

Structural characterization of anhydrous and bishydrated calcium hexafluorosilicate by powder diffraction methods

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The synthesis and X-ray powder diffraction data for the long-known CaSiF_6 and $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ species are reported. Their crystal structures have been determined from laboratory powder diffraction data by simulated annealing and full-profile Rietveld refinement methods. $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ was found to crystallize in the monoclinic $P2_1/n$ space group with unit-cell parameters: $a = 10.48107(9)$, $b = 9.18272(7)$, $c = 5.72973(5)$ Å, $\beta = 98.9560(6)^\circ$, $V = 544.733(8)$ Å³, and $Z = 4$. The crystal structure of $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$, eventually found to be isomorphous with $\text{SrSiF}_6 \cdot 2\text{H}_2\text{O}$ (but not with the Mg analogue—a hexahydrate phase), contains centrosymmetric $[\text{Ca}(\mu\text{-H}_2\text{O})_2\text{Ca}]^{4+}$ dimers, interconnected by hexafluorosilicate anions, in a dense 3D framework. The crystal structure is completed by a further water molecule, terminally bound to the Ca^{2+} ion, which, consequently, attains a F_5O_3 octacoordination. Thermodiffraction measurements allowed the determination of the linear and volumetric thermal expansion coefficients of $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$, which showed a minor contraction, along a , on heating. CaSiF_6 is trigonal, space group $R\bar{3}$, $a = 5.3497(3)$, $c = 13.5831(11)$ Å, $V = 336.66(5)$ Å³, and $Z = 3$, and isomorphous with several other species of $M^{\text{II}}\text{A}^{\text{IV}}\text{F}_6$ or $M^{\text{I}}\text{A}^{\text{V}}\text{F}_6$ formulation, among which several silicates, germanates, and stannates. © 2011 International Centre for Diffraction Data. [DOI: 10.1154/1.3641641]

Key words: powder diffraction, calcium fluorosilicate, structure solution, Rietveld refinement, thermodiffraction

I. INTRODUCTION

Calcium hexafluorosilicate bishydrate, $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$, CAS Number: 16961-80-1, is a widely marketed chemical, and a precursor of the anhydrous form, CaSiF_6 , both used as white pigments in ceramics, as preservatives in wood, rubber and textiles, as hardeners in concrete, as opalizers in glass and porcelain enamel and, finally as flotation agents or in insecticides. Medical applications for dentine remediation (Kawasaki *et al.*, 1996) and in bone surgery reconstruction (Hantson *et al.*, 1995) have also been devised.

Despite its wide use, the crystal structure of $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ remains unknown; except for some very limited structural information (unit-cell and experimental d/I list of powder diffraction peaks), in a form that is difficult to retrieve (NBS, 1982). Another occasional citation appeared several years later (Kondrashev and Bogdanov, 1987), in which the bishydrated form of calcium hexafluorosilicate cell was cited on the fly. Even more surprising is the absence of structural information, in the Inorganic Chemistry Structural Database (ICSD), of the purportedly simpler anhydrous CaSiF_6 phase, a crystalline material easily obtainable by thermal treatment, above 160 °C, of the hydrated phase (Patil and Secco, 1975).

In order to fill these gaps, we decided to determine the crystal structures of these species, using laboratory powder diffraction data and *ab initio* structure solution methods. These methods have been used successfully in the recent past by the authors of this paper (Masciocchi *et al.*, 2005) and others (David *et al.*, 2005), to retrieve the structural

features of polycrystalline species of moderately complex structures. A detailed knowledge of structural model at atomic resolution is indeed necessary in order to employ modern quantification techniques based on whole-pattern profile analysis, such as those implemented in widely used computer programs (e.g., QUANTO, Altomare *et al.*, 2001; TOPAS-R, Bruker AXS, 2005).

II. EXPERIMENTAL

A. Synthesis of $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$

A suspension of SiO_2 (particle sizes between 0.063 and 0.200 mm, 70-230 mesh ASTM, 3.30 g) in water (20 ml), was carefully treated with 14.45 ml of HF (40% w/w) at room temperature. To the resulting clear solution, CaCO_3 (5.50 g) was added in small portions until no further gas evolution was detected. The suspension was then oven-dried at $T = 120$ °C for about 150 min, giving a white crystalline powder.

