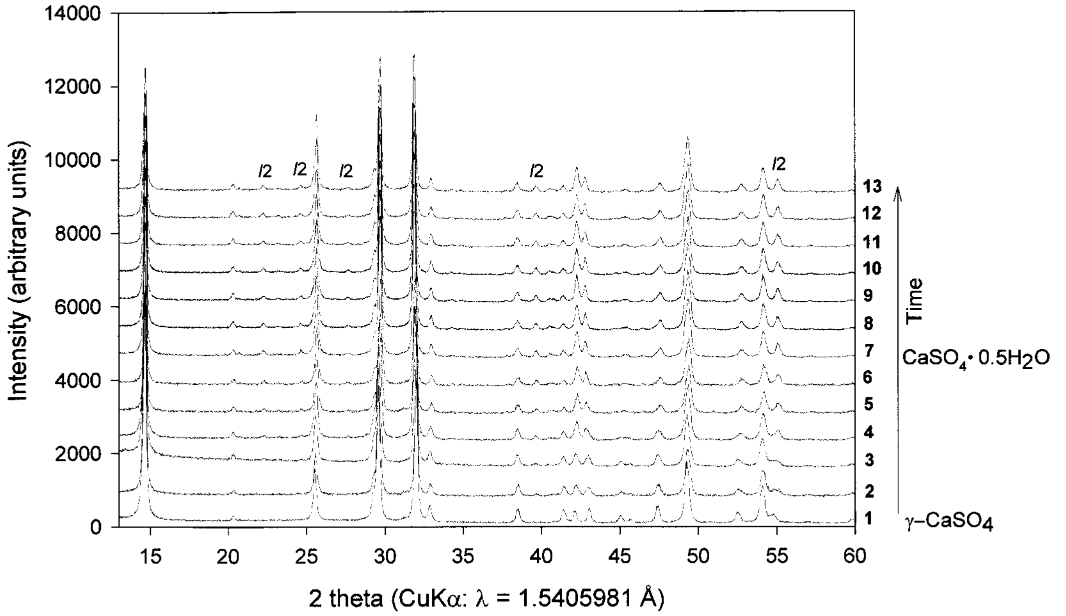

Fig. 1. Evolution of the powder diffraction patterns of γ-anhydrite with time. The appearance of some extra peaks during the evolution of the rehydration process, labelled as *I2*, is related to the formation of calcium sulfate hemihydrate.

power of the oxygen atoms of the water molecules was modified in order to include the electronic contribution of the bonded hydrogen atoms. An absorption correction was carried out as a part of the Rietveld refinements: the average value of the refined $\lambda A_B = \mu R$ was *ca.* 1.4, to be compared to calculated values for a rod-shaped single crystal of the same thickness, of ca. 5.0 (mass attenuation coefficients taken from the International Tables for Crystallography, Vol. C, 1995). The difference between the two values is caused by a reduced packing density. Peak shape was modelled by means of a pseudo-Voigt function modified to incorporate asymmetry (Finger *et al.*, 1994). Refined parameters included: $\tan^2 \theta$-, $\tan \theta$-dependent, and θ-independent Gaussian parameters (GU, GV, and GW respectively), $1/\cos \theta$- and $\tan \theta$-dependent Lorentzian parameters LX and LY, asymmetry parameters S/H and L/H. The peak cut-off was set to 0.2 % of the peak maximum. The background was fitted with a shifted Chebyshev polynomial of the first kind. The presence of texture was checked by means of a generalised spherical-harmonic description (Von Dreele, 1997). No significant improvement of the fits was observed as a result of texture indices J very close to unit, as expected for a capillary mount.

Refinements and discussion

The refinement of the starting material, identified as γ-$CaSO_4$, is fully consistent with that of Lager *et al.* (1984) on neutron data. The cell parameters (a = 6.9691(2) Å, c = 6.3033(2) Å) and bond distances and angles are within 1σ of the reference data.

