The crystal structures of cesanite and its synthetic analogue—A comparison

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ABSTRACT

Single crystals of a synthetic apatite-like phase with composition Na₆Ca₄(SO₄)₆(OH)₂ were grown under hydrothermal conditions. This compound crystallizes in the hexagonal space group P6₃/m (a = 9.4434(13) Å, c = 6.8855(14) Å, Z = 1). The structure was solved by direct methods, and subsequently refined using 655 independent reflections (R₁ = 0.0542). The chemical composition and the unit cell parameters indicated a close structural relationship with the mineral cesanite. A reinvestigation of the mineral showed that the natural and the synthetic phases are isostructural. Small differences result from the incorporation of both H₂O and (OH)⁻ into the structure of cesanite. Observed systematic absences revealed that the space group P6₃/m allocated to cesanite in earlier studies is incorrect. The crystal structure of a cesanite with composition Na₅Ca₃d(SO₄)₆(0H)₁d(H₂O)₀.n was successfully refined in space group P6₃ (a = 9.4630(8) Å, c = 6.9088(5) Å, Z = 1, R₁ = 0.0468 for 720 independent reflections [I > 2σ(I)]). The symmetry reduction can be attributed to ordering of the Na and Ca atoms among four symmetrically independent cation sites.

INTRODUCTION

Apatite, Ca₁₀(PO₄)₆F₂, shows a great flexibility concerning the substitution of the different cations and anions in the structure without changing the space group symmetry of P6₃/m. Several compounds are known with sulfate groups substituted for phosphate groups: Na₆Pb₄(SO₄)₆Cl₂ (caracolite; Schneider 1967), Na₆Ca₄(SO₄)₆(OH)₂ (cesanite; Tazzoli 1983), Na₆Cd₄(SO₄)₆Cl₂, Na₃Pd₂(SO₄)₃Cl (Perret and Bouillet 1975), Na₆Ca₄(SO₄)₆(P₃Cl₁₋₂)₂ (Piotrowski et al., unpublished manuscript).

In the course of our own investigations on the crystal chemistry of apatite-like sulfates we tried to synthesize a phase with formal composition Na₆Ca₄(SO₄)₆(OH)₂. The natural analogue of such a material would be the mineral cesanite, first described by Cavaretta et al. (1981). Cesarite has been found in core samples of the Cesano-I geothermal well (Cesano area, Latium, Italy). Chemical analysis and the X-ray powder pattern pointed towards a close structural relationship with apatite. Therefore, Tazzoli (1983) performed a single crystal structure analysis of cesanite in space group P6₃/m. Small differences resulted from the introduction of a split position for the cation site M₂ at (x,y,1/4). Furthermore, the structure refinement indicated the incorporation of both hydroxyl groups and water molecules into the crystal structure. The formula resulting from the structure investigation given by Tazzoli (1983) for cesanite was Na₇.02Ca₂.98(SO₄)₆(OH)₀.98·0.90H₂O. Further investigations by Deganello (1983, 1984) and Deganello and Artioli (1982) described the structural behavior of cesanite up to 390 °C. The single crystal structure refinements in these studies were based on the cesanite model proposed by Tazzoli (1983).

EXPERIMENTAL METHODS

Synthetic cesanite

For the synthesis of a compound with formal composition Na₆Ca₄(SO₄)₆(OH)₂, mixtures of Na₂SO₄, CaSO₄, and Ca(OH)₂ in stoichiometric proportions (3:3:1) were heated under hydrothermal conditions. Experiments were performed in externally heated Morey-type autoclaves with a teflon reaction vessel and a reaction volume of 125 mL. Water was used as pressure medium for all experiments. The synthesis experiment which yielded suitable single crystals for structural investigations was carried out at 250 °C for 14 days using 5 g of starting material and 50 mL H₂O saturated with Na₂SO₄ (corresponding to a pressure of about 100 bar). Prismatic single crystals with maximum dimensions of about 10 × 10 × 100 μm³ were found in a polycrystalline matrix containing Na₂SO₄. For phase analysis, X-ray powder patterns were recorded using a Philips PW 3050 powder diffractometer with CuKα₁ radiation. Data were collected at room temperature with a fixed-slit configuration in the range 10° and 120° 2θ in steps of 0.02° 2θ. For evaluation of the powder patterns the Philips PC-Rietveld plus program package (Fischer et al. 1993) was used.

Single-crystal data were collected at the SUNY X3A1 beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). Data were collected by fixing the Bruker SMART 1K CCD detector at 20° 2θ at a