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Isokite, $CaMg(PO_4)F_{0.8}(OH)_{0.2}$, isomorphous with titanite

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This study presents the first structural report of natural isokite (calcium magnesium phosphate fluoride), with the formula $CaMg(PO_4)F_{0.8}(OH)_{0.2}$ (*i.e.* some substitution of OH for F), based on single-crystal X-ray diffraction data. Isokite belongs to the $C2/c$ titanite mineral group, in which Mg is on an inversion centre and the Ca, P and F/OH atoms are on twofold axes. The structure is composed of kinked chains of corner-sharing MgO_4F_2 octahedra that are crosslinked by isolated PO_4 tetrahedra, forming a three-dimensional polyhedral network. The Ca^{2+} cations occupy the interstitial sites coordinated by six O atoms and one F anion.

Comment

The $C2/c$ titanite structure-type is very flexible and capable of accommodating a wide range of chemical components (Hawthorne, 1990; Sebastian *et al.*, 2002). Minerals belonging to this group include more than a dozen silicates, arsenates, phosphates and sulfates (Groat *et al.*, 1990). A list of synthetic analogues of titanite was given by Sebastian *et al.* (2002). Isokite is a fluoride-bearing calcium–magnesium phosphate mineral and was first described by Deans & McConnell (1955) with ideal chemical formula $CaMg(PO_4)F$. Recently, Hochleitner & Fehr (2005) presented a summary on the paragenesis, chemistry and physical properties of isokite on the basis of a new occurrence at Senhora de Assunção, Portugal, and experimental data. Although all previous studies (*e.g.* Deans & McConnell, 1955; Isaacs & Peacor, 1981; Strunz & Nickel, 2001; Hochleitner & Fehr, 2005) noted the similarities between isokite and minerals of the titanite group in terms of unit-cell parameters and crystal chemistry, the structure of isokite remained undetermined. This study presents the first structure refinement of isokite based on single-crystal X-ray diffraction data.

Isokite is homologous with minerals of the $C2/c$ titanite group (*e.g.* Hawthorne *et al.*, 1991; Oberti *et al.*, 1991; Troitzsch *et al.*, 1999) and is topologically very similar to the minerals of the $C\bar{1}$ amblygonite ($LiAlPO_4F$)–montebrasite ($LiAlPO_4OH$) group (Groat *et al.*, 1990). The structure, in which Mg is on an inversion centre and the Ca, P and F/OH atoms are on twofold axes, is characterized by kinked chains of corner-sharing MgO_4F_2 octahedra (parallel to *c*) that are crosslinked by isolated PO_4 tetrahedra, forming a three-dimensional polyhedral network. The Ca1 cations occupy the interstitial sites coordinated by six O atoms and one F anion (Fig. 1). Compared with the structure of tilasite ($CaMgAsO_4F$) (Bermanec, 1994), a member of the $C2/c$ titanite mineral group and the As analogue of isokite, both Mg—F and Ca—F bond distances in isokite, which are 1.872 (1) and 2.213 (1) Å, respectively, are noticeably shorter than the corresponding distances in tilasite [1.910 (1) and 2.246 (5) Å, respectively]. The calculation of bond-valence sums using the parameters given by Brese & O'Keeffe (1991) yields a value of 1.28 valence units (v.u.) for the bridging F^- anion in the octahedral chain in isokite, indicating that F^- is more over-bonded than in tilasite, which has a bond-valence sum of 1.16 v.u. In addition, the isokite structure appears to provide a better bonding environment for Ca^{2+}, as indicated by its bond-valence sum of 1.90 v.u., compared with that in tilasite (1.78 v.u.).

