

## COMPARISON OF PHASES FORMATION PROCESS IN INITIAL AND MECHANICALLY ACTIVATED BATCHES WITH PYROCHLORE FORMULATIONS

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### ABSTRACT

Formation of two pyrochlore ceramics with formulations  $\text{CaZr}_{0.25}\text{U}_{0.75}\text{Ti}_2\text{O}_7$  and  $\text{CaUTi}_2\text{O}_7$  within the temperature range 1000-1500 °C from batches prepared by grinding of oxide powders in a mortar and an activator with hydrostatic yokes AGO-2U as well as soaking of a Ca, Zr, and Ti oxide mixture with uranyl nitrate solution was studied. The pyrochlore ceramics are produced through intermediate calcium uranate formation. Phase formation reactions in the batch pre-treated in the AGO-2U unit were completed within the temperature range 1000-1100 °C that is lower than in the batches prepared by two other methods.

### INTRODUCTION

Pyrochlore based ceramics are considered as promising matrices for immobilization of actinide waste, including excess weapons plutonium [1,2]. Method of batch preparation are known to play significant role on mechanism and temperature range of target phase formation and final product properties. To reduce sintering temperature and improve quality of ceramics (higher density, homogeneity, lower porosity and elemental leaching) various methods are applied. The most widespread ways to get high reactive batch to produce ceramics, including those for radioactive waste immobilization, are solution methods (alkoxides hydrolysis, hydroxides co-precipitation, sol-gel) [3]. To produce homogeneous mixtures special methods of solutions and slurries drying and calcining (spray, impinging streams, etc.) are applied [4].

The promising method of the batch preparation is mechanical activation providing homogeneous fine-grained powdered mixtures with high specific surface area, active centers concentration, and reactivity [5]. Mechanical treatment/activation may be performed in various units, for example planetary mills, apparatuses with vortex layer of ferromagnetic particles, etc. Preliminary mechanical activation of ceramic batches reduces either temperature range of sintering and target phase formation or process duration. In our previous works [5-7] the zirconolite and pyrochlore formation process at heat-treatment of mechanically activated batches within temperature range of 1000-1500 °C was studied. It has been shown that temperature range of the target phases formation was reduced by 100-200 °C as compared to non-activated batch milled in a mortar. The present work continues this investigation. Process of pyrochlore composition batches ceramization is investigated in more details.

## EXPERIMENTAL

Batches for synthesis of pyrochlore ceramics with specified compositions  $\text{CaZr}_{0.25}\text{U}_{0.75}\text{Ti}_2\text{O}_7$  and  $\text{CaUTi}_2\text{O}_7$  were prepared by three different routes:

- grinding of  $\text{CaO-TiO}_2\text{-U}_3\text{O}_8$  and  $\text{CaO-TiO}_2\text{-ZrO}_2\text{-U}_3\text{O}_8$  mixtures (reagent grade) in specified quantities in agate mortar;
- milling and activation of  $\text{CaO-TiO}_2\text{-U}_3\text{O}_8$  and  $\text{CaO-TiO}_2\text{-ZrO}_2\text{-U}_3\text{O}_8$  mixtures in an activator with hydrostatic yokes (AGO-2U – Russian design) for 5 min.;
- milling and activation of  $\text{CaO-TiO}_2$  and  $\text{CaO-TiO}_2\text{-ZrO}_2$  mixtures in an activator with hydrostatic yokes (AGO-2U – Russian design) for 5 min. followed by soaking with uranyl nitrate solution.

The batches prepared were compacted under pressure of 200 MPa in pellets 10 mm in diameter and 3 mm in thickness, placed in alumina crucibles followed by heat-treatment in a resistive furnace at 1000, 1200, 1300, 1400, 1500 °C with exposure for 5 hours at each temperature as well as heating to 1550 °C with exposure for 20 min.

The ceramics produced were examined with X-ray diffraction (Philips diffractometer,  $\text{Co K}_\alpha$  radiation) and scanning electron microscopy with an energy dispersive system (SEM/EDS) using an JSM-5300+Link ISIS analytical unit.

