In nature, Europium is assumed to occur in two different valence states. In general, natural Eu is trivalent, but the well-known geochronological Eu anomaly of many rocks has been explained to be due to Eu⁺ in feldspar minerals. However, there is almost no information from experiments on the actual valence state of Eu in minerals. We have synthesized Eu-bearing anorthite (Ca,Eu)₂₃Si₂₄O₆₃(OH)₂₋₀.5H₂O and analysed the valence state of Eu using X-ray spectroscopy of ⁵⁷Eu. This method allows determination of trivalent, tetravalent, 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. To 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 Il for anorthite with 10 and 20 % Eu.

The "⁵⁷Eu spectra of the starting material (glass) showed only Eu⁺ without any trace of Eu²⁺. The spectra of Eu-bearing anorthite after synthesis, however, exhibited both Eu⁺ and Eu²⁺ with ratios Eu⁺/Eu²⁺ of 0.25 and 0.16 for contents of 10 and 20 % Eu, respectively.

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

\[
a_0 = 15.17 \text{ Å}, \quad c_0 = 8.77 \text{ Å}, \quad \gamma = 101.08°
\]

The crystals investigated are from Broken Hill, New South Wales, Australia. They were first observed during HREM 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,Fe]₃₂[Si₂₄O₆₀(OH)₂₋₀.5H₂O] with a = 13.481(3)Å and c₀ = 6.148(4)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)₂₋₀.5H₂O] is suggested for the unit cell.

The structure contains sheets parallel (001) of edge-sharing [Mn,Fe]₀₋₀.5(H₂O)₁₋₀.5 octahedra alternating with single layers of corner-sharing [Si₄O₁₁] 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 lower octahedral sheet, and those of the neighboring 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 Takeuchi, 1983, Can. Mineral. 21, 1-6). The structure of the new mineral contains two such units per cell (related by S axes), compared to only one for pyrosmalite. It can be considered as a polytypic structure within the pyrosmalite group, which was proposed by Takeuchi 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 (Fig.1). The apical oxygens of one of the six-membered rings are shared with the lower octahedral sheet, and those of the neighboring rings are shared with the lower octahedral sheet.

The structure of the new mineral contains two such units per cell (related by 6 axes), compared to only one for pyrosmalite. It can be considered as a polytypic structure within the pyrosmalite group, which was proposed by Takeuchi 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 (Fig.1). The apical oxygens of one of the six-membered rings are shared with the lower octahedral sheet, and those of the neighboring rings are shared with the lower octahedral sheet.