

Pyrochlores: hydrothermal synthesis, composition, properties

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According to the present day classification, minerals and artificial substances which have chemical formula $A_{2-m}B_2O_6(O,OH,F)_{1-n} \cdot pH_2O$ (where A – cations with charge (Z) from +1 to +4 and $r_A = 1.1-1.5\text{\AA}$, B – cations, Z from +3 to +5 and $r_B = 0.7-0.9\text{\AA}$, $m = 0.0-1.7$, $n = 0.0-1.0$ and $p = 0.0-2.5$) and crystal structure correspond to space group $Fd\bar{3}m$ are named pyrochlores (Hogarth, 1977, Atencio et al., 2010). Pyrochlores have a wide application as the matrixes for radionuclide fixation, they are also used in electronic industry (piezoelectric materials), and at the same time they could be considered as the indicators of geochemical processes for wide range of *PTX* parameters. The modern technologies let to synthesize wide range of pyrochlores of different chemical compositions, whereas natural pyrochlores have restrictions on the entry of the elements into A- and B-positions. There are three widespread groups of pyrochlores: the pyrochlores-group if $Nb > Ta + 2Ti$, microlite group if $Ta > Nb + 2Ti$, and betafite group if $2Ti \geq Nb + Ta$ (in moles). Thus, the estimation of maximum acceptance of other cations into pyrochlores formed in the appropriate geochemical conditions is of scientific interest.

The synthesis of pyrochlores was carried out in Pt capsules at $T = 800^\circ\text{C}$, $P = 2000$ bars, and oxygen fugacity appropriated to Co–CoO, Fe_2O_3 – Fe_3O_4 , and Cu_2O –CuO buffers. Initial materials were represented by well ground artificial mixtures of NaF (or Na_2CO_3), $CaCO_3$, Nb_2O_5 , Ta_2O_5 , TiO_2 , ZrO_2 , V_2O_5 , U_3O_8 , and $UO_4 \cdot 2H_2O$. Saturated at $T = 22^\circ\text{C}$ NaF solution was used as a medium for the synthesis. The runs duration was 7 days. The phase composition of the run products was studied with XRD powder diffraction analyses, while the chemical composition of crystals was defined on electron microscope VEGA–TESCAN.

The run products were represented by the fine crystal grains of 0.2–20 μm . The mixture with excess of Nb and Ta produced pyrochlores, whereas Ti, Zr and V enriched mixtures gave rise to perovskites (space group $Pm\bar{3}m$). We synthesized the full series of pyrochlores of pyrochlore-microlite solid solutions, including U-saturated. The maximum U^{4+} concentration in this pyrochlores reached 0.2–0.3 f.u. Run products of pyrochlore-microlite solid solutions have a constant $a_0 = 10.42 \pm 0.01\text{\AA}$. The pictures of the typical pyrochlores and perovskites from our experiments are shown on the fig. 1 and fig. 2.

When uranium was added into the betafite mixture, the pyrochlore crystal structure stabilized. The compositions of 0.25–0.4 X(U^{4+}) gave the 100 % yield of betafite $(Na_{0.79}Ca_{0.91}U_{0.38})(Nb_{1.04}Ti_{0.96})O_{6.19}F_{0.78}$ ($a_0 = 10.30 \pm 0.01\text{\AA}$), but a cubic perovskite $(Na_{0.92}Ca_{0.96})(Nb_{0.98}Ti_{1.02})O_{5.88}F_{0.06}$ ($a_0 = 3.851 \pm 0.003\text{\AA}$) grew in U-free mixtures. It was observed a straight relation between uranium content in an initial mixture and total titanium in pyrochlore and inverse one between a_0 and X(Ti^{4+}). Betafites synthesized in UO_2 and CaF_2 saturated conditions have 0.4–0.5 of U^{4+} and $a_0 = 10.27 \pm 0.01\text{\AA}$.

As at betafite synthesis, we could not get the Zr-rich & U-free pyrochlores. Zr^{4+} entering into pyrochlores and microlites is limited because value of ionic radius of $r(Zr^{4+}) = 0.98$ (c.n.=8) – 0.86 (c.n.=6) \AA is situated between limited values of radii of cations in A and B positions. The perovskites $(Na_{1.62}Ca_{0.36})(Nb_{1.9}Zr_{0.1})O_6$ and pyrochlores $(Na_{0.36}Ca_{1.36})(Nb_{1.93}Zr_{0.07})O_{6.33}F_{0.34}$ were formed at $T=800^\circ\text{C}$ and $P=2000$ bars from the mixture of composition $NaF+CaCO_3+0.5Nb_2O_5+ZrO_2$. The introduction of 30 wt. % of U_3O_8 into the initial mixture lead to increasing of yield of pyrochlore $(Na_{0.86}Ca_{0.69}U_{0.46})(Nb_{1.55}Zr_{0.45})O_{6.73}F_{0.16}$ with $a_0 = 10.45 \pm 0.01\text{\AA}$.