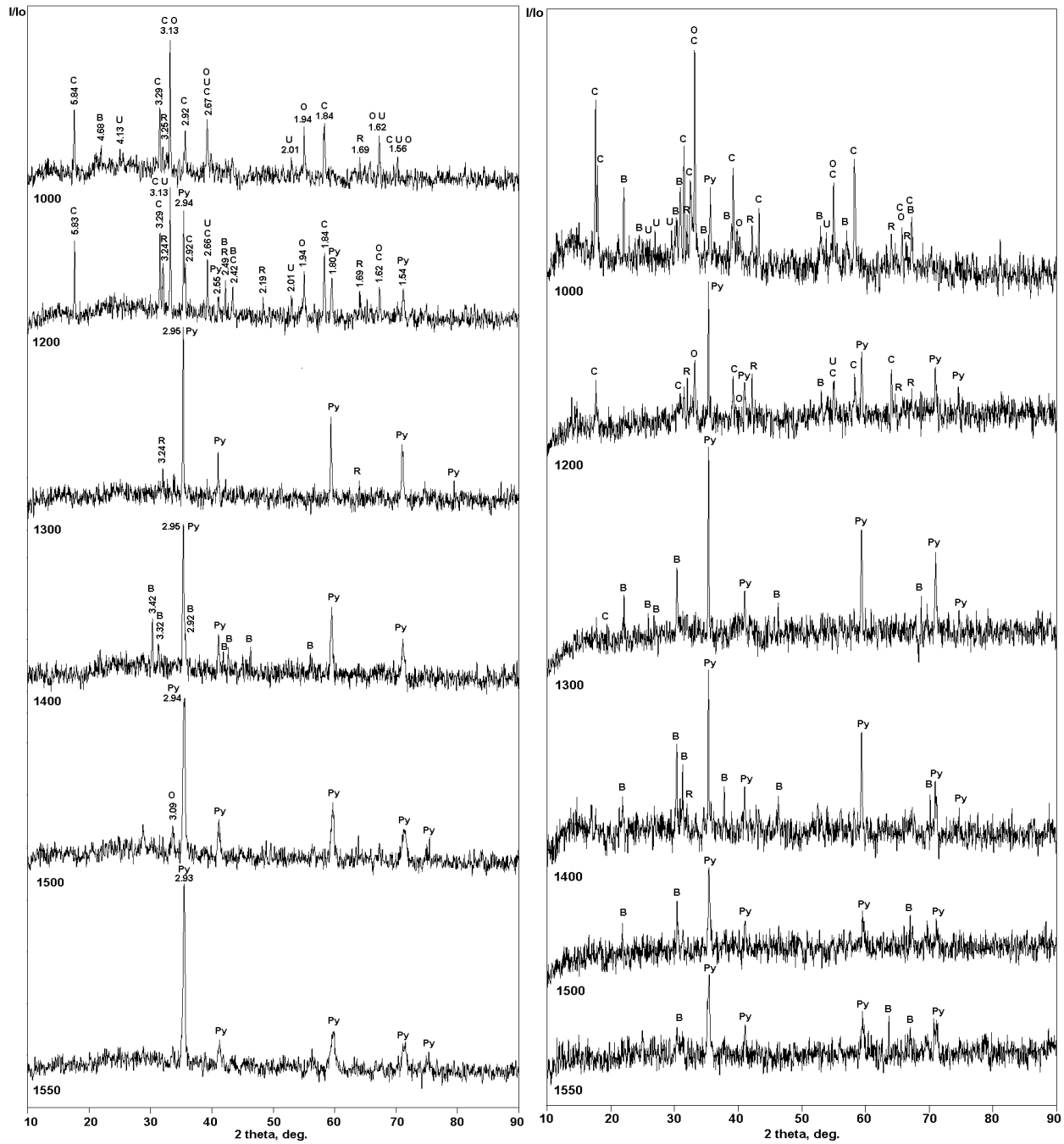
## RESULTS AND DISCUSSION

The samples sintered at 1000 and 1200 °C had low mechanical integrity, high porosity and were visually inhomogeneous. Only the samples heat-treated at 1300 °C and higher temperatures had acceptable strength. These were dark-gray (up to black) colored and free from visual inclusions. The best quality samples were obtained after heat-treatment at the highest temperatures – 1500 and 1550 °C. The samples with  $\text{CaZr}_{0.25}\text{U}_{0.75}\text{Ti}_2\text{O}_7$  formulation have been melted at 1550 °C, whereas the samples with  $\text{CaUTi}_2\text{O}_7$  formulation have not been melted at this temperature.

XRD data for the ceramic samples obtained from batches prepared by three routes are given on Figures 1-3.

