

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

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Abstract

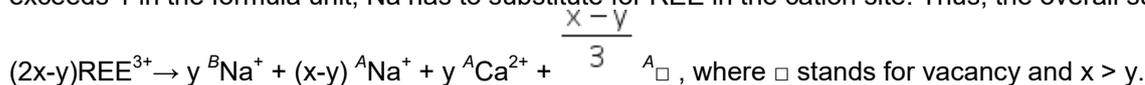
The Rare Earth Element (REE) fluoride, gagarinite-(Ce), ${}^A\text{Na}^B(\text{REE},\text{Ca})_2\text{F}_6$ has been synthesized in an experiment designed to examine the fluid-induced alteration of chevkinite-(Ce), $(\text{Ce}_{1.85}\text{La}_{0.79}\text{Nd}_{0.64}\text{Ca}_{0.39}\text{Pr}_{0.22})_{3.9}\text{Fe}^{2+}(\text{Fe}^{2+}_{1.03}\text{Ti}_{0.75}\text{Mn}_{0.16})_{1.9}\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_8$. 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: $(\text{Na}_{1.10}\text{Ce}_{0.69}\text{Ca}_{0.44}\text{Nd}_{0.31}\text{La}_{0.26}\text{Pr}_{0.12}\text{Sm}_{0.04}\text{Sr}_{0.03})_{3.0}\text{F}_{6.0}$.

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 ${}^B\text{Na}^+$ 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 $2{}^A\text{REE}^{3+} \rightarrow {}^A\text{Ca}^{2+} + {}^A\text{REE}^{3+} + {}^B\text{Na}^+$, the amount of extra Na^+ must equal Ca^{2+} in the final formula, giving $\text{Na}_x(\text{Ca}_x\text{REE}_{2-x})\text{F}_6$. 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:



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References

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