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Crystal structure of Kuzel's salt $3CaO\cdot Al_2O_3\cdot 1/2CaSO_4\cdot 1/2CaCl_2\cdot 11H_2O$ determined by synchrotron powder diffraction

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ABSTRACT

The crystal structure of Kuzel's salt has been successfully determined by synchrotron powder diffraction. It crystallizes in the rhombohedral $R\bar{3}$ symmetry with $a = 5.7508$ (2) Å, $c = 50.418$ (3) Å, V = 1444.04 (11) Å^3. Joint Rietveld refinement was realized using three X-ray powder patterns recorded with a unique wavelength and three different sample-to-detector distances. Kuzel's salt is the chloro-sulfoaluminate AFm phase and belongs to the layered double hydroxide (LDH) large family. Its structure is composed of positively charged main layer $[Ca_2Al(OH)_6]^+$ and negatively charged interlayer $[Cl_{0.50}\cdot(SO_4)_{0.25}\cdot 2.5H_2O]^-$. Chloride and sulfate anions are ordered into two independent crystallographic sites and fill successive interlayer leading to the formation of a second-stage compound. The two kinds of interlayer have the compositions $[Cl\cdot 2H_2O]^-$ and $[(SO_4)_{0.5}\cdot 3H_2O]^-$. The crystal structure explains why chloride and sulfate anions are not substituted and why the formation of extended solid solution in the chloro-sulfate AFm system does not occur.

1. Introduction

Calcium sulfoaluminate (CSA) cements may have a good potential to stabilize hazardous wastes such as heavy metals [1–8], ion exchange resins [9], aluminum-containing wastes [10] or radioactive streams containing high amounts of borate and sulfate ions [11]. Their outstanding confining properties are attributed to the structural flexibility of the two main hydrates formed, namely calcium monosulfoaluminate hydrate (an AFm phase [12]) and ettringite (an AFt phase [13]), which can accommodate many substitutions, both by cations and anions [14–18]. In this article, the focus is placed on chloride ions, which can be present as ^{36}Cl in many nuclear waste streams. AFm phases exhibit good capacities to bind chloride anions contrarily to AFt phases [15,19,20]. AFm phases belong to the lamellar double hydroxide (LDH) large family. The crystal structure of AFm phases is composed of positively charged main layers $[Ca_2Al(OH)_6]^+$ and negatively charged interlayers $[X\cdot nH_2O]^-$ where X is one monovalent anion or half a divalent anion. The following general formulae $3CaO\cdot Al_2O_3\cdot CaX_2\cdot nH_2O$ for a monovalent anion, or $3CaO\cdot Al_2O_3\cdot CaX\cdot nH_2O$ for a divalent anion, are generally used in cement chemistry. Several crystallographic studies have been performed on AFm compounds incorporating one type of anion only in the interlayer: SO_4^{2-} [12], Cl^- [21–23], CO_3^{2-} [24,25], NO_3^- [26,27], I^- [28,29] and Br^- [28,29]. Few crystallographic studies were devoted to bi anionic-AFm compounds formed by Cl^-–Br^- [29], CO_3^{2-}–OH^- [30] or CO_3^{2-}–Cl^- permutation [31–33].

The present study first aimed at providing a complete crystallographic description of the SO_4^{2-}–Cl^- bi anionic-AFm compounds – Kuzel's salt of composition $3CaO\cdot Al_2O_3\cdot 1/2CaCl_2\cdot 1/2CaSO_4\cdot\sim 11H_2O$ (which differs from Kuzelite, the mineral name of monosulfoaluminate of composition $3CaO\cdot Al_2O_3\cdot CaSO_4\cdot 12H_2O$ [12]) – by powder X-ray diffraction data. H. J. Kuzel proposed a description of Kuzel's salt in 1966 [34,35], involving ordering of chloride and sulfate anions which fill alternatively successive interlayer regions. However, accurate crystallographic data are still missing. The second objective was to investigate the chloride to sulfate permutation in the chloro-sulfate AFm system in order to explain the absence of any extended solid solution, as previously noticed by several authors [20].