The end of the rehydration process was reached during the sixth spectrum. The remaining seven diffraction patterns, therefore attributed to bassanite, were fitted with an *I*2 structure (unique axis *b*, cell choice 3) derived from the $P3_121$ substructure of Abriel & Nesper (1993). The space group *I*2 (more precisely *C*2 and therefore *I*2 after a different cell choice) represents, in fact, a maximal non-isomorphic *t*-subgroup of $P3_121$. The resulting structure has a volume quadruple with respect to that of the trigonal substructure and comprises four independent Ca sites (two in special and two in general positions), three S sites (all in general positions), and 12 O sites (all in general positions). This monoclinic structure allows ordering of water molecules: in fact they may be distributed over four independent sites, two in special (O_{W1}: 0, 0.85, 0 and O_{W3}: 0, 0.85, 0.5) and two in general positions (O_{W2}: 0.95, 0, 0.33 and O_{W4}: 0.95, 0, 0.83). As a starting model six water molecules were statistically distributed over the four sites, each one with occupancy of 50 %. The origin along the *b* axis was set with a Ca atom at 0, 0.5, 0.

The structure refinements were restrained, using a weight of 10, with S-O bond distances of 1.475 ± 0.01 Å (corresponding to the average S-O bond distance observed in gypsum and anhydrite), O-O distances of 2.408 ± 0.03 Å (corresponding to tetrahedral angles of 109.44°), and Ca-O distances of 2.50 ± 0.08 Å. Such a procedure has been proved to be very effective in order to avoid divergence or convergence toward false minima (Baerlocher, 1993). Isotropic displacement parameters for groups of equal atoms (all Ca atoms, all S atoms, all O atoms, and all O atoms of the water molecules) were also refined.

The following discussion will be focused in particular on the refinement of the last diffraction pattern recorded but applies equally well to the preceding six as the final results are very similar.

During the refinement, two of the water sites immediately refined to zero occupancy and for this reason were removed from the least-squares procedure whereas the remaining two sites (O_{W1} and O_{W2}) increased their occupancy near to one. At this point of the refinement the occupancy of O_{W1} and O_{W2} was fixed to one. Moreover the restraints on Ca-O bond distances were modified to 2.47 ± 0.08 or 2.53 ± 0.08 Å, depending on the presence of a water molecule inside the coordination polyhedron. These two values were chosen in order to be consistent with a bond strength of 2 v.u. (valence units) for Ca in both cases of an 8- and a 9-fold coordination (Brese & O'Keeffe, 1991). After convergence was reached, the refinement proceeded with the weight associated to each single restraint reduced to unit. No significant differences in bond distances ($\frac{\Delta}{\sigma}$ = 1.3) and angles ($\frac{\Delta}{\sigma}$ = 0.9 in the case of O-S-O bond angles) were observed comparing the two refinements. The only relevant difference is represented by the 1.5 times increment of the E.S.D. The refinement smoothly converged to Rp = 5.73 %, wRp = 7.49 %, R_{Bragg} = 2.85 %, reduced χ^2 = 1.104. The contribution to χ^2 of the restraints is 128 (corresponding to 0.85 % of χ^2). The J index is 1.08 for four Orientation-Distribution-Function (ODF) coefficients. Refined cell parameters are *a* = 12.0350(5) Å, *b* = 6.9294(3) Å, *c* = 12.6705(4) Å, β = 90.266(3)°.

Table 2. Miscellaneous data of the refinements of γ-anhydrite and $CaSO_4 \cdot 0.5H_2O$.

	γ-anhydrite	$CaSO_4 \cdot 0.5H_2O$	
		Scan n. 13	Average*
Rp (%)	6.70	5.73	5.85(7)
wRp (%)	8.73	7.49	7.65(7)
R_B (%)	3.35	2.85	3.3(2)
DWd	1.658	1.804	1.82(1)
Refined parms.	58	117	117
Reduced χ^2	1.236	1.104	1.13(2)
χ^2 restr.	0	128	117(12)
χ^2 restr./ χ^2 tot. (%)	0	0.85	1.2(3)
Peak cut-off (%)	0.2	0.2	0.2
$(\mu R)_{calc.}$	1.40	1.39	1.40(3)
J	1.020	1.079	1.06(1)
a (Å)	6.9691(2)	12.0350(5)	12.0340(6)
b (Å)	-	6.9294(3)	6.9284(6)
c (Å)	6.3033(2)	12.6705(4)	12.672(1)
β (°)	-	90.266(3)	90.265(3)
GU	294(23)	220(20)	214(15)
GV	-119(12)	-104(11)	-88(12)
GW	20(2)	23(2)	19(2)
LX	8.1(4)	8.0(4)	8.7(6)
LY	23(1)	16(1)	12(3)
S/H	0.0260(4)	0.0259(5)	0.0260(3)
L/H	0.0260(0)	0.0260(0)	0.0260(3)

* Average over the last seven scans.
Agreement indices as defined in Young (1993).