B. Synthesis of CaSiF_6

Anhydrous CaSiF_6 was obtained by heating powders of $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ in air, at $T = 140$ °C for about 30 min, in a custom-made furnace (assembled by Officina Elettrotecnica di Tenno, Ponte Arche, Italy) providing *in situ* heating of the samples directly in the diffractometer cradle.

C. X-ray powder diffraction characterization

Fine powders, obtained by thoroughly grinding the prepared material in an agate mortar, were deposited on a quartz zero-background plate. Diffraction data were recorded on a Bruker AXS D8 Advance diffractometer operating in the $\theta:\theta$ mode, equipped with a Lynxeye position-sensitive

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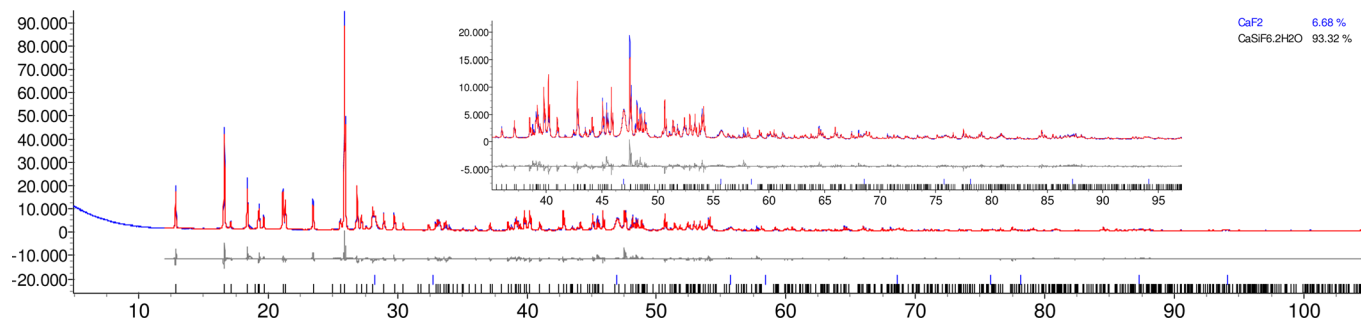


Figure 1. (Color online) Rietveld Refinement plot for $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ with difference plot and peak markers at the bottom. Horizontal axis $2\theta(^{\circ})$; vertical axis: counts. The insert shows the high-angle region at a magnified scale ($5\times$).

detector and Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray generator and diffractometer settings were: 40 kV, 40 mA, and DS 0.5° . The experimental conditions were: step scan mode, with $5 \leq 2\theta \leq 105^{\circ}$, $\Delta 2\theta = 0.02^{\circ}$, total time (in recycling mode) = 18 h. Silicon NBS 640b was used as an external standard.

The recorded pattern of $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ is in agreement with that reported in the PDF 00-33-0307 (ICDD, 2005), for which a tentative unit cell (but not a structural model) was proposed (NBS, 1982). Peak search methods and indexing of the first 20 lines ($2\theta < 31^{\circ}$) by TOPAS-R (Bruker AXS, 2005) allowed the preliminary determination of a monoclinic structure with approximate unit-cell parameters $a = 10.48 \text{ \AA}$, $b = 9.18 \text{ \AA}$, $c = 5.74 \text{ \AA}$, $\beta = 98.95^{\circ}$, $V = 545 \text{ \AA}^3$, and $\text{GoF} = 119.8$. A survey of the 2011 version of the ICSD showed an absence of this phase. It was, therefore, decided to solve the structure by *ab initio* XRPD methods using the experimental data collected as described above. Systematic absences indicated a probable space group, $P2_1/n$, later confirmed by successful structure solution and refinement. The structural model employed in the final whole-pattern Rietveld refinement was determined *ab initio* using simulated annealing