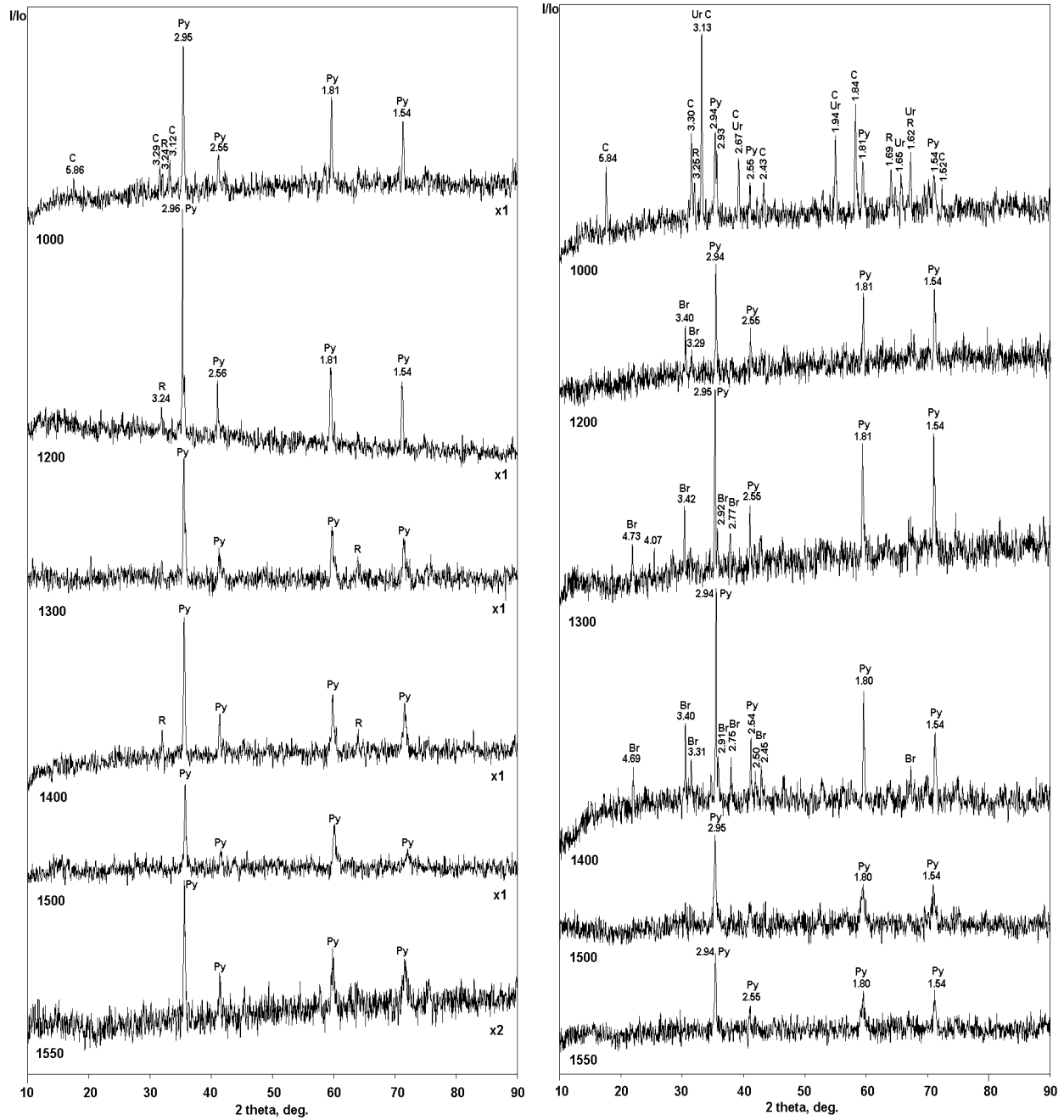
Reactions in all the batches ground in mortar were completed at temperatures over 1300 °C only. The samples heat-treated at lower temperatures are composed of a number of intermediate phases and residual source components (calcium uranates, uranium and zirconium oxides, rutile, and brannerite) as well as new-formed pyrochlore (Figure 1).

