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REFINEMENT OF THE STRUCTURE OF GAGARINITE-(Y), $Na_x(Ca_xREE_{2-x})F_6$

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ABSTRACT

The crystal structure of gagarinite-(Y), $Na_x(Ca_xREE_{2-x})F_6$, *a* 5.987(1), *c* 3.5413(7) Å, $P6_3/m$, has been redetermined to an index of $R = 0.012$ using X-ray data obtained on a single crystal. Gagarinite-(Y) is a stuffed derivative of the UCl_3 structure, a common structure-type among lanthanide and actinide halides and hydroxides. Calcium and the rare-earth elements occupy a tricapped trigonal prism; charge balance for the $Ca^{2+} \leftrightarrow REE^{3+}$ substitution is maintained by inserting Na atoms into interstices at (0,0,0) and (0,0,½). The maximum occupancy of Na_1 per unit cell (½ occupancy) results from the short *c*-dimension (3.54 Å) and the close proximity of the Na sites.

Keywords: gagarinite, crystal structure.

SOMMAIRE

Nous avons redéterminé la structure cristalline de la gagarinite-(Y), $Na_x(Ca_xTR_{2-x})F_6$ (*TR*: terres rares), *a* 5.987(1), *c* 3.5413(7) Å, $P6_3/m$, jusqu'à un résidu *R* de 0.012 avec des données de diffraction X obtenues sur cristal unique. Il s'agirait d'une structure dérivative gonflée du type structural UCl_3, commune parmi les halogénures et les hydroxydes des lanthanides et des actinides. Le calcium et les terres rares occupent un site dont les ligands définissent un prisme trigonal à trois sommets; suite à la substitution des terres rares trivalentes pour le Ca^{2+}, l'électroneutralité est assurée par l'insertion d'atomes de Na dans les interstices à (0,0,0) et (0,0,½). La teneur maximale d'un seul atome de Na par unité réticulaire (position à demi occupée par le sodium) découle de la courte dimension *c* (3.54 Å) et de la courte distance entre les sites Na.

(Traduit par la Rédaction)

Mots-clés: gagarinite, structure cristalline.

INTRODUCTION

Gagarinite-(Y), $Na_x(Ca_xREE_{2-x})F_6$, was originally described by Stepanov & Severov (1961). Although the phase was defined relatively recently, it is not a rare mineral, and may be a precursor to other common minerals enriched in the rare-earth elements (*REE*), such as bastnäsite-(Y) (Mineev *et al.* 1970), tengerite, synchysite and yttrofluorite (Stepanov & Severov 1961).

The atomic arrangement of gagarinite was solved by Voronkov *et al.* (1962), who described the structure as a derivative of the UCl_3 arrangement. They proposed the space group $P\bar{3}$, but noted pronounced $P6_3/m$ pseudosymmetry. However, location of the (Ca, *REE*) and F atoms at $z = 0.250$, positions that are unconstrained in $P\bar{3}$ but are special positions in space group $P6_3/m$, as well as Na occupancy at (0,0,0) but *not* at (0,0,½), a site with identical ligation within error, invited re-examination of the atomic arrangement.

EXPERIMENTAL

A small sample that contains quartz, feldspar, and massive gagarinite-(Y) was sampled from the granitoid rocks of the Katugino Massif, Irkutsk region, Kazakhstan, C.I.S. X-ray intensity data for gagarinite-(Y) were collected on an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo*K*α radiation. Unit-cell parameters were refined without symmetry constraints using diffraction angles from

TABLE 1. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENT

Location:	Katungino Massif, Kazakhstan, C.I.S.
Dimensions (mm):	0.08 x 0.08 x 0.08
a: (Å)	5.987(1)
c:	3.5413(7)
Theta limits:	0–34°
Scan type, time (s):	$\theta/2\theta$, ≤120
Data collected:	1019, ±h, ±k, +l
# unique data:	174
R_{merge} (%):	2.0
# data > $5\sigma_I$:	145
R (%):	1.2
R_w (%):	2.0
Goodness–of–fit:	0.499
Peaks on difference map (e/Å^3): +/–	0.37/0.20

25 automatically centered reflections; the resulting values are compatible with hexagonal symmetry. Crystal data are given in Table 1, together with details of data collection and structure refinement.

Intensity data were reduced to structure factors and corrected for Lorentz and polarization effects. Absorption effects were corrected using 360° psi-scans for two reflections; the nearly spherical nature of the crystal was confirmed by the small range of transmission values.

STRUCTURE REFINEMENT

Refinement in space group $P6_3/m$ converged routinely to an R index of 1.2%. Thus gagarinite-(Y) crystallizes in space group $P6_3/m$; there is no need to invoke lower symmetry.

The SDP package of computer programs (Frenz 1985) was used for the full-matrix least-squares refinement. Refinement in space group $P6_3/m$ included reflections with $I > 5\sigma(I)$, with a ratio of observations/parameters greater than 10; neutral-atom scattering factors were used, including terms for anomalous dispersion, and observed reflections were assigned unit weights. Final refinement was done using the Yb scattering factor to represent the *REE* atoms, and constrained by (Yb + Ca) = 2; the refinement gave 31.5 electrons at the ($Ca_{0.77}Yb_{0.23}$) site. Na occupancy was released to model the partial occupancy of the Na site.