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2. Experimental section

2.1. Synthesis

Powder samples with nominal compositions $[Ca_2Al(OH)_6]\cdot[Cl_{1-x}\cdot(SO_4)_{x/2}\cdot(2+x/2)H_2O]$ were synthesized in aqueous solution. The starting powders $Ca_3Al_2O_6$, $CaCl_2\cdot2H_2O$ (Aldrich, ≥99%) and $CaSO_4\cdot2H_2O$ (Aldrich, ≥99%) were mixed in pure boiled water (decarbonated) to reach a water/solid mass ratio of 50.

Two series of syntheses were prepared, each of them with $x=0.25$, 0.50 and 0.75. The first one was performed at room temperature for one month in closed polypropylene bottles, and the second one at 85 °C for three weeks in closed Teflon reactors. The six suspensions were stored under nitrogen and continuous stirring. At the end of the experiments, the products were centrifuged twice in demineralised and decarbonated water before performing a third centrifugation with isopropanol. The obtained precipitates were subsequently dried in a dessiccator, under slight vacuum, over potassium acetate (≈20% r.h.) at room temperature.

The three samples from the series synthesized at room temperature were named AFm-$[Cl^-_{3/4}(SO_4^{2-})_{1/8}]$-25 °C, AFm-$[Cl^-_{1/2}(SO_4^{2-})_{1/4}]$-25 °C, AFm-$[Cl^-_{1/4}(SO_4^{2-})_{3/8}]$-25 °C for $x=0.25$, 0.50, 0.75 respectively. The three samples from the series synthesized at 85 °C were named AFm-$[Cl^-_{3/4}(SO_4^{2-})_{1/8}]$-85 °C, AFm-$[Cl^-_{1/2}(SO_4^{2-})_{1/4}]$-85 °C, AFm-$[Cl^-_{1/4}(SO_4^{2-})_{3/8}]$-85 °C.

2.2. SEM analysis (EDS)

Scanning electron microscopy (SEM) analyses were performed with a field emission gun electron microscope (FEI QUANTA 200 ESEM FEG model) coupled with a Bruker SDD 5010 energy dispersive spectrometer (EDS). As the compounds to be analyzed may be damaged under the electron beam, the beam current was lowered by using a 30 µm aperture, whereas the acceleration voltage was maintained at 15 kV and the acquisition time limited to 30 s.

Kuzel's salt sample synthesized at room temperature was analyzed to check its chemical composition. It was prepared by dispersion in ethanol, deposited on a carbon holder, and fully coated with carbon. The particle sizes ranged between 0.5 and 20 µm. Fifty measurements were performed on one sample, and each analysis was recorded on different crystals. A statistical treatment of the chemical analyses allowed rejecting outliers.

2.3. Thermogravimetry analyses (TGA)

Thermogravimetric analyses (TGA) were performed with a Netzsch STA 409 PC instrument between 20 °C and 1200 °C under nitrogen atmosphere using a heating rate of 2 °C/min. TGA were used to determine the amount of water contained in the interlayer region and to check the anionic stoichiometry.

2.4. Raman spectroscopy

Micro-Raman spectra were recorded at room temperature in the back scattering geometry using a Jobin-Yvon T64000 device. The spectral resolution, about 1 cm^{-1}, was obtained with an excitation source at 514.5 nm (argon ion laser line, Spectra Physics 2017). The Raman detector was a charge coupled device (CCD) multichannel detector cooled down at 140 K by liquid nitrogen. The laser beam was focussed onto the sample through an Olympus confocal microscope with ×100 magnification. The laser spot was about 1 µm². The measured power at the sample level was kept low (<15 mW) in order to avoid any damage of the material. The Raman scattered light was collected with a microscope objective at 360° from the excitation and filtered with an holographic Notch filter before being dispersed by a single grating (1800 grooves per mm).