Residual  $\text{U}_3\text{O}_8$  grains (major peaks are 4,15-4,20; 3,51-3,54; 3,34-3,37; 2,59-2,61 Å - JCPDS 20-1345 and 31-1426) are still present in the products of heat-treatment at 1000 °C. Up to this temperature calcium oxide has reacted with formation of defect structure uranates [8] whose major reflections on XRD patterns are 5,83-5,84; 5,73; 3,33; 3,28-3,29; 3,17-3,20; 3,13-3,14; 2,66-2,68 Å that is close to tabulated values (JCPDS 4-187 and 20-1327). Uraninite  $\text{UO}_{2+x}$  as a product formed from  $\text{U}_3\text{O}_8$  is also present. Peaks at 3,13-3,14; 2,67-2,68; 1,94 Å and some others are due to uraninite and mixed oxide  $(\text{Zr,U})\text{O}_2$  (in Zr-containing batches). Minor pyrochlore is also present in these samples with major reflection at 2.94 Å. Rising temperature to 1200 °C increases fraction of the target phase – pyrochlore (major peaks are 2,94-2,95; 2,55; 1,84; 1,54;



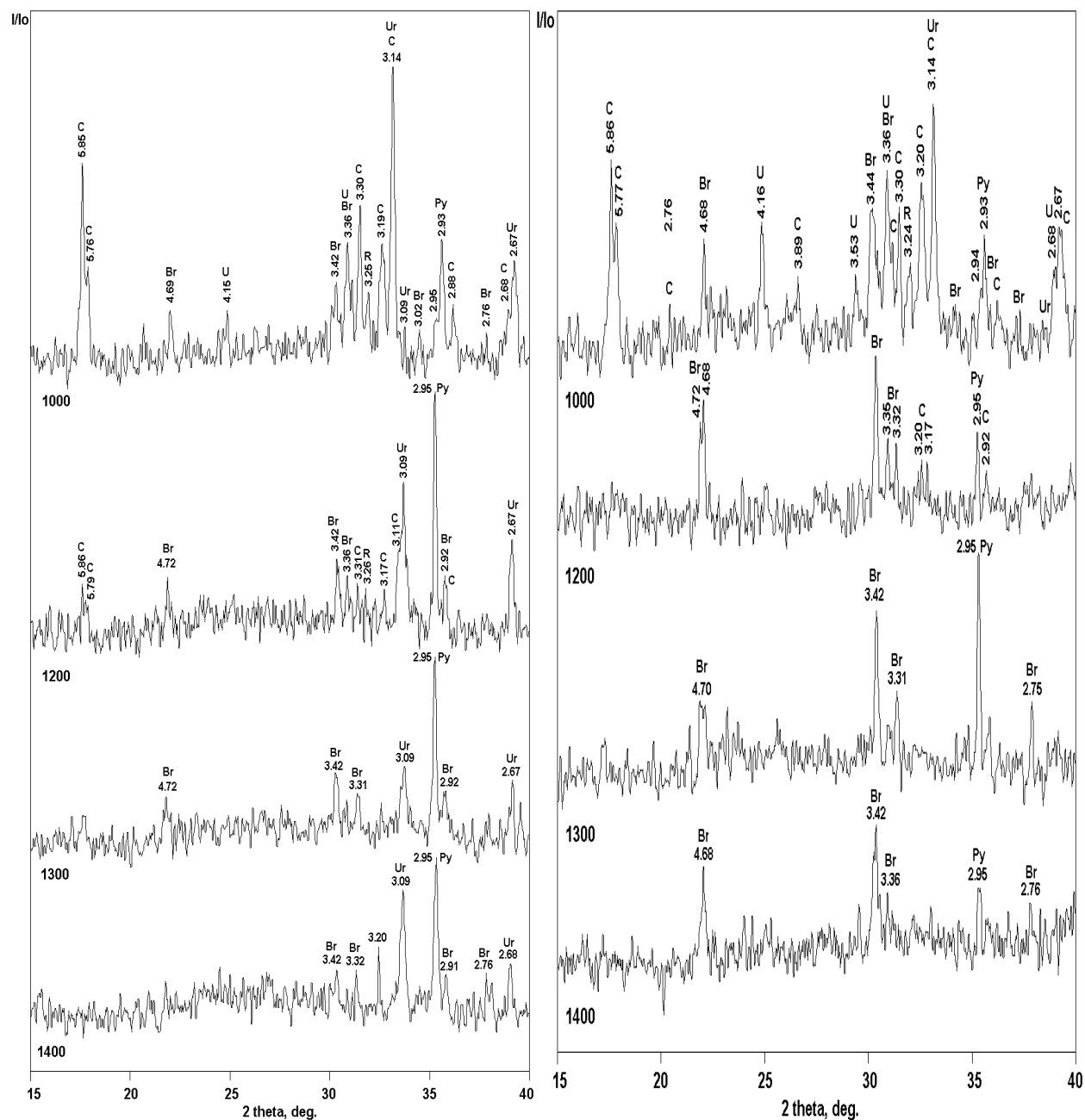
**Fig. 1. XRD patterns of the samples prepared from non-activated batches with  $\text{CaZr}_{0.25}\text{U}_{0.75}\text{Ti}_2\text{O}_7$  (left) and  $\text{CaUTi}_2\text{O}_7$  (right) formulations after sintering at various temperatures.**