(Kirkpatrick *et al.*, 1983) as implemented in TOPAS-R (Coelho, 2000). According to this real space method, many “tentative” structural models are randomly generated (by positioning a set of atoms or rigid fragments, randomly, within the crystal lattice) and optimized by a combined global optimization algorithm, minimizing the differences between the calculated and the measured diffraction pattern (R_{wp}) and the “potential energy” of the system (as defined by a set of user-defined, properly weighted, penalty functions addressing the “correct” stereochemistry). The magnitude of the randomization is related to the so-called temperature of the process, while solutions are accepted and ranked according to R_{wp} only. In our final model, one independent Ca^{2+} ion, two water molecules (including hydrogen atoms in idealized positions) and independent silicon and fluorine atoms (with soft-restrained Si-F distances) were located in the asymmetric unit, all eventually found to lie in general positions. The final refinement showed evidence of a small contribution from a contaminant phase, identified as nanocrystalline CaF_2 (with crystal size near 40 nm), whose contribution was included in the total pattern simulation—using the known fluorite structural parameters—resulting in a weight percent fraction near 8%.

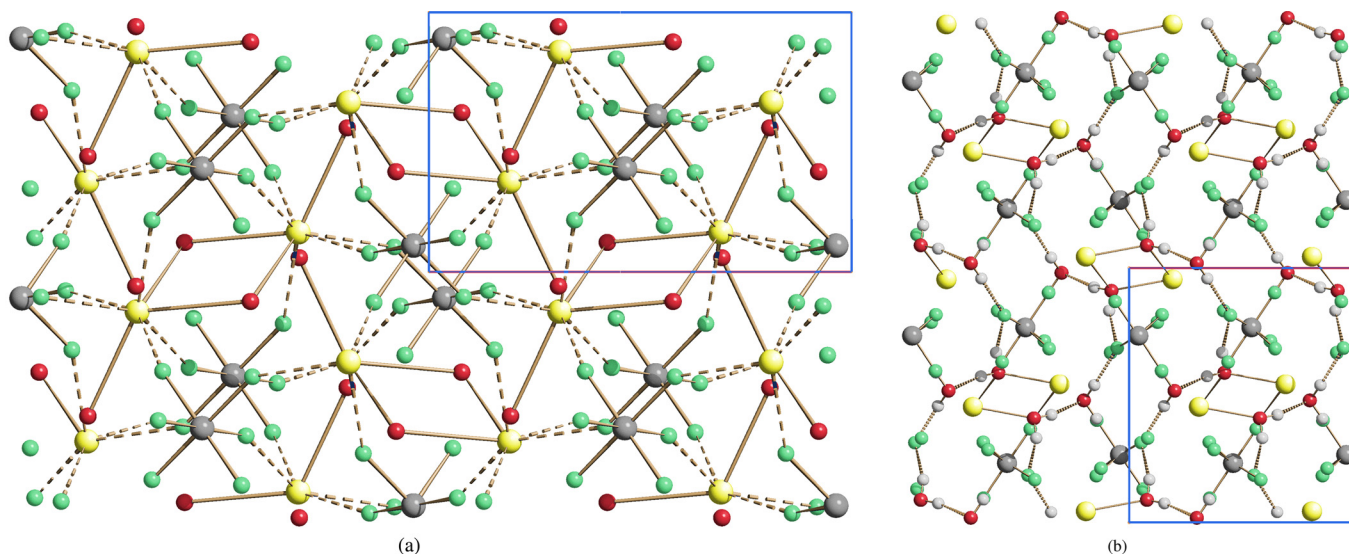


Figure 2. (Color online) Schematic drawing of the crystal packing of the $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ species. Calcium and silicon atoms drawn as large spheres; Calcium ions connected to hexafluorosilicates by fragmented lines. (a) View down $[100]$. Vertical axis: c . Relevant bond distances (\AA) and angles ($^{\circ}$): Ca-O1 2.453(4) to 2.554(6) \AA , Ca-O2 2.404(5), Ca-O1-Ca 108.8(2); Ca-F (fragmented lines): range: 2.235(3)- to 2.444(3), average: 2.356 (statistical dispersion value 0.076); Si-F 1.648(4) to 1.701(3), average value: 1.672. (b) View down $[001]$. Vertical axis: a . Fragmented lines indicate $\text{OH}\cdots\text{O}$ and $\text{OH}\cdots\text{F}$ hydrogen bonds interactions (discussed in the text).