The substitution of OH for F in minerals of the $C2/c$ titanite group has been a matter of discussion (*e.g.* Cooper & Hawthorne, 1995; Troitzsch *et al.*, 1999). Both tilasite $CaMg(AsO_4)F$ (Bermanec, 1994) and synthetic $CaAl(SiO_4)F$ (Troitzsch *et al.*, 1999) have monoclinic $C2/c$ symmetry, but their OH analogues, *viz*. adelite $CaMg(AsO_4)OH$ (Effenberger *et al.*, 2002) and vuagnatite $CaAl(SiO_4)OH$ (McNear *et al.*, 1976), respectively, are orthorhombic (space group $P2_12_12_1$). Interestingly, Isaacs & Peacor (1981) reported a new mineral, panasqueiraite, with stoichiometry $CaMg(PO_4)(OH_{0.7}F_{0.3})$ and unit-cell parameters a = 6.535 (3) Å, b = 8.753 (4) Å and c = 6.919 (4) Å, and β = 112.33 (4)°, suggesting that panasqueiraite and isokite are isomorphous.

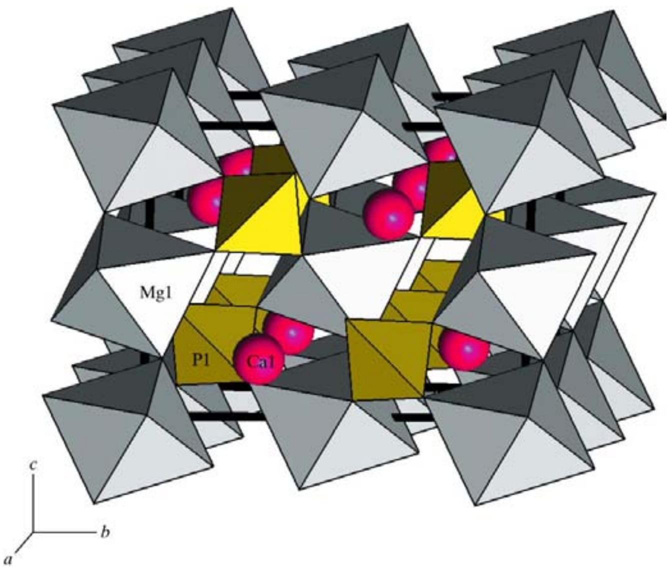

Figure 1
The crystal structure of isokite, $CaMg(PO_4)F_{0.8}(OH)_{0.2}$. The octahedra and tetrahedra represent the MgO_4F_2 and PO_4 groups, respectively.

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Apparently, further research is needed to clarify whether a complete solid solution exists between the two phosphate end-members of $CaMg(PO_4)F$ and $CaMg(PO_4)OH$, and if not, to what extent OH can substitute for F without modifying the *C*2/*c* titanite-type structure.

Experimental

The isokite specimen used in this study is from Kjorrestad, near Bamle, Norway, and is in the collection of the RRUFF project (deposition No. R070526; http://rruff.info), donated by the University of Arizona Mineral Museum (No. 4797). It formed a rim on a large sample of wagnerite, $Mg_2(PO_4)F$ (RRUFF deposition No. R050519). The average chemical composition of the sample studied, $CaMg(PO_4)[F_{0.8}(OH)_{0.2}]_{\Sigma=1}$, was determined with a CAMECA SX50 electron microprobe.

Crystal data

$CaMg(PO_4)F_{0.8}(OH)_{0.2}$
$M_r = 177.76$
Monoclinic, $C2/c$
$a = 6.5109$ (3) Å
$b = 8.7301$ (5) Å
$c = 6.9046$ (5) Å
$\beta = 112.246$ (2)°
$V = 363.25$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.25$ mm^{-1}
$T = 293$ (2) K
0.06 × 0.05 × 0.05 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2005) $T_{min} = 0.877$, $T_{max} = 0.896$
3037 measured reflections
801 independent reflections
660 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.081$
$S = 1.05$
801 reflections
40 parameters
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

The atomic occupancy of the octahedral chain bridging site was constrained to that determined by microprobe analysis (0.8 F + 0.2 OH) throughout the structure refinements.

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XtalDraw* (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3103). Services for accessing these data are described at the back of the journal.

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