B – brannerite, C- calcium uranate, O – complex oxide, Py – pyrochlore, R – rutile, U –  $\text{U}_3\text{O}_8$ .



**Fig. 2. XRD patterns of the samples prepared from activated batches with  $\text{CaZr}_{0.25}\text{U}_{0.75}\text{Ti}_2\text{O}_7$  (left) and  $\text{CaUTi}_2\text{O}_7$  (right) formulations after sintering at various temperatures.**

Phase symbols are the same as on Figure 1.



**Fig. 3. XRD patterns of the samples prepared from partially activated batches with CaZr<sub>0.25</sub>U<sub>0.75</sub>Ti<sub>2</sub>O<sub>7</sub> (left) and CaUTi<sub>2</sub>O<sub>7</sub> (right) formulations after sintering at various temperatures.**

1.48 Å). However, noticeable calcium uranate and rutile contents also occurred. After heat-treatment of the batches at 1300 and 1400 °C pyrochlore structure phase was predominant but Zr-bearing and Ca-U-Ti samples contained minor rutile and calcium uranate relicts, respectively. Brannerite formation especially in the samples with Ca-U-Ti composition was observed. The same effect was described in [5]. The samples sintered at 1500 and 1550 °C consisted of

predominant pyrochlore type phase and traces of one more cubic phase, probably complex U-Zr-Ti oxide.

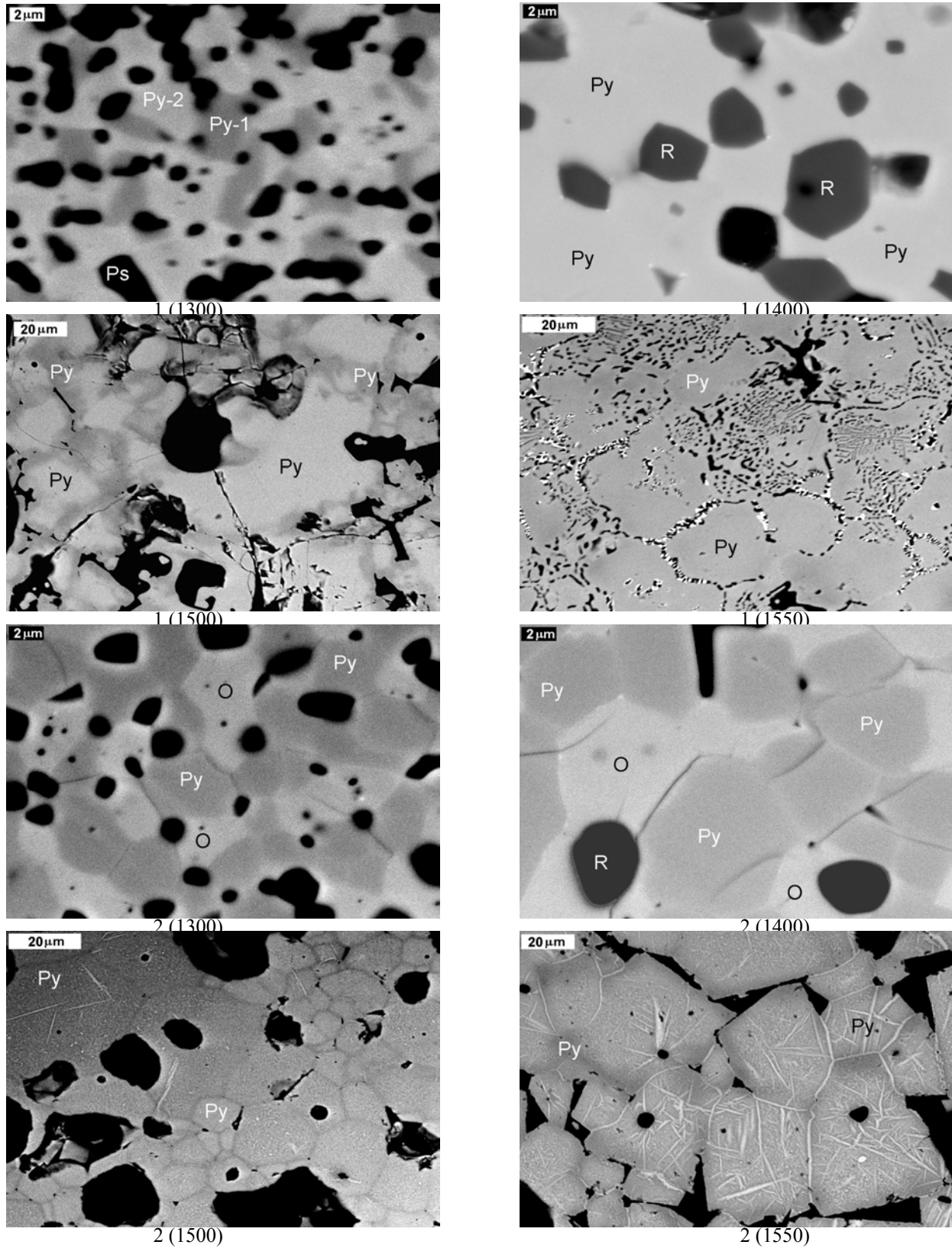
Reactions in the batch with Ca-Zr-U-Ti composition pre-activated in the AGO-2U unit are mainly completed at temperatures about 1000 °C (Figure 2). Major phase was found to be pyrochlore. Residual grains of calcium uranate, rutile, and baddeleyite or (Zr,U)O<sub>2</sub> solid solution were also found.

