

08.4-9 CRYSTAL CHEMISTRY OF EUROPIUM IN FELDSPARS.

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In nature, Europium is assumed to occur in two different valence states. In general, natural Eu is trivalent, but the well known geochemical Eu anomaly of many rocks has been explained to be due to Eu²⁺ in feldspar minerals. However, there is almost no information from experiment on the actual valence state of Eu in minerals. We have synthesized Eu-bearing anorthite (Ca,Eu)Al₂Si₂O₈ and analysed the valence state of Eu using Mössbauer spectroscopy of ¹⁵²Eu. This method allows determination of bivalent, trivalent, or mixed states of Eu unambiguously.

As starting material for the synthesis, glasses of anorthite composition were produced by melting Al₂O₃, CaO, Eu₂O₃, and SiO₂ at 1550°C under oxidizing conditions, part of Ca being replaced by 10 and 20 % Eu. Eu-bearing anorthite was obtained at 750°C and 1 kbar water vapor pressure using a reducing metallic iron buffer. No crystalline phase other than anorthite could be observed, neither in powder x-ray diffraction patterns nor with the scanning electron microscope. Electron diffraction photographs revealed sharp b type reflections indicative of space group I1 for anorthite with 10 and 20 % Eu.

The ¹⁵²Eu spectra of the starting material (glass) showed only Eu³⁺ without any trace of Eu²⁺. The spectra of Eu-bearing anorthite after synthesis, however, exhibited both Eu²⁺ and Eu³⁺ with ratios Eu²⁺/Eu³⁺ of 0.26 and 0.16 for contents of 10 and 20 % Eu, respectively.

Refinement of lattice constants from more than 30 lines of powder patterns of the Guinier type yielded typical values for anorthite, i.e.

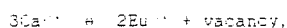
	a ₀	b ₀	c ₀	α	β	γ	V
1. 0% Eu	8.177	12.873	14.171	93.13	115.85	91.27	1338.6
2. 10% Eu	8.202	12.836	14.164	92.83	115.74	91.15	1345.2
2. 20% Eu	8.204	12.892	14.185	92.50	115.80	91.23	1347.2
3. 100% Eu	8.341	12.972	7.112	90	115.50	90	1399.2

a, b, c in Å; α, β, γ in degrees, V in Å³.

1. Pentinghaus (1980), 2. this work, 3. Sasaki and Kimizuka (1978)

The systematic changes of the cell dimensions (cf. Table) indicate that only Eu²⁺ enters anorthite, substituting for Ca at the position of Ca. Thus, the yield of anorthite in the synthesis is determined by the system of the buffer. The Eu²⁺/Eu³⁺ ratio obtained from the ¹⁵²Eu spectrum measures the fraction of glass still present after synthesis.

Small amounts of Eu³⁺ might be expected to be present at the position of Ca in anorthite according to the substitution



considering the ionic radii of Ca²⁺ and Eu³⁺. However, we have no indication of this for the conditions of our synthesis within the experimental error.

08.4-10 STRUCTURE DETERMINATION AND HRTEM INVESTIGATION OF A NEW PYROSMALITE-GROUP MINERAL.

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The crystals investigated are from Broken Hill, New South Wales, Australia. They were first observed during HRTEM studies on natural pyroxenoids from this location. The cell dimensions and qualitative chemical analyses, both obtained from EM data, suggested that the crystals represent a new member of the pyrosmalite group.

Electron microprobe analyses gave a composition of (Mn_{4.79} Fe_{3.00} M_{1.15} □_{0.06}) [Si_{6.0} O_{14.88} (OH)_{1.12}] (OH)_{7.19} Cl_{2.81}, calculated on the basis of 6Si and divalent Mn and Fe; M is for trace elements.

The new mineral, for which the name "Brokenhillite" will be proposed, crystallizes in space group P₆3mc with a₀ = 13.481(3)Å and c₀ = 14.084(3)Å. Its structure has been determined from single crystal X-ray diffraction data. Based on the structure refinement (R = 0.029), the composition (Mn,Fe)₃₂[Si₂₄O₆₀](OH)₂₉Cl₁₁ is suggested for the unit cell.

The structure contains sheets parallel (001) of edge-sharing [(Mn,Fe)(O,Cl,OH)₆] octahedra alternating with single layers of corner-sharing [SiO₄] tetrahedra. The tetrahedral sheet is composed of six-membered rings, which are linked together to form twelve-membered and four-membered rings (Fig.1). The apical oxygens of one of the six-membered rings are shared with the upper octahedral sheet, and those of the neighbouring rings are shared with the lower octahedral sheet.

One octahedral and one tetrahedral sheet form a basic unit, which is similar to that in the pyrosmalite structure (Kato and Takéuchi, 1983, Can. Mineral. 21, 1-6). The structure of the new mineral contains two such units per cell (related by 6₃ axes), compared to only one for pyrosmalite. It can be considered as a polytypic structure within the pyrosmalite group, which was proposed by Takéuchi et al. (1983, Can. Mineral. 21, 19-27). Here the six-membered rings, having tetrahedra with apices pointing up, lie around the hexagonal axes, while the other six-membered rings alternate with the twelve-membered rings (together with the cavities within them) around the trigonal axes by z = 1/2. As a result, the packing of the basic units can be denser. Thus, c₀ is 0.25Å shorter than 2 x c₀ of pyrosmalite, although the mean cation radii, as well as the mean anion radii, are larger for the new mineral.

HRTEM studies reveal the real-structure of the mineral: the crystals contain different stacking faults (R=1/4a₀, R=1/2a₀ and unidentified ones) and rotation faults, with both types having (001) as the fault plane. In addition, crystal grains with various other ordered stacking sequences were found. Many of these were recognized as polytypes, which were described by Takéuchi et al. (1983, Can. Mineral. 21, 19-27). However, the most commonly observed polytype was a rhombohedral variant of the new structure with c₀=42.24Å.

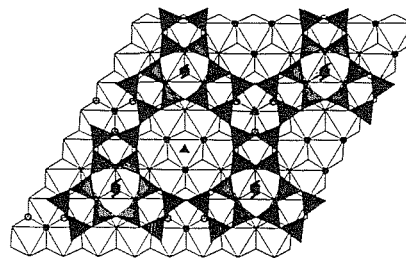


Fig.1 Schematic presentation of the structure (0sz ≤ 0.55; space group: P₆3mc) in [001] projection. Tetrahedral sheet is shaded and the positions occupied mainly by Cl are signed • (upper) and o (lower).