Table 2 contains atomic positions and equivalent isotropic displacement-factors. Anisotropic displacement factors and observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 2. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC DISPLACEMENT FACTORS IN GAGARINITE–(Y)

Atom	x	y	z	U_{eq}(Å^2)
(Ca, REE)	2/3	1/3	1/4	0.0108
Na	0	0	0	0.0308
F	0.3089(3)	0.3933(3)	1/4	0.0277

$U_{eq} = 1/(6\pi^2)\Sigma_i\Sigma_j\beta_{ij}\, a_i\, a_j$ (Fischer & Tillmans 1988), where $a_1 = a$, $a_2 = b$, $a_3 = c$.

DISCUSSION OF THE STRUCTURE

The atomic arrangement of gagarinite-(Y) is depicted in Figure 1. As noted by Voronkov *et al.* (1962), the structure is a stuffed derivative of the UCl_3 arrangement. In gagarinite-(Y), the (Ca,*REE*) atoms are coordinated in a tricapped trigonal prism. The cations bond to three F atoms in the mirror plane below [2.366(2) Å], three F atoms in the mirror plane above [2.366(2) Å], and also form bonds with three coplanar F atoms through the prism faces [2.342(2) Å]. In the UCl_3 structure (Zachariasen 1948), symmetry-equivalent interstices that are surrounded by anions in an octahedral array exist at (0,0,0) and (0,0,½). In gagarinite-(Y) these interstices are partly filled with Na to balance the charge deficiency produced by the $Ca^{2+} \leftrightarrow REE^{3+}$ substitution [Na–F = 2.323(1) Å (×6)].

The (0,0,0) site has a rank of 2 in space group $P6_3/m$, thus the most Na-rich gagarinite is ideally $Na_2Ca_2F_6$. However, the small c-dimension (3.5 Å) prohibits full occupancy of the interstices, which would result in Na–Na distances of 1.75 Å. The maximum possible occupancy is Na_1 per unit cell, giving $Na_1(Ca_1REE_1)F_6$; for this occupancy, Na–Na distances would be 3.5 Å, the length of the c dimension. In the hexagonal structure described here, the vacancies and the Na-occupied sites must be disordered, but no two adjacent sites can be occupied, leading to the unit cell in Table 1.

Refinement of the Na occupancy gave $Na_{0.90(1)}$, yielding a composition of $Na_{0.90}(Ca_{0.90}REE_{1.10})F_6$ on the basis of the charge-balancing substitution. Electron-microprobe analysis of a crystal from the same sample of granitic rock as that used for structure refinement gave $Na_{0.6}(Ca_{0.95}Y_{0.72}Dy_{0.10}Gd_{0.09}Er_{0.04}Ho_{0.03}Sm_{0.03}Yb_{0.01}Nd_{0.01}Tb_{0.01}Ce_{0.01})F_{5.41}$ on the basis of (Ca + *REE*) = 2. The discrepancies between the results of the electron-microprobe analysis and the crystal-structure results lie principally in F and, to a lesser extent, Na; repeated electron-microprobe analysis of the mineral with a variety of standards gave similar results. It is not known whether the deficiency in F is a result of differences in the analyzed crystals, difficulties inherent in analyzing the crystal for fluorine in a matrix of *REE* elements, or if it results from fluorine vacancies in the gagarinite structure that are balanced by Na deficiencies. The latter case cannot be ruled out, as the electron-microprobe-derived composition is well balanced, and such vacancies were suggested in the original work of Voronkov *et al.* (1962).

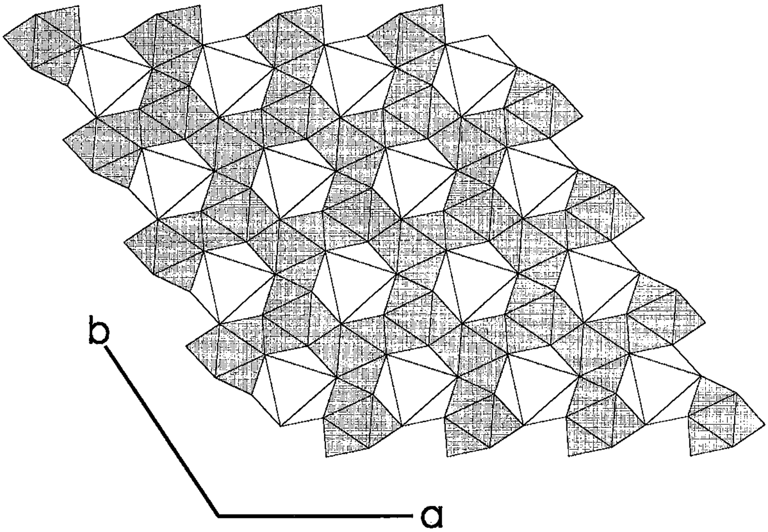

FIG. 1. Atomic arrangement of gagarinite-(Y) projected on (001). Tricapped trigonal prisms (stippled) contain Ca and *REE* atoms, and Na atoms partly occupy the intervening octahedral sites at (0,0,0) and (0,0,½).

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