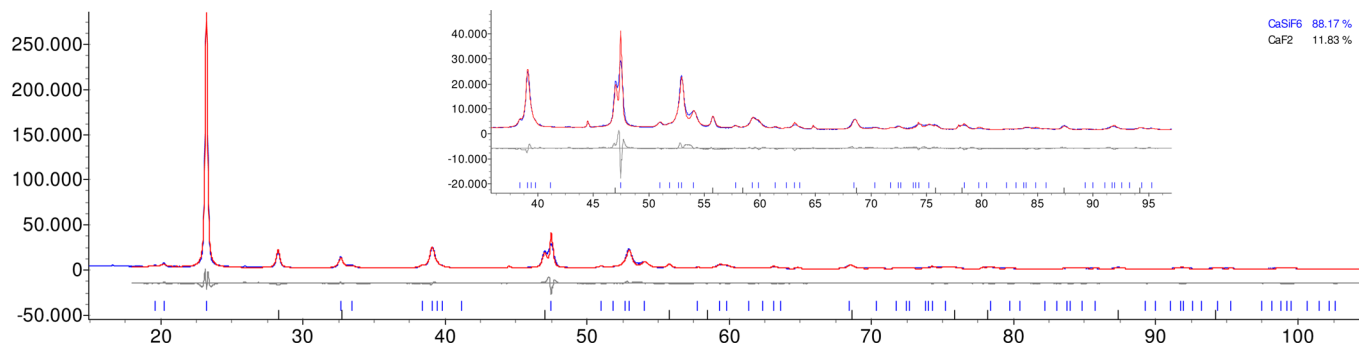


Figure 3. (Color online) Rietveld Refinement plot for CaSiF_6 with difference plot and peak markers at the bottom. Horizontal axis: 2θ ($^\circ$); vertical axis: counts. The insert shows the high-angle region at a magnified scale ($5\times$).

The pattern of anhydrous CaSiF_6 , apart from the expected contamination of residual fluorite (see above), gave broad(er) peaks, which, nevertheless, allowed an easy indexation [$\text{GOF}(18) = 34.7$] and the determination of trigonal unit-cell parameters (R-centered lattice), later refined by the Le Bail method as $a = 5.349$ and $c = 13.596$ Å. A quick search in the ICSD allowed the detection of a number of isomorphous species (among which germanates, stannates, and plumbates), from which initial coordinates of the crystallographically independent ions were taken: Ca in 0, 0, 0; Si in 0, 0, $1/2$ and F in a general (x, y, z) position.

In the final steps of the Rietveld refinements, again performed by TOPAS-R, the background contribution was modelled by a polynomial function, a preferred orientation was applied (only for $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ —in the second-order spherical harmonics description approximation), and three different isotropic thermal parameters were separately refined for the Ca, Si and F/O/H atoms. Ionic scattering factors were used for Ca^{2+} , Si^{4+} , and F^- ions, while neutral ones were employed for the (more) covalently bound O and H atoms. Peak shapes were described by the fundamental parameters approach with anisotropic peak broadening. These specimen-dependent effects, following a $1/\cos\theta$ trend, are attributed to small crystallite sizes, or, more specifically, small coherent scattering domains. Comparison of the average peak widths before and after water molecules elimination allowed the detection of the deterioration of crystallinity, which is attributed to crystal fragmentation. The final Rietveld refinement plots and a sketch of the crystal structures are shown in Figures 1–4. Table I contains the relevant crystal data and data analysis parameters, and Tables II and III contain the final fractional atomic coordinates. While for $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ a suitable entry is present in the PDF 00-33-0307 (ICDD, 2005), the absence of powder diffraction data for CaSiF_6 requires database deposition of the contents of Table IV, in which the observed peaks, in terms of d -spacings, 2θ -angles, relative intensities and their pertinent hkl indices, are listed.

