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Structure Refinement and Thermal Stability of Creedite

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Abstract—The crystal structure of the mineral creedite (hydrous calcium aluminum sulfate fluoride, $Ca_3Al_2(F,OH)_{10}(SO_4) \cdot 2H_2O$) has been determined by Rietveld powder diffraction analysis. X-ray diffraction data obtained in the temperature range from 25 to 470°C indicate that the crystal structure of creedite is stable up to 390°C. We have measured the unit-cell parameters of creedite as functions of temperature and determined its thermal expansion coefficients. Above 390°C, the mineral decomposes.

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INTRODUCTION

The crystal structure of creedite, $Ca_3Al_2(F,OH)_{10}(SO_4) \cdot 2H_2O$, was first determined in 1964 by Borisov et al. [1]. A year later, Brusentsev et al. [2] reexamined the structure of creedite and were able to distinguish between the oxygen and fluorine atoms [2]. Nevertheless, the arrangement of the water molecules and the role of the hydrogen atoms remained unclear. In 1983, Giuseppetti and Tadini [3] studied in detail the crystal structure of a creedite single crystal from Bolivia and considerably improved the *R* factor. They more accurately determined the cell metrics and atomic coordinates, including the hydrogen atoms.

The water molecules and OH groups in creedite are responsible for the formation of hydrogen bonds, which influence the stability of the crystal structure. To assess the stability of creedite, this mineral was characterized by high-temperature X-ray diffraction (XRD). The results are presented in this paper.

EXPERIMENTAL

The chemical composition of creedite from the Akchatau mine (Kazakhstan) [4, 5] was determined by electron probe X-ray microanalysis (CAMEBAX SX50 microanalyzer). Average over six points (wt %): Al_2O_3, 21.23; CaO, 32.74; SO_3, 15.59; F, 31.52; $O{=}F_2$, 13.97; Σ, 87.11. As follows from the chemical analysis data, the formula of the sample studied is $Ca_{2.93}Al_{2.09}(SO_4)_{0.98}F_{8.34}(OH)_{1.49}O_{0.17} \cdot 2H_2O$. The formula was derived under the constraints Ca + Al + S = 6 and $(F,OH,O)_{10}$. The O/OH ratio was found from the electroneutrality condition. For molecular water, we took an idealized content, $2H_2O$, inferred from structure analysis results. XRD patterns of creedite were collected at room temperature and above on an STOE STADI MP powder diffractometer (bent Ge(111) monochromator, strictly monochromatic CuK_{α_1} radiation, $\lambda = 1.54056$ Å). The data were collected over overlapping scan intervals using a linear position-sensitive detector covering an angular range of 5° 2θ, with a channel width of 0.02°.

After thorough grinding, the powder was pressed into a 0.3-mm-diameter glass capillary tube, which was secured on a rotating goniometer head. The measurements were made in Debye–Scherrer geometry. The crystal structure was refined using room-temperature experimental data. All calculations were performed using the WYRIET 3.3 program [6] and WinX^{Pow} package [7]. As the input model, we used the creedite structure reported by Giuseppetti and Tadini [3]. Line shapes were fitted with Pearson VII functions. First, the structural model was fixed, and we refined only the scale factor, the zero point of the detector, unit-cell parameters, peak asymmetry ($2\theta < 50°$), and full width at half maximum parameters with constant graphical modeling of the background. In the next step, we refined the crystal structure by gradually adding refinement parameters until the *R*-factors stabilized for isotropic thermal parameters. The positional and thermal parameters of the H atoms, taken from Ref. [3], were fixed, without refinement. The refinement converged to the following agreement factor:

$$R_{wp} = 100\left[\sum w|I_{obs} - I_{calc}|^2 \Big/ \sum w I_{obs}^2\right]^{1/2} = 3.62,$$

where I_{obs} and I_{calc} are the observed and calculated intensities. The Durbin–Watson test was DWD = 1.01 [8]. Intensity data collection conditions and refinement parameters are given in Table 1. The calculated profile (continuous line) and raw XRD data (asterisks) for creedite are presented in Fig. 1. Table 2 lists the atomic position coordinates and isotropic thermal parameters.