Table 3. Fractional coordinates and displacement parameters of $CaSO_4 \cdot 0.5H_2O$ as derived from the refinement of the last pattern.

	x	*y*	*z*	B_{iso}(Å^2)
Ca1	0	0.500(0)	0	0.91(5)
Ca2	½	0.011(2)	0	0.91(5)
Ca3	0.2380(5)	0.199(2)	0.1677(8)	0.91(5)
Ca4	0.2217(6)	0.165(2)	0.6648(8)	0.91(5)
S1	-0.0016(8)	0.499(2)	0.2493(6)	0.75(6)
S2	0.2247(7)	0.164(2)	0.9183(8)	0.75(6)
S3	0.2282(8)	0.185(2)	0.4146(8)	0.75(6)
O1	0.127(1)	0.211(3)	0.984(1)	0.90(7)
O2	0.125(1)	0.230(3)	0.473(2)	0.90(7)
O3	0.074(1)	0.616(3)	0.315(1)	0.90(7)
O4	0.075(1)	0.620(3)	0.816(1)	0.90(7)
O5	0.196(1)	0.044(3)	0.332(1)	0.90(7)
O6	0.205(2)	-0.015(3)	0.858(1)	0.90(7)
O7	0.057(1)	0.366(3)	0.178(1)	0.90(7)
O8	0.058(1)	0.376(2)	0.673(1)	0.90(7)
O9	0.272(2)	0.359(3)	0.361(1)	0.90(7)
O10	0.238(1)	0.317(3)	0.838(1)	0.90(7)
O11	0.319(1)	0.161(3)	0.991(1)	0.90(7)
O12	0.308(1)	0.103(3)	0.491(1)	0.90(7)
O_{W1}	0	0.843(4)	0	6.4(3)
O_{W2}	0.953(2)	0.004(4)	0.353(2)	6.4(3)

Miscellaneous data both for the last pattern and

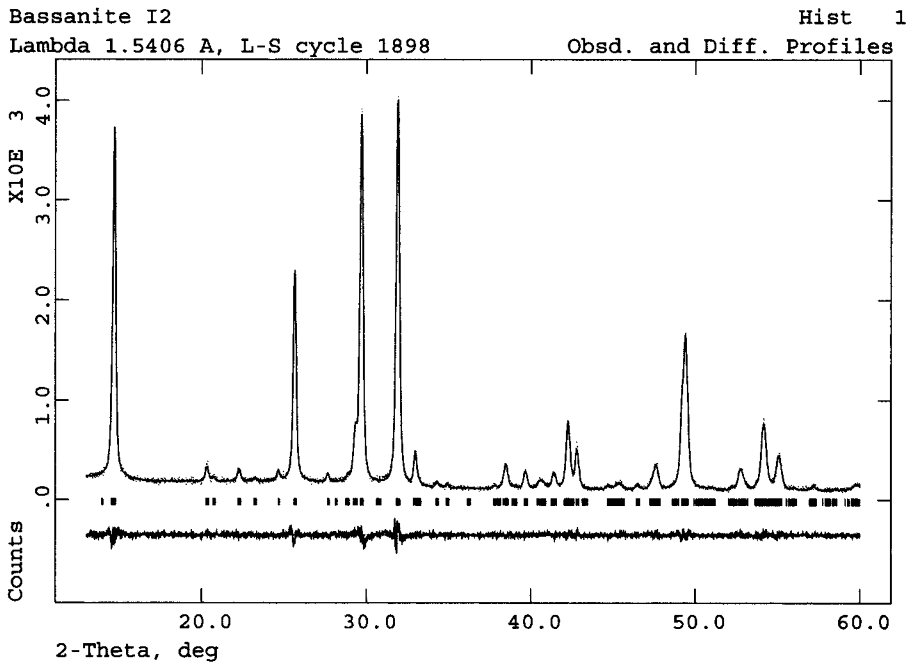

Fig. 2. a) Experimental (dots) and calculated (continuous line) plots for the *I*2 structure of $CaSO_4 \cdot 0.5H_2O$. The difference profile is shown at the bottom of the figure. Vertical markers refer to the positions of the calculated Bragg reflections.