III. DISCUSSION

The crystal structure of $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ contains Ca^{2+} ions in square antiprismatic coordination, connected to five fluorine atoms from neighbouring SiF_6^{2-} anions, and three

oxygen atoms from coordinated water molecules, two of the bridging type (Ca-O1 2.453(4) to 2.554(6) Å, Ca-O1-Ca $108.8(2)^\circ$) and one terminally bound (Ca-O2 2.404(5) Å). $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ is, therefore, isomorphous with its heavier analogue, $\text{SrSiF}_6 \cdot 2\text{H}_2\text{O}$, the structure of which was determined from conventional single-crystal methods by Golovastikov and Belov (1982). In the latter species, six crystallographically independent Si-F bond distances were determined, averaging 1.686 Å, with a very narrow statistical distribution (0.008 Å). Such observations strengthen our choice in using a restrained description of the complex anion in $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$, which gave a slightly larger (0.018 Å) statistical spread of Si-F distances (range: 1.648(4) to 1.701(3) Å, average value: 1.672 Å), likely dependent on the inherent limitations of the powder vs single-crystal, diffraction method. As expected, the presence, in $\text{SrSiF}_6 \cdot 2\text{H}_2\text{O}$, of a slightly larger cation than in the calcium analogue (r^{VIII} 1.26 vs 1.12 Å, respectively, Shannon and Prewitt, 1969), inflates all pertinent values, locally (see for example, Sr-O 2.65 to 2.68 Å, Sr-O 2.59 Å), or globally (unit-cell parameters are inflated by *ca.* 2.6%, the maximum increase ($>3.0\%$) being observed along c).

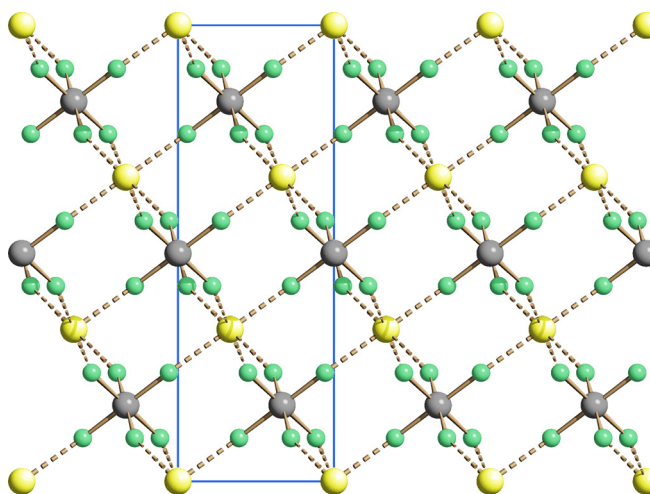


Figure 4. (Color online) Schematic drawing of the crystal packing of the CaSiF_6 species, viewed down $[100]$. Vertical axis: c . Color codes: calcium: yellow; silicon: grey; fluorine: green. Relevant bond distances (Å): Ca-F (fragmented lines) 2.269(3); Si-F 1.659(3) Å.

TABLE I. Crystal data and data-analysis parameters for CaSiF₆·2H₂O and CaSiF₆.

Formula	H ₄ CaF ₆ O ₂ Si	CaF ₆ Si
fw, g mol ⁻¹	218.18	182.15
System	Monoclinic	Trigonal
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>R</i> -3
<i>a</i> , Å	10.48107(9)	5.3497(3)
<i>b</i> , Å	9.18272(7)	5.3497(3)
<i>c</i> , Å	5.72973(5)	13.5831(11)
β°	98.9560(6)	—
<i>V</i> , Å ³	544.733(8)	336.66(5)
<i>Z</i>	4	3
ρ, g cm ⁻³	2.659	2.692
μ(Cu-Kα), mm ⁻¹	13.2	15.4
F(000)	432	264
2θ range	12 to 105	18 to 105
R _p , R _{wp}	0.082, 0.108 ^a	0.064, 0.069
R _{Bragg}	0.065	0.022

^aProfile agreement factors from conventional Rietveld refinement, as defined in TOPAS-R (Bruker AXS, 2005), have been calculated without background subtraction.

The analysis of the short O···O and O···F contacts in the structure allowed to uniquely define the network of hydrogen bonds further connecting the different units in a complex manner (see Figure 2(b)); with hydrogen atoms positioned in ideal locations at 0.90 Å from the pertinent O atoms, the following contacts can be devised: O1-H11···O2 2.78 Å, O1-H12···F4 2.76 Å, O2-H22···F4 2.77 Å, while H21 belongs to a more complex, bifurcated O2-H21-(F3,F4) interaction.