Rutile grains are present in the ceramics sintered at higher temperatures. Pyrochlore structure phase composition is varied within the individual grain even after sintering at 1300 °C. Two types of grains with different Ca:U:Zr ratio occurred (Figure 4). Average compositions of these grains from SEM/EDS data are Ca<sub>1.19</sub>Zr<sub>0.34</sub>U<sub>0.55</sub>Ti<sub>1.92</sub>O<sub>6.81</sub> and Ca<sub>1.34</sub>Zr<sub>0.20</sub>U<sub>0.62</sub>Ti<sub>1.84</sub>O<sub>6.66</sub>. In the ceramics sintered at 1400 and 1500 °C or melted at 1550 °C pyrochlore compositions are more uniform: Ca<sub>1.30</sub>Zr<sub>0.23</sub>U<sub>0.64</sub>Ti<sub>1.85</sub>O<sub>6.74</sub>, Ca<sub>1.04</sub>Zr<sub>0.31</sub>U<sub>0.53</sub>Ti<sub>2.13</sub>O<sub>6.98</sub>, and Ca<sub>1.17</sub>Zr<sub>0.31</sub>U<sub>0.56</sub>Ti<sub>1.93</sub>Al<sub>0.02</sub>O<sub>6.80</sub>, respectively. However, these samples also contain traces of extra phases: grains of partially reacted rutile Ti<sub>0.90</sub>Zr<sub>0.07</sub>U<sub>0.02</sub>Ca<sub>0.01</sub>O<sub>1.99</sub> (in the ceramic sintered at 1400 °C), aggregates of pyrochlore and rutile with representative combined composition Ca<sub>0.95</sub>Zr<sub>0.26</sub>U<sub>0.33</sub>Ti<sub>2.44</sub>O<sub>7</sub> (in the ceramic sintered at 1500 °C), and fine (~1 μm) inclusions located at the pyrochlore grain boundaries with higher uranium and zirconium content and lower titanium concentration than major pyrochlore (just in the melted ceramic). Composition of these grains is Ca<sub>0.99</sub>Zr<sub>0.52</sub>U<sub>1.39</sub>Ti<sub>1.08</sub>Al<sub>0.02</sub>O<sub>7.00</sub>. It should be noted, that the sample melted at 1550 °C is slightly contaminated with alumina from crucible material.