High-temperature XRD studies of creedite were performed in two steps. First, a powder sample was cemented to tungsten holder, which was then placed in

Table 1. Crystal data and structure refinement statistics for creedite

Crystal system	Monoclinic
Space group, *Z*	*C*2/*c*, 4
a, Å	13.948(1)
b, Å	8.6051(1)
c, Å	9.9823(1)
β, deg	94.37(1)
V, $Å^3$	1194.60(4)
2θ, deg	10–85
Observed reflections	535
Refinement parameters	58
R_p	2.75
R_{wp}	3.62
R_{exp}	2.30
R_B	2.98
R_F	2.91
GoF	1.57
DWD	1.01

a graphite heater. The heating rate was 10°C/min, and the sample was equilibrated for 10 min before measurements. XRD patterns were collected at $t = 100$, 200, 300, 350, 375, and 400°C in the range $2\theta = 10°–90°$. At 400°C, we observed additional, weak reflections, and the intensity of the reflections from creedite decreased. To more accurately determine the temperature at which the additional reflections emerged, we performed XRD measurements at 380, 385, and 390°C. The sample was pressed into a 0.3-mm-diameter quartz capillary tube. Data were collected in the range $2\theta = 20°–35°$, and the heating rate was 20°C/min, with 5-min equilibration.

Figure 2 shows the XRD patterns obtained at 375, 380, 385, and 390°C (the dots mark extra reflections). As seen in Fig. 2, the reflections from creedite become weaker with increasing temperature, and extra reflections emerge in the XRD pattern at $t = 390°C$. The unit-cell parameters *a, b, c*, and *V* of creedite in the range $t = 25–400°C$ are listed in Table 3, and their variation with temperature is illustrated in Fig. 3. The increase in *c* is the largest: $\Delta c = 0.103$ Å. The *a* and *b* cell parameters increase by roughly the same value: $\Delta a = 0.077$ Å and $\Delta b = 0.057$ Å. The unit-cell volume increases by $\Delta V = 26.2$ $Å^3$. The coefficients of linear thermal expansion are $\bar{\alpha}_a = 1.48 \times 10^{-5}$ K^{-1}, $\bar{\alpha}_b = 1.73 \times 10^{-5}$ K^{-1}, $\bar{\alpha}_c = 2.\ 97 \times 10^{-5}$ K^{-1}, and $\bar{\alpha}_V = 6 \times 10^{-5}$ K^{-1}.

RESULTS AND DISCUSSION

The data obtained by refining the crystal structure of creedite from Kazakhstan lend support to the structural model reported by Giuseppetti and Tadini [3]. The structure of creedite contains two types of eight-vertex Ca polyhedra, which share corners and edges to form a framework. The Ca(1) polyhedra are Thompson cubes with five F and three O atoms as their vertices. The Ca(1)–F and Ca(1)–O bond distances range

Table 2. Atomic position coordinates, temperature factors, and site occupancies in the structure of creedite

Atom	*x*	*y*	*z*	B_{iso}, $Å^2$	Occupancy
Ca(1)	0.2475(2)	0.2193(4)	0.1923(4)	0.54(12)	0.99(2)
Ca(2)	0	0.0251(6)	0.025	0.88(17)	0.98(2)
Al	0.2982(4)	0.3996(7)	0.4875(6)	0.25(14)	0.99(4)
S	0	0.6575(7)	0.25	0.85(19)	0.96(4)
F(1)	0.1404(6)	0.1227(11)	0.3473(7)	0.4(3)	1
F(2)	0.4070(6)	0.4524(9)	0.4271(9)	0.8(3)	1
F(3)	0.2649(6)	0.4027(9)	0.028(9)	0.4(2)	1
F(4)	0.234(7)	0.4388(11)	0.322(9)	0.8(3)	1
O(1)	0.4183(7)	0.2612(11)	0.1906(11)	0.7(3)	1
O(2)	0.4702(7)	0.0585(13)	0.3622(11)	1.2(3)	1
O(3)	0.0724(7)	0.2613(13)	0.1166(9)	1.1(3)	1
O(4)	0.3062(7)	0.1869(11)	0.4363(11)	0.5(3)	1
H(1)	0.064	0.246	0.038	3.3	1
H(2)	0.054	0.349	0.128	3.1	1
H(3)	0.355	0.154	0.434	1.4	1

Note: The positional and thermal parameters of the hydrogen atoms were taken from Giuseppetti and Tadini [3] and were not refined.