2.5. X-ray diffraction

2.5.1. Laboratory powder diffraction

Powder X-ray diffraction (PXRD) patterns were recorded using Cu Kα radiation ($\lambda=1.54184$ Å) on an X'Pert Pro PANalytical diffractometer, with θ–θ geometry, equipped with a *X'Celerator* solid detector and a Ni filter. PXRD patterns were recorded at room temperature in the interval $3°<2\theta<120°$, with a step size $\Delta2\theta=0.0167°$ and a total counting time of about 3 h.

2.5.2. Synchrotron powder diffraction

Synchrotron powder diffraction data were recorded at the Swiss–Norwegian Beam Lines at ESRF (Grenoble, France) for the Kuzel's salt sample synthesized at 25 °C; i.e. AFm-$[Cl^-_{1/2}(SO_4^{2-})_{1/4}]$-25 °C sample. White powder was introduced into a Lindeman capillary (0.5 mm by diameter). Data collection was performed at 295 K with a MAR345 Image Plate detector by using a monochromatic wavelength ($\lambda=0.70093$ Å). The calculated absorption coefficient $\mu\cdot R$ ($\mu=$ linear absorption coefficient, $R=$ radius of the capillary) was estimated at 0.338. Repetitive measurements showed the non-destructive nature of the X-ray dose. Three sample-to-detector distances were used (150, 250 and 400 mm) in order to combine the advantages of high structural and angular resolutions. The detector parameters and the wavelength were calibrated with NIST LaB_6 (660b). An instrumental resolution function was determined from the LaB_6 data for each sample-to-detector distance.

2.5.3. Indexation and Le-Bail procedure

Indexing was made for the pattern recorded with a sample-to-detector distance of 400 mm (high angular resolution). Standard peak search method was used to locate the diffraction peak maxima with the Reflex program from Material Studio system software (Accelrys). The X-Cell indexing program allowing space group determination was used [36] and solution was found in rhombohedral $R\bar{3}$ space group. Proposed lattice parameters were $a=5.758$ Å, and $c=50.4313$ Å (figure of merit FOM = 1 700 for the 18 first reflections). A Le-Bail fitting was made using Fullprof [37]. The peak shape was described with the Thomson–Cox–Hastings function [38]. The profile matching refinement using the first pattern recorded with a sample-to-detector distance of 150 mm (large angular range) led to the following good agreement factors: $R_p=1.27\%$ and $R_{wp}=1.53\%$ with $a=5.7508(1)$ Å, $c=50.4184(7)$ Å and $V=1444.02(2)$ $Å^3$. No superstructure peaks were observed, and the previously proposed hexagonal axis $c=100.6$ Å by H. J. Kuzel [34,35] was not considered at this stage of the study.

2.5.4. Structure solution and refinement strategy

The structure was solved by using the direct methods from the EXPO 2004 program [39] working on the extracted intensities from Le-Bail procedure. The centrosymmetric $R\bar{3}$ space group symmetry was confirmed, and not $R\bar{3}c$. The absence of the c glide mirror could be explained by the ordering of the anions: chlorides, and sulfur atoms from sulfate groups were located on the 3*a* and 3*b* Wyckoff sites respectively. The structure was refined with Fullprof program [37] using joint refinement from the three patterns. The model contained 11 atomic sites. Ow were water molecules (Ow1, Ow2: linked molecules, Ow3: weakly bonded molecules), O1 and O2 were the apical and basal oxygen atoms of the sulfate groups respectively. The refinement of 61 parameters (36 intensity dependent parameters, 25 profile parameters) including: 1 zero shift, 1 scale factor, 2 lattice parameters, 13 atomic coordinates, 9 temperature factors, led to the final agreement factors $R_{Bragg}1,2,3\ (\%)=7.01, 6.78, 6.47$, and $R_F1,2,3\ (\%)=7.87, 6.98, 5.69$ for the sample-to-detector distances of 150, 250 and 400 mm respectively. Refinement parameters are collected in Table 1.

The four following constraints on occupancy factors were used: occ(S) = 0.5, occ(O1) = occ(O2) = 0.25, occ(Ow3) = 0.1667. It