To complete reactions in the batch with Ca-U-Ti composition pre-activated in the AGO-2U some higher temperatures (1200-1300 °C) are required. However, process mechanism is approximately the same as in the batch with Ca-Zr-U-Ti composition. The difference is in brannerite phase formation like in the samples produced from non-activated batch. The strongest peaks of the brannerite phase in the sample sintered at 1300 °C are close to tabulated JCPDS 12-477 values, although its composition (U<sub>0.60</sub>Ca<sub>0.33</sub>)Ti<sub>2.07</sub>O<sub>5.67</sub> demonstrates excess Ca and deficiency of U relatively nominal stoichiometry.

Pyrochlore composition corresponds to Ca<sub>1.44</sub>U<sub>0.68</sub>Ti<sub>1.88</sub>O<sub>6.56</sub>. Pyrochlore grains have some darker color than brannerite grains on SEM images (Figure 4). After sintering at 1400 °C pyrochlore and brannerite as well as rare rutile grains (black on SEM images) with compositions Ca<sub>1.40</sub>U<sub>0.68</sub>Ti<sub>1.92</sub>O<sub>6.60</sub>, (U<sub>0.63</sub>Ca<sub>0.32</sub>)Ti<sub>2.04</sub>O<sub>5.66</sub>, and Ti<sub>0.98</sub>U<sub>0.01</sub>Ca<sub>0.01</sub>O<sub>1.99</sub>, respectively, have been found. In the ceramic sintered at 1500 °C pyrochlore with slightly variable composition of grains is dominating phase (Figure 4). Major bulk has composition Ca<sub>1.00</sub>U<sub>0.74</sub>Ti<sub>2.26</sub>O<sub>7.00</sub>. Fine crystals (lighter on SEM images) incorporated in the major bulk of the sample have cationic shortfall: Ca<sub>0.75</sub>U<sub>0.75</sub>Ti<sub>2.37</sub>O<sub>7.00</sub>. Occurrence of two types of pyrochlore in the sample is also seen from pyrochlore peaks splitting on XRD pattern (Figure 2). Rare needle-like crystals, probably brannerite, (U<sub>0.60</sub>Ca<sub>0.57</sub>)Ti<sub>1.83</sub>O<sub>5.43</sub> were also found. Pyrochlore phase composition is slightly varied even in the sample heat-treated at 1550 °C. Major grains have average composition Ca<sub>1.19</sub>U<sub>0.70</sub>Ti<sub>2.11</sub>O<sub>6.81</sub> but some sections of grains are enriched with titanium and depleted with uranium having average composition (Ca<sub>1.02</sub>U<sub>0.65</sub>Ti<sub>2.33</sub>O<sub>6.98</sub>). Needle-like brannerite crystals (U<sub>0.66</sub>Ca<sub>0.45</sub>)Ti<sub>2.14</sub>O<sub>5.55</sub> are incorporated within the pyrochlore bulk. Moreover, partially reacted uraninite grain with U<sub>0.86</sub>Ti<sub>0.06</sub>Ca<sub>0.08</sub>O<sub>1.92</sub> formulation has been found (Figure 4).

Mechanism of the mineral formation process in the batches prepared with soaking of pre-activated Ca-Zr-Ti oxide mixtures with uranyl nitrate solution is similar to that in the batches prepared by two other methods. However, in this case reactions are less intensive and unreacted and intermediate phases occurred even in the ceramics sintered at 1400 °C (Figure 3). Apparently



**Fig. 4. SEM images of the ceramics with  $\text{CaZr}_{0.25}\text{U}_{0.75}\text{Ti}_2\text{O}_7$  (1) and  $\text{CaUTi}_2\text{O}_7$  (2) formulations sintered at various temperatures.**

soaking of mechanically activated additives with uranyl nitrate solution results in deactivation of centers and agglomeration of batch grains reducing surface area of the particles contact and their bond strength effecting negatively on mineral formation kinetics.

## CONCLUSIONS

Pyrochlore type phase formation process in oxide batches goes through the defect calcium uranate formation step following by its interaction with  $ZrO_2$  and  $TiO_2$  in spite of batch preparation method. In the batches mechanically activated in the planetary mill AGO-2U phase formation processes are mainly completed at temperature about  $1000\text{ }^{\circ}\text{C}$  which is lower by  $200\text{-}300\text{ }^{\circ}\text{C}$  than in non-activated batch or in the batch prepared by soaking of mechanically activated Ca-Zr-Ti additives with uranyl nitrate solution.

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