Thermodiffraction experiments were performed in order to determine the linear thermal expansion coefficients and to verify the solid-to-solid transformation of the bishydrated phase into CaSiF₆. The refined unit-cell parameters, corrected for specimen-displacement errors, showed unexpected variations (see Figure 5), with a negative trend for *a* ($\partial \ln a / \partial T = -2.8 \times 10^{-6} \text{ K}^{-1}$) and positive values for *b* and *c* ($\partial \ln b / \partial T = 7.9 \times 10^{-6}$; $\partial \ln c / \partial T = 8.4 \times 10^{-6} \text{ K}^{-1}$),

TABLE II. Fractional atomic coordinates for CaSiF₆·2H₂O.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	B _{iso}
Ca	0.0445(2)	0.1917(2)	0.3421(4)	1.44(5)
O(1)	0.0894(4)	-0.0785(4)	0.3680(9)	1.81(5)
H(11)	0.0760	-0.1557	0.271	1.81(5)
H(12)	0.1677	-0.0887	0.457	1.81(5)
O(2)	-0.0189(4)	0.2992(4)	-0.04101(8)	1.81(5)
H(21)	-0.0907	0.3545	-0.060	1.81(5)
H(22)	0.0411	0.3456	-0.110	1.81(5)
Si	-0.2664(2)	-0.0406(2)	0.0931(3)	0.32(6)
F(1)	-0.3321(3)	0.0818(3)	-0.1036(6)	1.81(5)
F(2)	-0.1835(3)	-0.1454(3)	0.3026(5)	1.81(5)
F(3)	-0.2131(3)	-0.1248(3)	-0.1268(5)	1.81(5)
F(4)	-0.3144(3)	0.0528(3)	0.3128(5)	1.81(5)
F(5)	-0.4029(3)	-0.1433(3)	0.0685(7)	1.81(5)
F(6)	-0.1316(3)	0.0623(3)	0.1313(8)	1.81(5)

TABLE III. Fractional atomic coordinates for CaSiF₆.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	B _{iso} , Å ²
Ca	0	0	0	0.79(9)
Si	0	0	1/2	0.77(12)
F	0.3908(5)	-0.0575(6)	0.2378(2)	1.62(7)

resulting in an overall (rather small) volumetric coefficient of $\partial \ln V / \partial T = 14.1 \times 10^{-6} \text{ K}^{-1}$. Why the structure tends to shrink along *a*, upon mild heating, is not evident, even after a detailed analysis of the Ca²⁺ coordination geometry and of the subtle intermolecular contacts. In the absence of further experimental evidence, we tentatively put forward the hypothesis that a slight tilting (reorientation) of the rather stiff hexafluorosilicate anion, modifying the (flexible) octacoordination of the Ca²⁺ (not possessing stereochemically active *d* electrons) to a very limited extent, can indeed be invoked for such an unexpected (but small) effect.

The CaSiF₆ phase was prepared upon heating the bishydrated species in air at 140 °C for about 30 min. Interestingly, this transformation occurred at a significantly lower temperature than the values of 160 to 165 °C reported by Patil and Secco (1975) and by Zachara and Wiśniewski (1995), and showed that fragmentation of the pristine polycrystalline material occurred, down to coherent domain sizes of less than 40 nm (as measured by the lorentzian peak

TABLE IV. List of observed diffraction peaks for CaSiF₆ (λ = 1.5406 Å).