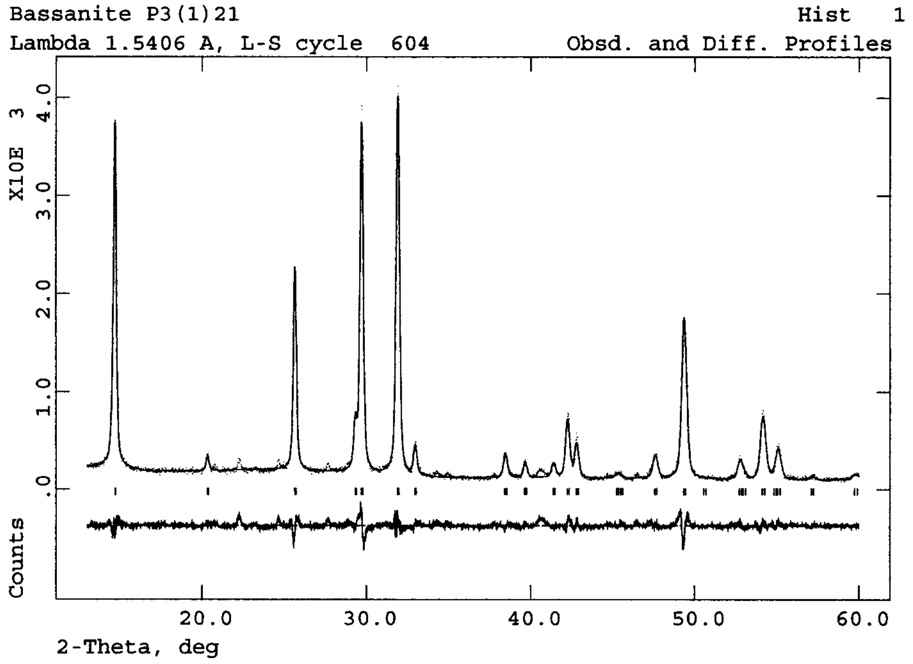

Fig. 2. b) Experimental (dots) and calculated (continuous line) plots for the $P3_121$ structure of $CaSO_4 \cdot 0.5H_2O$.