In the condition of Hem-Mt oxygen buffer, the pyrochlores and microlites with X(V^{3+} , V^{4+}) = 0.18–0.19 ($a_0 = 10.39$ – 10.40\AA) mixed with VO_2 were obtained from the mixtures of composition $(NaCa)(NbV)O_6F$ and $(NaCa)(TaV)O_6F$. In uraninite saturated system we synthesized pyrochlores $(Na_{0.66}Ca_{0.99}U_{0.26})(Nb_{1.67}V_{0.33})O_{6+x}F_{0.52}$ ($a_0 = 10.35 \pm 0.01\text{\AA}$). In spite of V-bearing pyrochlores were synthesized in conditions of VO_2 stability, the valance of vanadium in pyrochlores remain unsolved. The analysis of

composition influence to the a_0 parameter indicates that V^{4+} ($r=0.72\text{\AA}$) and V^{3+} ($r=0.78\text{\AA}$) might be present in B position, while V^{5+} ($r=0.68\text{\AA}$) presence would be improbable.

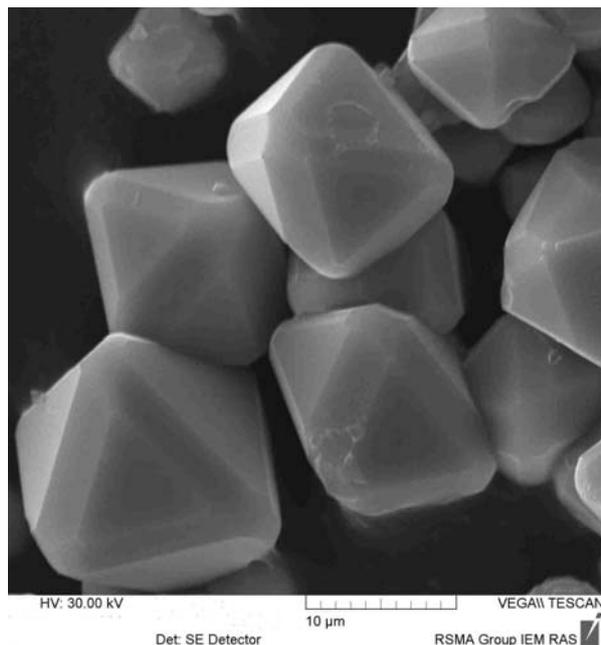


Fig. 1. Picture of pyrochlores

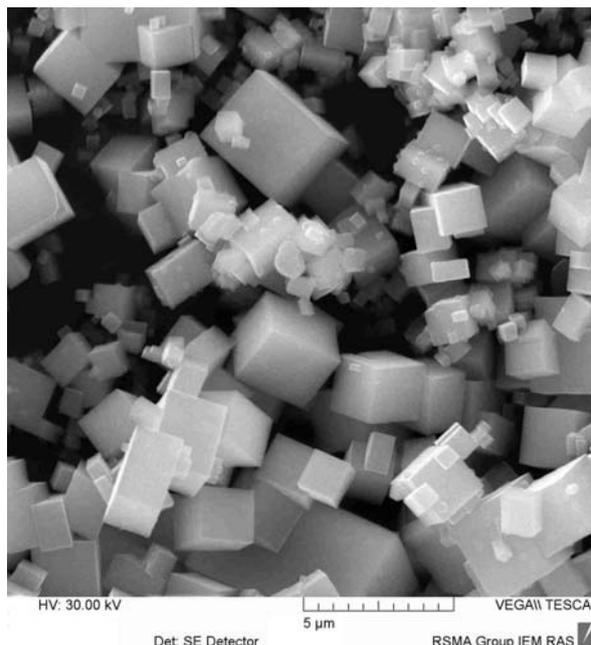


Fig. 2. Picture of perovskites

Thus, pyrochlore and microlite could be synthesized at 800°C and 2000 bars. There is a continuous Nb and Ta composition row in pyrochlore-microlite solid solutions. The data obtained show that Nb^{5+} and Ta^{5+} crystal radius are close indeed, they also have full isomorphic miscibility in pyrochlores.

Uranium entrance does not effect to the size of the elementary cell in pyrochlores of the pyrochlore-microlite group, obtained in $1m\text{NaF}$ solutions. The maximum uranium content in pyrochlores of the pyrochlore-microlyte group does not exceed 0.2–0.3 f.u.

Replacement of 50 mol % Nb by Ti in pyrochlores leads to unit cell changing from 10.42 to 10.27 \AA , and also to the increasing of U^{4+} isomorphic capacity up to 0.4–0.5 f.e.

Some features of cations from A-position replacement (i.e. Ca^{2+} and Na^{+} by U^{4+}) are noted. Ca^{2+} was replaced by U^{4+} in pyrochlores of pyrochlore-microlite solid solutions, while in betafites and Zr-bearing pyrochlores the Na^{+} was replaced by U^{4+} . Obtained data allow to believe that such replacements in A position do not lead to the change of pyrochlore unit cell size.

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