2θ _{obs} , °	<i>d</i> _{obs} , Å	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>	2θ _{calc} , °	<i>d</i> _{calc} , Å	2θ _{obs} -2θ _{calc} , ° ^a
19.596	4.5265	0.7	0	0	3	19.591	4.5277	0.005
20.228	4.3864	1.6	1	0	1	20.235	4.3849	-0.007
23.210	3.8292	100	0	1	2	23.222	3.8273	-0.012
32.681	2.7379	4.6	1	0	4	32.669	2.7389	0.012
33.440	2.6775	1.6	1	1	0	33.474	2.6749	-0.034
38.410	2.3417	1.3	0	1	5	38.380	2.3435	0.030
39.116	2.3011	8.2	1	1	3	39.082	2.3030	0.034
47.477	1.9135	9.9	0	2	4	47.473	1.9136	0.004
50.958	1.7906	1.1	1	0	7	50.984	1.7898	-0.026
52.937	1.7283	7.8	1	1	6	52.945	1.7280	-0.008
54.058	1.6951	2.9	1	2	2	54.037	1.6956	0.021
57.767	1.5947	0.6	0	1	8	57.788	1.5942	-0.021
59.407	1.5544	1.7	2	1	4	59.331	1.5564	0.076
61.308	1.5108	0.4	0	0	9	61.380	1.5092	-0.072
62.411	1.4857	0.3	0	2	7	62.375	1.4875	0.036
63.147	1.4701	0.7	1	2	5	63.116	1.4718	0.031
68.529	1.3682	1.6	2	0	8	68.457	1.3694	0.072
70.303	1.3379	0.3	2	2	0	70.333	1.3374	-0.030
71.709	1.3151	0.3	1	1	9	71.752	1.3144	-0.043
72.451	1.3035	0.5	1	0	10	72.452	1.3034	-0.001
74.303	1.2755	0.9	3	0	6	74.285	1.2758	0.018
78.450	1.2181	0.7	1	2	8	78.385	1.2190	0.065
79.751	1.2015	0.3	1	3	4	79.727	1.2018	0.024

^aA few larger than usual Δ2θ values appear in this table, since several peaks are (i) partially overlapped and (ii) significantly broadened by limited coherent domain sizes, lower than 40 nm (see text).

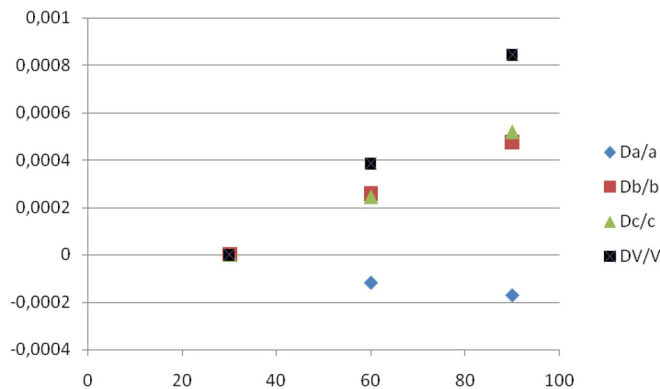


Figure 5. (Color online) Relative $\Delta x/x$ ($=\Delta \ln x$) variations of unit-cell parameters and volume, vs. T ($^{\circ}\text{C}$). Derived linear thermal expansion coefficients are: $\partial \ln a / \partial T = -2.8 \times 10^{-6}$; $\partial \ln b / \partial T = 7.9 \times 10^{-6}$; $\partial \ln c / \partial T = 8.4 \times 10^{-6}$; and $\partial \ln V / \partial T = 14.1 \times 10^{-6} \text{ K}^{-1}$.

broadening attributed to isotropic crystal-size effects after corrected for the instrumental contribution by the fundamental parameters approach). The refined structure of the highly symmetric CaSiF_6 phase allowed an independent determination of Si-F bond distances [$1.659(3) \text{ \AA}$, $6\times$], only marginally lower the average value cited above for $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$, 1.672 \AA .

IV. CONCLUSION

The crystal structures of $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ and CaSiF_6 , two species for which single crystals amenable to conventional diffraction techniques were not available, were determined by employing laboratory X-ray powder diffraction data and, for the bishydrated phase, state-of-the-art *ab initio* techniques. The final model of $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$ was eventually refined, in $P2_1/n$, by the Rietveld method. At variance, the structure of highly symmetric anhydrous salt was refined starting from the knowledge of isomorphous species found in the ICSD database. Accordingly, the detailed knowledge of their crystal structures makes it now possible to meaningfully apply quantitative analytical methods based on the Rietveld technique in the characterization of polyphasic mixtures containing one or both crystal phases, bearing significant industrial interest.

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