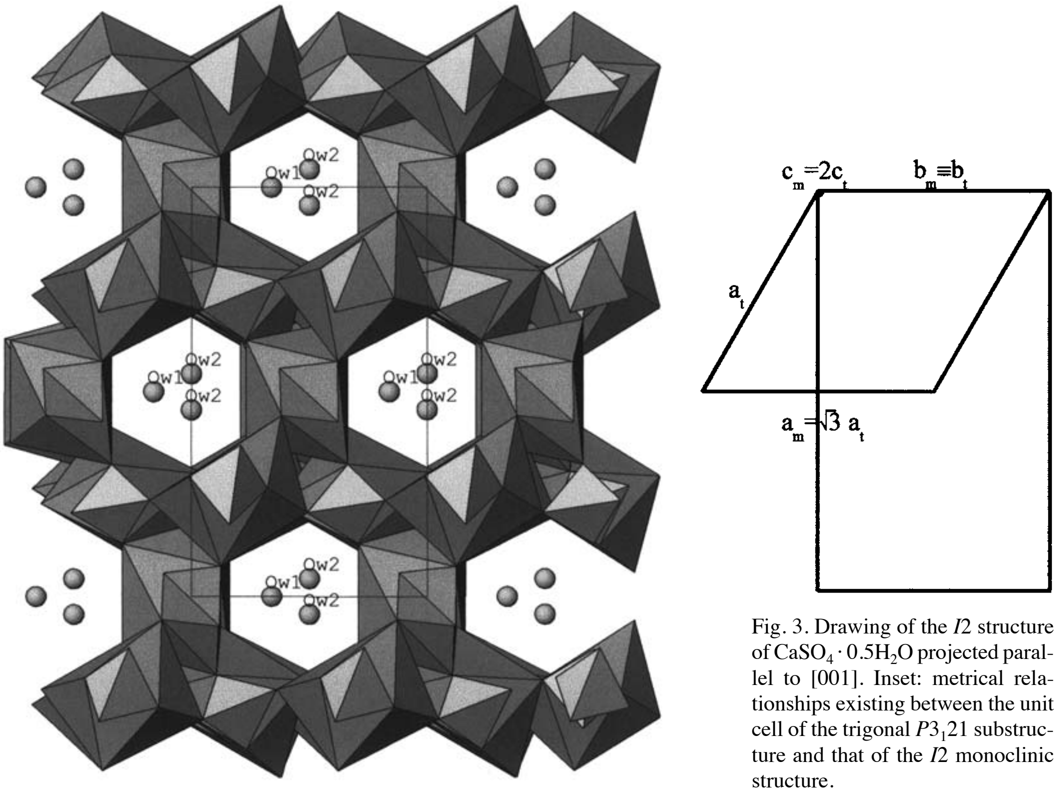

Fig. 3. Drawing of the *I*2 structure of $CaSO_4 \cdot 0.5H_2O$ projected parallel to [001]. Inset: metrical relationships existing between the unit cell of the trigonal $P3_121$ substructure and that of the *I*2 monoclinic structure.

for the averaged values over the seven scans are collected in Table 2. Fractional coordinates and displacement parameters are reported in Table 3, relevant bond distances and angles referring to the refinement of the last pattern, carried out with unit weight, in Table 4. Experimental, calculated, and difference plots are presented in Fig. 2a. For comparison the refinement of $CaSO_4 \cdot 0.5H_2O$ in $P3_121$ is also given (Fig. 2b). A drawing of the corresponding structure, as viewed along [001], is shown in Fig. 3.

According to our data $CaSO_4 \cdot 0.5H_2O$ is characterised by the occupancy of one H_2O (O_{W1}) site with multiplicity two (0, 0.84, 0) and one (O_{W2}) with multiplicity four (0.95, 0, 0.35). In this way no short distances between adjacent water molecules are present in the structure (Fig. 4). This fact confirms the statement of Putnis *et al.* (1990), on the basis of IR spectroscopy, that neighbouring water molecules are sufficiently isolated to prevent vibrational coupling.

As previously indicated, two of the four Ca cations are 8-fold coordinated (Ca2, Ca3) whereas the remaining two are 9-fold coordinated (Ca1, Ca4). The Ca-O bond distances are in the 2.35-2.76 Å range (Table 4): the average bond-distance for Ca-O in 9-fold coordination is 2.51 Å whereas that in 8-fold coordination is 2.50. This spreading is larger than that reported for other calcium sulphates but is comparable to that observed in many other minerals as, for example, aragonite, apatites, zoisite, melilites, and Ca-pyroxenes (for a comprehensive list see for example Smyth & Bish, 1988). As in the case of γ-anhydrite, the geometry of the SO_4 polyhedron is distorted despite of nearly constant S-O bond distances of 1.474(1.458-1.485) Å. In fact three of the six O-S-O bond angles are significantly smaller (average value over the three independent tetrahedra of 106.3(103-108)°) than the remaining three (112.7(111-116)°). The average Ca-O_W distance has been refined to 2.38(1) Å: this value is in good agreement with the average value of 2.42 Å of Einspahr & Bugg (1980) for calcium hydrates. It is, however, significantly shorter than the distance of 2.59(2) Å reported by Abriel (1983) for $CaSO_4 \cdot 0.81H_2O$. The O_{W1} site forms six contacts with the oxygen atoms pertaining to the sulphate groups, namely 2 x O_{W1}-O1, 2 x O_{W1}-O4, and 2 x O_{W1}-O12. Contact distances are in the 2.85-2.98 Å range. On

Table 4. Relevant bond distances and angles of $CaSO_4 \cdot 0.5H_2O$ as derived from the refinement of the last pattern.

