

THE SINGLE-CRYSTAL X-RAY STRUCTURE OF GAGARINITE-(Ce)

MATTHEW J. SCIBERRAS, PETER LEVERETT AND PETER A. WILLIAMS[§]

School of Natural Sciences, University of Western Sydney, Locked Bag 1797, Penrith South DC, NSW 1797, Australia

DAVID E. HIBBS

School of Pharmacy, University of Sydney, Sydney, NSW 2001, Australia

ANDREW C. ROBERTS

Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8, Canada

JOEL D. GRICE

Research Division, Canadian Museum of Nature, PO Box 3443, Station "D", Ottawa, Ontario K1P 6P4, Canada

ABSTRACT

The single-crystal X-ray structure of gagarinite-(Ce) has been solved using a cleavage fragment taken from the type specimen of "zajacite-(Ce)". The mineral is hexagonal, space group $P6_3/m$, with a 6.0861(12) and c 3.6810(8) Å. It is isomorphous with gagarinite-(Y), with Ce^{3+} dominating the *REE* site. The mineral name "zajacite-(Ce)" is discredited, and the mineral is renamed gagarinite-(Ce).

Keywords: gagarinite-(Ce), crystal structure, redefinition.

SOMMAIRE

Nous avons résolu la structure cristalline de la gagarinite-(Ce) en prélevant un fragment de clivage de l'échantillon type de la "zajacite-(Ce)". Il s'agit d'un minéral hexagonal, groupe spatial $P6_3/m$, dont les paramètres réticulaires sont a 6.0861(12) et c 3.6810(8) Å. Le minéral et la gagarinite-(Y) démontrent une relation isomorphique, le Ce^{3+} étant ici la terre rare dominante. Le nom "zajacite-(Ce)" se trouve discrédité, et le minéral se nomme maintenant gagarinite-(Ce).

(Traduit par la Rédaction)

Mots-clés: gagarinite-(Ce), structure cristalline, redéfinition.

INTRODUCTION

Gagarinite-(Y), whose ideal end-member formula is $NaYCaF_6$, was originally described by Stepanov & Severov (1961). A better way to represent its stoichiometry is $Na_x(Ca_xREE_{2-x})F_6$, with Y dominant over other *REE*; all published analyses give $x < 1.0$ (Anthony *et al.* 1997, p. 214). The crystal structure of gagarinite was first reported by Voronkov *et al.* (1962), who assumed an ideal formula of $NaCa(REE,Y)F_6$. They noted first that the structure is a derivative of that of

UCl_3 . They proposed the trigonal space-group $P\bar{3}$ in order to avoid unacceptably short Na–Na distances along the *z* axis. The crystal structure of gagarinite-(Y), $Na_{0.90}(Ca_{0.90}REE_{1.10})F_6$, was subsequently solved by Hughes & Drexler (1994), who showed it to crystallize in space group $P6_3/m$, with a 5.987(1) and c 3.5413(7) Å. The Na ions are sited at $2b$ (0,0,0), the F ions at $6h$ ($x,y,1/4$), and the Ca and *REE* ions are disordered at site $2d$ ($2/3,1/3,1/4$). In the same year, Frank-Kamenetskaya *et al.* (1994) reported the single-crystal X-ray structure of gagarinite of composition $Na_{0.95}(Ca_{0.94}Sr_{0.02})$

[§] E-mail address: p.williams@uws.edu.au

($REE_{0.56}Y_{0.52}F_6$). This study confirmed the space group as being $P6_3/m$, and both studies revealed disorder of the Na ions in the structure.