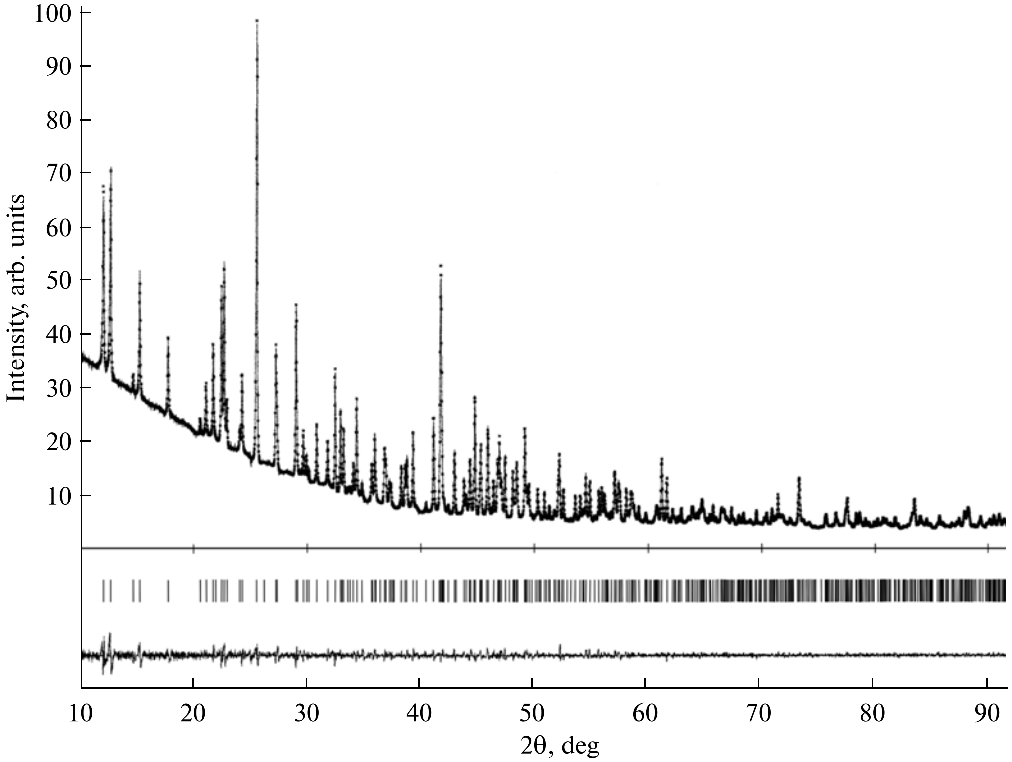

Fig. 1. Calculated profile (asterisks) and raw XRD data (continuous line) for creedite, $Ca_3Al_2(OH)_2F_8(SO_4) \cdot 2H_2O$.