Ca1	-O1 x 2		2.53(2) Å	Ca2	-O2 x 2		2.51(2) Å
	-O4 x 2		2.64(2) Å		-O3 x 2		2.61(2) Å
	-O7 x 2		2.53(2) Å		-O8 x 2		2.48(2) Å
	-O12 x 2		2.42(1) Å		-O11 x 2		2.41(2) Å
	-O_{W1}		2.37(3) Å				
average			*2.51 Å*				*2.50 Å*
Ca3	-O1		2.68(2) Å	Ca4	-O2		2.72(2) Å
	-O3		2.35(1) Å		-O4		2.48(1) Å
	-O5		2.40(2) Å		-O6		2.76(2) Å
	-O5		2.51(2) Å		-O6		2.40(2) Å
	-O7		2.48(1) Å		-O8		2.45(1) Å
	-O9		2.72(2) Å		-O10		2.44(2) Å
	-O9		2.39(2) Å		-O10		2.46(2) Å
	-O11		2.46(2) Å		-O12		2.47(2) Å
					-O_{W2}		2.39(2) Å
average			*2.50 Å*				*2.51 Å*
S1	-O3		1.471(7) Å	S2	-O1		1.478(7) Å
	-O4		1.464(7) Å		-O6		1.470(7) Å
	-O7		1.469(7) Å		-O10		1.485(7) Å
	-O8		1.473(7) Å		-O11		1.462(7) Å
average			*1.469 Å*				*1.474 Å*
S3	-O2		1.458(7) Å	O3	-S1-	O4	112(1)°
	-O5		1.483(7) Å			O7	114(1)°
	-O9		1.480(7) Å			O8	103(1)°
	-O12		1.473(7) Å	O4	-S1-	O7	108(1)°
						O8	115(1)°
				O7	-S1-	O8	106(1)°
average			*1.474 Å*				
O1	-S2	O6	111(1)°	O2	-S3-	O5	106.6(9)°
		O10	108(1)°			O9	111(1)°
		O11	106(1)°			O12	107(1)°
O6	-S2-	O10	105(1)°	O5	-S3-	O9	108(1)°
		O11	116(1)°			O12	112(1)°
O10	-S2-	O11	111(1)°	O9	-S1-	O12	112.6(9)°

the other side the $O2_W$ site makes six contacts distributed as 2 x O_{W2}-O2, O_{W2}-O3, O_{W2}-O5, O_{W2}-O8, and O_{W2}-O10. The contact distances are more dispersed, being in the 2.60-3.09 Å range. Such contact distances are in agreement with the 3.02 Å O-H...O distance as calculated from the correlation function $\nu = 3592–3.04 \times 10^{11}\exp\left(-\frac{d_{O...O}}{0.1321}\right)$ of Libowitzky (1999) considering the O-H asymmetric stretching IR vibrational frequency ν of 3560 cm^{-1} reported by Bensted & Prakash (1968). The presence of H atoms along the O_{W2}-O8 directions seems to be ruled out because of the occurrence of a too short (O_{W2}-O8 = 2.60 Å) contact as compared to IR spectroscopic evidence.

The room temperature ordering of the water molecules we observed in hemihydrate seems to be in disagreement with the study of Winkler & Hennion (1994) on the dynamics of molecular H_2O, as investigated by high-resolution incoherent inelastic neutron scattering. In fact these authors found significant differences in the hemihydrate spectra recorded at 150 and 3 K. In particular a significant narrowing of the bands assigned to H_2O motion as well as band splitting was observed for the 3 K spectrum. These differences were attributed to a dynamical disorder of the water molecules at a temperature greater than 3 K. In effect in our molecular dynamics study on calcium sulphate hydrates (Meloni *et al.*, in prep.) we have found that the water molecules are relatively free to move inside the channel. However their mobility cannot result in a free migration toward a neighbouring site because the energy involved in the adjustment of the frame is high enough to prevent this movement.