More recently, Jambor *et al.* (1996) described the mineral “zajacite-(Ce)” from the Strange Lake deposit, Quebec–Labrador, Canada. The mineral, of composition $Na_{0.90}(Ca_{0.90}REE)_{1.10}F_6$, is characterized by extensive solid-solution involving the REE at the REE–Ca site, with cerium the dominant REE cation. They also reported that an X-ray study showed the mineral to be trigonal, space group $P\bar{3}$, with a 6.0942(3) and c 11.048(1) Å. They noted the presence of a subcell corresponding to the unit cell reported for gagarinite-(Y) with $a' = a$ and $c' = c/3$. Specifically, Jambor *et al.* (1996) wrote the following: “Precession photographs of a fragment of zajacite-(Ce) extracted from a polished thin section showed trigonal symmetry, space groups $P3$ or $P\bar{3}$, a 6.08, c 11.03 Å. The cell dimensions were subsequently refined from the indexed powder-diffraction pattern, as given in Table 2. The crystal-structure study gave a 6.0942(3), c 11.048(1) Å, and indicated that the space group is $P\bar{3}$. The precession X-ray photographs revealed a pronounced subcell, with $a' = a$ and $c' = c/3$. This subcell approximates the true cell of gagarinite-(Y),” and “The X-ray powder patterns of the two minerals are readily distinguishable...”

Unfortunately, no records of the structure study of “zajacite-(Ce)” can be located, and the person responsible for the study (J.T. Szymański) cannot be contacted. Jambor *et al.* (1996) listed observed and calculated powder X-ray data for a refined cell of dimensions a 6.099(2), c 11.064(2) Å. Data are reproduced in Table 1. As well as hkl indices, a second set of indices, $h'k'l'$, is given, corresponding to the subcell which for the experimental data of Jambor *et al.* (1996) would refine

to a 6.099(2), c 3.688(1) Å. The sole reflection that cannot be indexed with this subcell is that with $d_{meas} = 4.77$ Å, and it is weak, with $I_{est} = 5$. Otherwise, the dataset is entirely consistent with either the larger or smaller cell. The claim that the X-ray powder patterns of the two minerals are readily distinguishable cannot be substantiated from the data given.

Although it was stated that a description of the single-crystal structure of zajacite-(Ce) was in preparation, this was never published. This prompted a re-examination of the structure of “zajacite-(Ce)” in order to clarify its true nature.

SINGLE CRYSTAL X-RAY STRUCTURE OF GAGARINITE-(CE)

A small, equant crystal of “zajacite-(Ce)” was selected from a number that had been deposited with the type specimen in National Mineral Collection of the Geological Survey of Canada. Intensity data were collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer with graphite-monochromatized $MoK\alpha$ radiation and corrected for Lorentz and polarization effects. An empirical absorption-correction was made based on psi-scans. Data reduction gave a cell of dimensions a 6.084(1) and c 3.6805(8) Å, space group $P6_3/m$. The structure was refined using the atom positions of Hughes & Drexler (1994) as a starting point, with La being used for the REE position as this best reflected the weighted-average site-occupancy based upon the electron-microprobe results of Jambor *et al.* (1996). Refinement on F^2 by full-matrix least-squares methods (Sheldrick 2008) gave an R_1 value of 0.0316 [$I > 2\sigma(I)$]. The structure is in complete agreement with that of gagarinite-(Y), reported by Hughes & Drexler (1994) and Frank-Kamenetskaya *et al.* (1994). Details are available from the authors upon request.

In order to settle the matter, given that the material examined was not *sensu stricto* from the type specimen, a second single-crystal X-ray structure study was undertaken. The type specimen of “zajacite-(Ce)” (National Mineral Collection of the Geological Survey of Canada specimen number NMC 67314) consists of a polished resin block containing eight fragments corresponding to numbered electron-microprobe compositions given in Jambor *et al.* (1996). A crystal fragment (0.25 × 0.20 × 0.10 mm) was retrieved from grain number 4, the majority of which remains intact in the resin block.