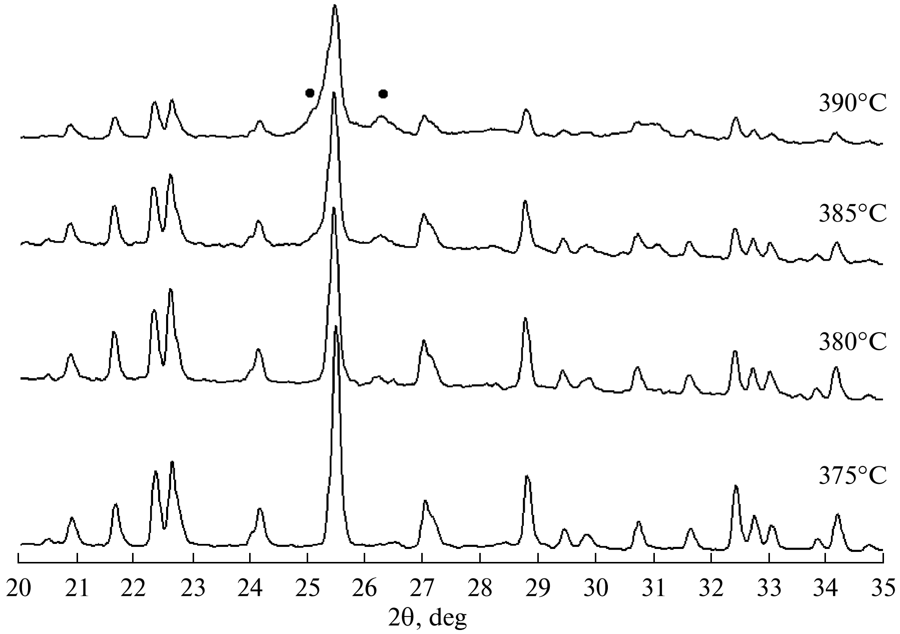

Fig. 2. Portions of XRD patterns obtained at $t = 375$, 380, 385, and 390°C. The dots mark extra reflections.

Table 3. Unit-cell parameters of creedite in the range 25–400°C

t, °C	25	100	200	300	350	375	400
a, Å	13.948(1)	13.970(3)	13.988(3)	14.005(3)	14.015(3)	14.018(5)	14.025(4)
b, Å	8.6051(1)	8.6222(21)	8.6348(12)	8.6505(16)	8.6546(19)	8.659(3)	8.6622(23)
c, Å	9.9823(1)	10.0088(22)	10.0309(14)	10.053(3)	10.0667(22)	10.074(3)	10.0847(25)
β, deg	94.37(1)	94.444(13)	94.539(9)	94.675(17)	94.757(14)	94.789(19)	94.832(14)
V, Å^3	1194.6(4)	1201.9(7)	1207.8(5)	1213.9(7)	1216.8(7)	1218.5(10)	1220.8(8)

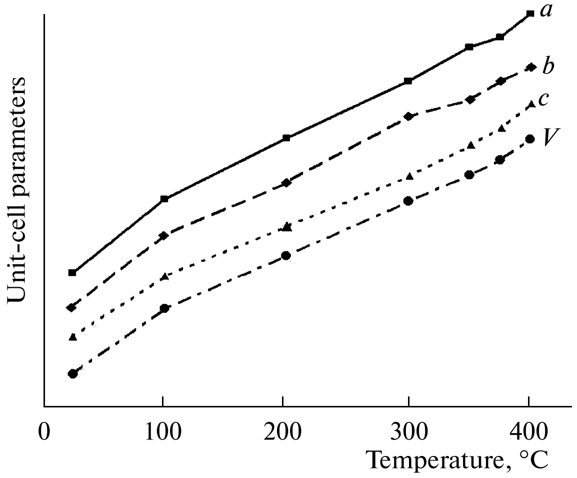

Fig. 3. Temperature dependences of unit-cell parameters.

from 2.302 to 2.433 and from 2.411 to 2.525 Å, respectively. In contrast to Ca(1), the Ca(2) cations are coordinated by four F atoms, at distances from 2.279 to 2.356 Å, and four O atoms, at distances from 2.589 to 2.671 Å.

The Al atoms are coordinated by octahedra of four F atoms, with Al–F bond distances in the range 1.736(5)–1.849 Å, and two O atoms, at distances of 1.850(7) and 1.906(6) Å. The Al octahedra share the edge formed by two O(4) atoms, with a center of inversion at its midpoint. The SO_4 polyhedra have the form of isolated tetrahedra with an average S–O bond distance of 1.522 Å. The Ca(2) polyhedra and SO_4 tetrahedra share the O(1)–O(1) edge.

The present experimental data lead us to conclude that the structure of creedite is stable up to ≃390°C, where the mineral begins to decompose. Characterization of creedite by differential thermal analysis and thermogravimetry [9] reveals a prominent endotherm at $t = 375$–470°C.

Heating creedite powder to 420°C leads to complete structure breakdown, and the XRD pattern shows reflections from $CaSO_4$ and weak peaks attributable to Ca_2AlF_7 and α-CaAlF.

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