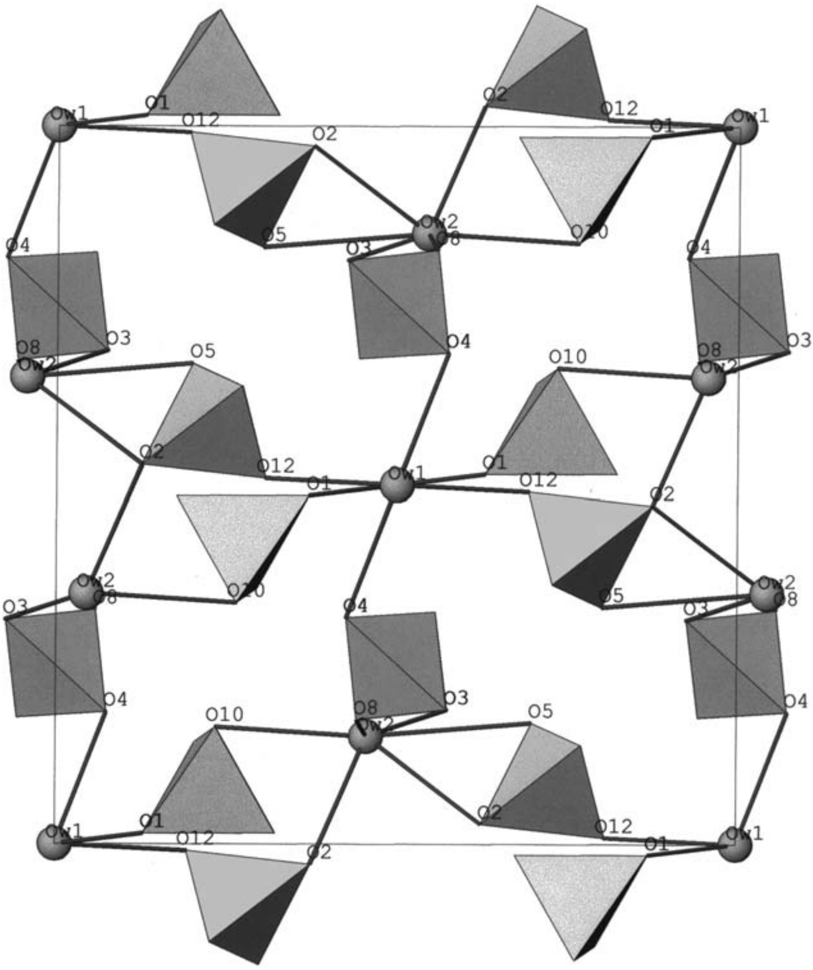

Fig. 4. Drawing of the coordination of water molecules inside the channels. Projection parallel to [010]. O_W-O contact distances in the 2.6-3.1 Å range are reported for clarity.

Conclusions

The structures of γ-anhydrite ($CaSO_4$) and calcium sulphate hemihydrate ($CaSO_4 \cdot 0.5H_2O$), two dehydration products of gypsum, have been investigated. The refined structure of γ-anhydrite is in remarkable agreement with that of Lager *et al.* (1984) obtained from neutron diffraction data. The structure of $CaSO_4 \cdot 0.5H_2O$ has been determined and refined in space group *I*2. The structure is only slightly distorted from the trigonal substructure presented by Abriel & Nesper (1993). The structural data indicate that symmetry lowering from space group $P3_121$ to *I*2 is caused by ordering of the water molecules inside the channels. However, small adjustments of the framework are necessary in order to reach a correct coordination of the oxygen atoms of the CaO_8 polyhedra as required by the bond valence sum. In fact two of the four Ca sites are 8-fold and two 9-fold coordinated. As a result the average bond-distance for Ca-O in 9-fold coordination is 2.51 Å whereas that in 8-fold coordination is 2.50 Å. Despite the reported weakness of the hydrogen bonds (Putnis *et al.*, 1990; Winkler & Hennion, 1994) preliminary results of molecular dynamics calculations indicate that a free interchange of the positions of the water molecules seems to be strongly hindered by the presence of different coordination spheres around the various water sites.

Acknowledgements: Financial support of CNR and MURST is gratefully acknowledged as well as the thorough revision work by Eugen Libowitzky and two anonymous referees.

References

Abriel, W. (1983): Calcium Sulfat Subhydrat, $CaSO_4 \cdot 0.8H_2O$. *Acta Cryst.*, **C39**, 956-958.

Abriel, W. & Nesper, R. (1993): Bestimmung der Kristallstruktur von $CaSO_4 \cdot (H_2O)_{0.5}$ mit Röntgenbeugungsmethoden und mit Potentialprofil-Rechnungen. *Z. Krist.*, **205**, 99-113.

Abriel, W., Reisdorf, K., Pannettier, J. (1988): Kinetisch stabile Phasen bei der Dehydratationsreaktion von Gips. *Z. Krist.*, **182**, 1-2.

Baerlocher, Ch. (1993): Restraints and constraints in Rietveld refinement. *in* "The Rietveld method", R.A. Young, ed. Oxford Science, Oxford, p. 186-196.

Ball, M.C. (1977): A discussion of the paper "The dehydration kinetics of calcium sulfate dihydrate, influence of the gaseous atmosphere and the temperature" by J.J. Gardet, B. Guilhot and M. Soustelle. *Cem. Concr. Res.*, **7**, 351-352.