Intensity data were collected at 150(2) K on a Bruker Smart 1000 CCD diffractometer with graphite-monochromatized $MoK\alpha$ radiation and corrected for Lorentz and polarization effects. Again, no superstructure reflections pointing to $c' = 3c$ were observed. The structure was refined on F^2 by full matrix least-squares methods (Sheldrick 2008) in space group $P6_3/m$ using anisotropic displacement parameters for all atoms, to a final R_1 value of 0.0313 for 109 reflections with $I > 2\sigma(I)$. The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 +$

TABLE 1. POWDER X-RAY DATA FOR “ZAJACITE-(Ce)”

I_{est}	d_{meas}	d_{calc}	hkl	$h'k'l'$	I_{est}	d_{meas}	d_{calc}	hkl	$h'k'l'$
70	5.29	5.28	100	100	25	1.273	1.273	306*	302
5	4.77	4.77	101		5	1.243	1.243	403	401
100	3.036	3.050	110	110	10	1.197	1.197	109*	103
		3.024	103	101	10	1.175	1.175	226*	222
20	2.633	2.641	200	200	40	1.152	1.153	410*	410
30	2.351	2.350	103*	101	10	1.149	1.147	316*	312
70	2.146	2.147	203*	201	20	1.115	1.115	209*	203
20	1.994	1.996	210*	210	10	1.073	1.074	406*	402
20	1.842	1.844	006*	002	30	1.047	1.047	219*	213
80	1.757	1.761	300	300	10	1.016	1.017	330	330
		1.756	213	211			1.016	503	501
10	1.740	1.741	106*	102	10	1.013	1.013	326*	322
20	1.577	1.578	116*	112	30	0.9775	0.9774	416*	412
20	1.423	1.525	220*	220	30	0.9635	0.9635	423*	421
10	1.509	1.512	206	202	5	0.9488	0.9487	510	510
5	1.466	1.465	310	310	25	0.9419	0.9417	319*	313
30	1.361	1.361	313*	311	40	0.9189	0.9187	513*	511
20	1.355	1.355	216*	212					

The data are taken from Jambor *et al.* (1996). Reflections used by those authors for cell refinement are marked with an asterisk. The reflection with $d_{calc} = 0.9847$ Å is a typographical error; the d_{calc} value should be 0.9487 Å.

3.41P], where $P = [\max(0, F_o)^2 + 2(F_c)^2]/3$, as defined by SHELX-97 (Sheldrick 2008). Average analytical data for the mineral in Jambor *et al.* (1996) give an empirical formula based on 6 F atoms *pfu* of $\text{Na}_{0.90}\text{Ca}_{0.92}(\text{Ce}_{0.51}\text{La}_{0.26}\text{Y}_{0.08}\text{Nd}_{0.18}\text{Gd}_{0.06}\text{Sm}_{0.02}\text{Dy}_{0.01})_{\Sigma 1.12}\text{F}_6$ or, more simply, $\text{Na}_{0.9}\text{Ca}_{0.9}\text{REE}_{1.1}\text{F}_6$. The REE distribution gives a weighted average of 57.2 e^- per REE, and

thus the scattering curve for La was used as a proxy for REE. Site-occupancy factors corresponding to the simplified formula were included in the calculation. Details concerning data collection and refinement are given in Table 2, and final coordinates and displacement parameters of atoms are listed in Table 3. The Na ion site is somewhat anisotropic, but no real evidence of a split site was found in the Fourier-difference map.

Figure 1 shows the crystal structure of the mineral. The structure is isotopic with that reported by Hughes & Drexler (1994) for gagarinite-(Y). As they pointed out,

