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 Eu^{2+} in feldspar minerals.
However, there is almost no information from experiment
on the actual valence state of Eu in minerals. We have
synthezised Eu-bearing anorthite $(Ca,Eu)Al_2Si_2O_8$ and
analysed the valence state of Eu using Mössbauer spec-
troscopy of ^{151}Eu. This method allows determination of
bivalent, trivalent, or mixed states of Eu unambigously.

As starting material for the synthesis, glasses of anor-
thite composition were produced by melting Al_2O_3, CaO,
Eu_2O_3, and SiO_2 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 cry-
stalline 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 anothite with 10 and 20 % Eu.

The ^{151}Eu spectra of the starting material (glass)
showed only Eu^{3+} without any trace of Eu^{2+}. The spectra
of Eu-bearing anorthite after synthesis, however, exhi-
bited both Eu^{3+} and Eu^{2+} with ratios Eu^{3+}/Eu^{2+} 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.

	a₀	b₀	c₀	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	12.886	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 Eu^{2+} enters anorthite, substi-
tuting for Ca at the postion of Ca. Thus, the yield of
anorthite in the synthesis is determined by the system
of the buffer. The Eu^{3+}/Eu^{2+} ratio obtained from the
^{151}Eu spectrum measures the fraction of glass still
present after synthesis.

Small amounts of Eu^{3+} might be expected to be present at
the postion of Ca in anorthite according to the substi-
tution

$$3Ca^{2+} \rightarrow 2Eu^{3+} + vacancy,$$
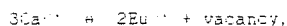
considering the ionic radii of Ca^{2+} and Eu^{3+}. However,
we have no indication of this for the conditions of our
synthesis within the experimental error.

08.4-10 STRUCTURE DETERMINATION AND HRTEM INVESTIGA-
TION 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
$(Mn_{4.79} Fe_{3.00} M_{.15} \square_{.06}) [Si_{6.0} O_{14.88} (OH)_{.12}]$
$(OH)_{7.19}Cl_{2.81}$, calculated on the basis of 6Si and diva-
lent Mn and Fe; M is for trace elements.
The new mineral, for which the name "Brokenhillite"
will be proposed, crystallizes in space group $P6_3mc$ with
$a_0 = 13.481(3)$Å and $c_0 = 14.084(3)$Å. Its structure has
been determined from single crystal X-ray diffraction
data. Based on the structure refinement (R = 0.029), the
composition $(Mn,Fe)_{32}[Si_{24}O_{60}](OH)_{29}Cl_{11}$ 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 $[SiO_4]$ 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 octahe-
dral 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 6_3 axes), compared to only one
for pyrosmalite. It can be considered as a polytypic
structure within the pyrosmalite group, which was pro-
posed 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, c_0 is
0.25Å shorter than 2 x c_0 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 mine-
ral: the crystals contain different stacking faults
($\bar{R}=1/4\bar{a}$, $\bar{R}=1/2\bar{a}$ and unindentified 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 recog-
nized 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
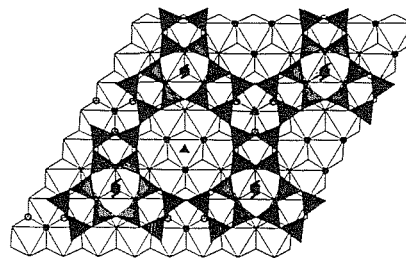the new structure with $c_0=42.24$Å.

Fig.1 Schematic presentation of the structure ($0 \le z \le 0.55$;
space group: $P6_3mc$) in [001] projection. Tetrahedral
sheet is shaded and the positions occupied mainly by Cl
are signed ● (upper) and o (lower).