Bensted, J. & Prakash, S. (1968): Investigation of the calcium sulfate-water system by infrared spectroscopy. *Nature*, **219**, 60-61.

Brese, N.E. & O'Keeffe, M. (1991): Bond-valence parameters for solids. *Acta Cryst.*, **B47**, 192-197.

Bushuev, N.N. (1982): Water of crystallization in the $CaSO_4 \cdot 0.67H_2O$ and $CaSO_4 \cdot 0.50H_2O$ structures. *Russ. Jour. Inorg. Chem.*, **27**, 344-347.

Bushuev, N.N. & Borisov, V.M. (1982): X-ray diffraction investigation of $CaSO_4 \cdot 0.67H_2O$. *Russ. Jour. Inorg. Chem.*, **27**, 341-343.

Deer, W.A., Howie, R.A., Zussman, J. (1962): Rock forming minerals, vol. **5.** The Geological Society, London, p. 202-218.

Einspahr, H. & Bugg, C.E. (1980): The geometry of calcium-water interactions in crystalline hydrates. *Acta Cryst.*, **B36**, 264-271.

Finger, L.W., Cox, D.E., Jephcoat, A.P. (1994): A correction for powder diffraction peak asymmetry due to axial divergence. *J. Appl. Cryst.*, **27**, 892-900.

Flörke, O.W. (1952): Kristallographische und röntgenometrische Untersuchungen im System $CaSO_4 - CaSO_4 \cdot 2H_2O$. *N. Jb. Miner. Abh.*, **84**, 189-240.

Frik, M. & Kuzel, H.-J. (1982): Röntgenographische und thermoanalytische Untersuchungen an Calciumsulfat-Halbhydrat. *Fortschr. Mineral.*, **60**, 80-81.

Gallitelli, P. (1933): Ricerche sul solfato di calcio semidrato e sull'anidro solubile. *Per. Mineral.*, **4**, 133-171.

International Tables for Crystallography (1995): Vol. **C.** Kluwer Academic Publishers, Dordrecht, p. 200-206.

Kuzel, H.-J. (1987): Hydratationswärmen von α-Calciumsulfaten. *N. Jb. Miner. Abh.*, **156**, 155-174.

Kuzel, H.-J. & Hauner, M. (1987): Chemische und kristallographische Eigenschaften von Calciumsulfat-Halbhydrat und Anhydrit III. *Zement-Kalk-Gips*, **40**, 628-632.

Lager, G.A., Armbruster, Th., Rotella, F.J., Jorgensen, J.D., Hinks, D.G. (1984): A crystallographic study of the low-temperature dehydration products of gypsum, $CaSO_4 \cdot 2H_2O$: hemihydrate $CaSO_4 \cdot 0.5H_2O$, and γ-$CaSO_4$. *Am. Mineral.*, **69**, 910-918.

Larson, A.C. & Von Dreele, R.B. (1985): GSAS: General Structure Analysis System. LAUR 86-748, Los Alamos National Laboratory, Copyright, 1985-1994, The Regent of the University of California.

Libowitzky, E. (1999): Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals. *Mh. Chemie*, **130**, 1047-1059.

Putnis, A., Winkler, B., Fernandez-Diaz, L. (1990): In situ IR spectroscopic and thermogravimetric study of the dehydration of gypsum. *Mineral. Mag.*, **54**, 123-128.

Saito, T. (1961): Dehydration and rehydration of gypsum by proton magnetic resonance. *Bull. Chem. Soc. Japan*, **34**, 1454-1457.

Smyth, J.R. & Bish, D.L. (1988): Crystal structures and cation sites of the rock-forming minerals. Allen & Unwin, Boston, MA.

Von Dreele, R.B. (1997): Quantitative texture analysis by Rietveld refinement. *J. Appl. Cryst.*, **30**, 517-525.

Winkler, B. & Hennion, B. (1994): Low temperature dynamics of molecular H_2O in bassanite, gypsum and cordierite investigated by high resolution incoherent inelastic neutron scattering. *Phys. Chem. Minerals*, **21**, 539-545.

Young, R.A. (1993): Introduction to the Rietveld method. *in* "The Rietveld method", R.A. Young, ed. Oxford Science, Oxford, p. 1-38.

Received 4 December 2000
Modified version received 16 February 2001
Accepted 22 March 2001