TABLE 2. GAGARINITE-(Ce): CRYSTAL DATA AND DETAILS ABOUT THE STRUCTURE REFINEMENT

Empirical formula*	$\text{Na}_{0.90}(\text{Ca}_{0.90}\text{REE}_{1.10})\text{F}_6$	Temperature	150(2) K
Formula weight	323.56		
Wavelength	0.71073 Å		
Crystal system	Hexagonal	Space group	$P6_3/m$
Unit-cell dimensions			
<i>a</i> , <i>c</i> (Å)	6.0861(12), 3.6810(8)		
<i>V</i> (Å ³)	118.08(4)	<i>Z</i>	1
Density (calculated)	4.55 Mg m ⁻³	μ	11.0 mm ⁻¹
<i>F</i> (000)	145		
Crystal size	0.25 × 0.20 × 0.10 mm		
θ range for data collection	3.87 to 28.16°		
Index ranges	$-8 \leq h \leq 7, -7 \leq k \leq 7, -4 \leq l \leq 4$		
Reflections collected	903		
Independent reflections	109 [R(int) = 0.052]		
Completeness to $\theta = 28.16^\circ$	96.5%		
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	109/0/12		
Goodness-of-fit on F^2	1.46		
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.031, wR_2 = 0.091$		
<i>R</i> indices (all data)	$R_1 = 0.031, wR_2 = 0.091$		
Extinction coefficient	0.11(3)		
Largest diff. peak and hole	0.81 and $-1.03 e \text{ \AA}^{-3}$		

* Ce is the dominant REE: $(\text{Ce}_{0.50}\text{La}_{0.26}\text{Nd}_{0.18}\text{Y}_{0.08}\text{Gd}_{0.06}\text{Sm}_{0.02}\text{Dy}_{0.01})$. The formula $\text{Na}_{0.90}(\text{Ca}_{0.90}\text{La}_{1.10})\text{F}_6$ is used for *M*, *D*, μ and *F*(000).

TABLE 3. GAGARINITE-(Ce): FINAL COORDINATES, SITE-OCCUPANCY FACTORS AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	occ.	<i>U</i> (eq)	
REE	0.6667	0.3333	0.2500	0.55	6(1)	
Ca	0.6667	0.3333	0.2500	0.45	6(1)	
Na	0.0000	0.0000	0.0000	0.45	12(4)	
F	0.3046(12)	0.3890(12)	0.2500	1.00	8(1)	
	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	
REE	0.007(1)	<i>U</i> ₁₁	0.003(1)	0	<i>U</i> ₂₃	0.5 <i>U</i> ₁₁
Ca	0.007(1)	<i>U</i> ₁₁	0.003(1)	0	<i>U</i> ₂₃	0.5 <i>U</i> ₁₁
Na	0.002(4)	<i>U</i> ₁₁	0.033(11)	0	<i>U</i> ₂₃	0.5 <i>U</i> ₁₁
F	0.008(3)	<i>U</i> ₁₁	0.008(3)	0	<i>U</i> ₂₃	0.5 <i>U</i> ₁₁

* (Å² × 10³). The exponent of the anisotropic displacement factor takes the form $-2\pi^2(h^2a^2U_{11} + \dots + 2hka^*b^*U_{12})$; $U(\text{eq}) = 1/3(U_{11} + U_{22} + U_{33})$.

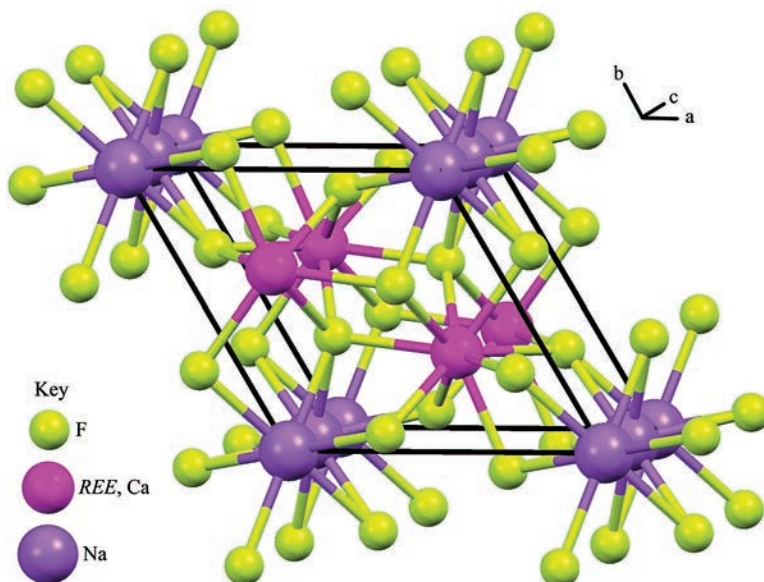


FIG. 1. The structure of gagarinite-(Ce). Both Na positions (0,0,0) and (1/2,0,0) are shown to illustrate their coordination. The unit cell is outlined in black.

