MS15-1-17 A revised structure for the rare earth fluoride gagarinite-(Ce) from experimental synthesis by fluid-induced alteration of chevkinite-(Ce)
#MS15-1-17

M. Stachowicz [1], P. Jokubauskas [1], B. Bagiński [1], R. MacDonald [1], D.E. Harlov [2]

[1]Department of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw, Żwirki i Wigury 93, 02-089 - Warszawa (Poland), [2]Section 3-3, GeoForschungsZentrum, Telegrafenberg, 14473 - Potsdam (Germany)

Abstract

The Rare Earth Element (REE) fluoride, gagarinite-(Ce), $^{A}Na^{B}(REE,Ca)_2F_6$ has been synthesized in an experiment designed to examine the fluid-induced alteration of chevkinite-(Ce), $(Ce_{1.85}La_{0.79}Nd_{0.64}Ca_{0.39}Pr_{0.22})_{3.9}Fe^{2+}(Fe^{2+}_{1.03}Ti_{0.75}Mn_{0.16})_{1.9}Ti_2(Si_2O_7)_2O_8$. The experiments were conducted at 600 °C and 400 MPa for 21 days; 550 °C and 200 MPa for 63 days; and 600 °C and 200 MPa for 42 days. The formula of crystallized gagarinite-(Ce) analogue, calculated on the basis of 3 cations and 6 F *pfu*, can be written as: $(Na_{1.10}Ce_{0.69}Ca_{0.44}Nd_{0.31}La_{0.26}Pr_{0.12}Sm_{0.04}Sr_{0.03})_{3.0}F_{6.0}$.

The mineral, previously named zajacite-(Ce), is known from only one natural occurrence, a hypersolvus granite from the Strange Lake Zr-Y-REE-Nb-Be deposit, Quebec-Labrador. The space group was identified as $P\bar{3}$, with unit cell parameters *a*=6.099(1), *c*=11.064(2)(2) Å [1]. A subsequent single-crystal determination showed that it is isostructural with gagarinite-(Y) and its name was changed, with IMA-CNMNC approval, to gagarinite-(Ce), space group $P6_3/m$, with *a*=6.0861(12) and *c*=3.6810(8) Å [2].

The gagarinite-(Ce) in our experiments crystallized in $P\bar{6}$, with *a* = 6.1465(2), *c*= 3.75950(10), R_1=1.37%. We observed 26% twinning by a twin centre. The structure is derived from that of UCl_3 [3] with the addition of extra $^{B}Na^{+}$ into the crystal lattice, where REE^{3+} and Ca^{2+} fill both the cation sites (*A*) of the uranium salt [4,5].

Previous studies assumed full occupancy of the REE+Ca, compositionally disordered, site. To charge balance the substitution $2^{A}REE^{3+} \rightarrow {}^{A}Ca^{2+} + {}^{A}REE^{3+} + {}^{B}Na^{+}$, the amount of extra Na^{+} must equal Ca^{2+} in the final formula, giving $Na_x(Ca_xREE_{2-x})F_6$. Gagarinite-(Ce) from the experiment shows surplus Na over Ca with a ratio close to 2:1, respectively. A vacancy in the REE site is necessary, equal to $\frac{1}{3}$ of the redundant Na to remain in charge balance. If the Na content exceeds 1 in the formula unit, Na has to substitute for REE in the cation site. Thus, the overall substitution mechanism is:

$(2x-y)REE^{3+} \rightarrow y\ {}^{B}Na^{+} + (x-y)\ {}^{A}Na^{+} + y\ {}^{A}Ca^{2+} + \frac{x-y}{3}\ {}^{A}\square$, where □ stands for vacancy and x > y.

We gratefully acknowledge funding by NCN Harmonia grant no. 2017/26/M/ST10/00407.

References

1. J.L. Jambor, A.C. Roberts, D.R. Owens, J.D. Grice, The Canadian Mineralogist, 34 (1996) 1299–1304.
2. M.J. Sciberras, P. Leverett, P.A. Williams, D.E. Hibbs, A.C. Roberts, J.D. Grice, The Canadian Mineralogist, 49 (2011) 1111–1114.
3. W.H. Zachariasen, Acta Crystallographica, 1 (1948) 265–268.
4. A.A. Voronkov, N.G. Shumyatskaya, Y.A. Pyatenko, Journal of Structural Chemistry, 3 (1962) 665–669.
5. J.M. Hughes, J.W. Drexler, The Canadian Mineralogist, 32 (1994) 563–565.