TABLE 4. COMPARATIVE DATA FOR GAGARINITE-(Y) AND GAGARINITE-(Ce)

Mineral	gagarinite-(Y) ^{a,b}	gagarinite-(Y) ^c	gagarinite-(Y) ^d	gagarinite-(Ce) ^e	gagarinite-(Ce) ^f
Formula	NaCaY (F,Cl,OH) ₆ ^a	Na _{0.8} Ca _{0.8} REE _{1.2} F ₆	Na _{0.95} (Ca _{0.94} Sr _{0.02}) (REE _{0.56} Y _{0.52})F ₆	Na _{0.9} Ca _{0.9} REE _{1.1} F ₆	Na _{0.9} Ca _{0.9} REE _{1.1} F ₆
Crystal system	Hexagonal ^b	Trigonal	Hexagonal	Trigonal	Hexagonal
Space group	<i>P</i> 6 ₃ / <i>m</i> ^b	<i>P</i> 3̄	<i>P</i> 6 ₃ / <i>m</i>	<i>P</i> 3̄	<i>P</i> 6 ₃ / <i>m</i>
<i>a</i> (Å)	5.987(1) ^b	5.99(3)	6.0403(1)	6.099(1)	6.084(1) ^g ; 6.0861(12) ^h
<i>c</i> (Å)	3.5413(7) ^b	3.53(2)	3.5899(1)	11.064(2)	3.6805(8) ^g ; 3.6810(8) ^h
<i>Z</i>	1 ^b	1	1	3	1
Optical character	uniaxial (+) ^a			uniaxial (+)	
ω	1.472-1.475 ^a			1.483(1)	
ϵ	1.490-1.493 ^a			1.503(1)	

^a Stepanov & Severov (1961), ^b Hughes & Drexler (1994), ^c Voronkov *et al.* (1962), ^d Frank-Kamenetskaya *et al.* (1994), ^e Jambor *et al.* (1996) for "zajacite-(Ce)", ^f this work, ^g data collected at 293 K, ^h data collected at 150 K.

it is important to note that the 2*b* site for Na⁺ ions can never be more than half occupied, as this would require Na⁺ ions to occupy adjacent positions with a separation of *c*/2. The most Na-rich phase would have cell contents Na_{1.0}[(REE)_{1.0}Ca_{1.0}]F₆ where, for this occupancy, the Na⁺-Na⁺ distance is *c*. In the single-crystal structure described here, and supported by electron-microprobe data, the sodium content of the cell is Na_{0.9}, meaning that only 45% of sites are occupied; occupied sites and vacancies must be disordered such that no two adjacent sites are occupied.

NOMENCLATURE

"Zajacite-(Ce)" is isomorphous with gagarinite-(Y), with Ce³⁺ dominating the REE site. Comparative data for "zajacite-(Ce)" and gagarinite-(Y) are given in Table 4. Because of the priority of the name gagarinite-(Y) (Stepanov & Severov 1961), the mineral name "zajacite-(Ce)" is discredited, and the mineral is renamed gagarinite-(Ce). The discreditation of the name "zajacite-(Ce)" and the renaming of the mineral as gagarinite-(Ce) have been approved by the IMA-CNMNC (2010 proposal 10-C).

SUPPLEMENTARY DATA

Full lists of crystallographic data excluding structure-factor tables have been deposited with the Inorganic Crystal Structure Database (ICSD), Fachinformationszentrum, Karlsruhe, Germany; CRYSDATA@FIZ-Karlsruhe.DE. Any request to the ICSD for this material should quote the full literature citation and the CSD number 421715 (filename Ca0.90 F6 La1.10 Na0.90). A table of structure factors is available from the Depository of Unpublished Data on the Mineralogical Association of Canada website [document Gagarinite-(Ce) CM49_1111].

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