

EFFECT OF MECHANICAL ACTIVATION OF BATCHES ON PHASE COMPOSITION AND ELEMENTS PARTITIONING IN ZIRCONOLITE-BASED CERAMICS

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ABSTRACT

An effect of mechanical treatment in a planetary ball mill and an apparatus with rotating magnetic field of batches with zirconolite composition on temperature range of sintering was studied. Three variants of batch preparation: blending without mechanical activation, blending of mechanically treated additives with untreated calcined actinide waste surrogate, mechanical treatment of the whole batch were considered. Formation of zirconolite and pyrochlore-structured phases has been established. Zirconium titanate and rutile were found to be extra phases. Mechanical activation of the batches with zirconolite composition reduces temperature range of zirconolite and pyrochlore formation by 100-200 °C as compared to initial batch (from 1500-1550 °C to 1350-1400 °C).

INTRODUCTION

Zirconolite-based ceramics are considered as one of the most promising forms for actinide waste immobilization [1-4]. They can be produced by ceramic (cold pressing and sintering [CPS] or hot-pressing) [5,6] or melting (preferably the cold crucible melting [7,8]) routes. The CPS method is believed to be the cheapest and simplest from technological point of view, therefore, it has been accepted as basic at development of excess weapon plutonium immobilization process at LLNL [5]. However, the CPS method is quite sensitive to quality of batch preparation. To reduce sintering temperature and improve product quality special methods such as co-precipitation, sol-gel, wet milling, jet milling are being considered. Alternative method is mechanical activation of oxide/nitrate mixture by high-speed ferromagnetic particles rotating in a magnetic field [6] to obtain very fine-grade and homogeneous batch. Moreover such high energy mechanical treatment forms freshly cracked surfaces with high concentrations of active centers (dislocations, displaced atoms, ion-radicals, etc.) as a result of which material becomes higher reactive.

The goal of the present work is investigation of an effect of mechanical treatment/activation of the oxide batch on temperature range of sintering of zirconolite-based ceramics.

EXPERIMENTAL

To produce ceramics oxides of calcium (lime), titanium (rutile), uranium (uraninite), and zirconium (baddeleyite) were used as raw materials (all the oxides were reagent-grade). Calculated compositions of the zirconolite ceramics were $\text{CaZrTi}_2\text{O}_7$ and $\text{CaZr}_{0.75}\text{U}_{0.25}\text{Ti}_2\text{O}_7$ (Table I). The samples were prepared by compaction of powders into pellets under pressure of 300 MPa followed by sintering in a resistive furnace as follows: heating to 400 °C for 1 hour and

exposure for 1 hour, heating to sintering temperature (ranging between 1100 and 1550 °C) for 2 hours and exposure at this temperature for 2 hours, temperature reduction to 900 °C for 1 hour, and cooling down to room temperature in turned-off furnace for about 16 hours. Four procedures of batch preparation were tested (Table I):

- Blending of initial oxides in an agate mortar without mechanical activation;
- Blending of initial oxides followed by mechanical treatment in a planetary mill Pulverisette-7 (Fritsh, GmbH);
- Blending of initial oxides followed by mechanical treatment/activation in an apparatus with rotating magnetic field;
- Blending of CaO, TiO₂, and part of ZrO₂ (75 mol.% of total amount) followed by mechanical treatment/activation in the apparatus with rotating magnetic field to prepare a “precursor”, and blending of this precursor with residual part of ZrO₂ (25 mol.% of total amount) or with initial UO₂ (actinide waste surrogate).

The latter procedure simulates a case when just non-radioactive additives will be mechanically treated and radioactive constituent (calcine) is admixed to precursor.

The samples obtained were examined with X-ray diffraction (XRD) using a DRON-4 diffractometer (Cu K_α radiation), scanning (SEM) and transmission (TEM) electron microscopy equipped with energy dispersive system (EDS) using a JSM-5300 + Link ISIS analytical unit.

Table I. Samples preparation methods

Sample	Formulation	Preparation method
1	$\text{CaZrTi}_2\text{O}_7$	Grinding of $\text{CaO-TiO}_2\text{-ZrO}_2$ mixture in the mortar, compaction in pellets, sintering at $1300\text{ }^\circ\text{C}$
2	--	Treatment of $\text{CaO-TiO}_2\text{-ZrO}_2$ mixture in the planetary mill, compaction in pellets, sintering at $1300\text{ }^\circ\text{C}$
3	--	Treatment of $\text{CaO-TiO}_2\text{-ZrO}_2$ mixture in the apparatus with rotating magnetic field, compaction in pellets, sintering at $1300\text{ }^\circ\text{C}$
4	--	Treatment of part of $\text{CaO-TiO}_2\text{-ZrO}_2$ mixture ($\text{CaZr}_{0.75}\text{Ti}_2\text{O}_{6.5}$) in the apparatus with rotating magnetic field, blending with non-treated ZrO_2 ($\text{Zr}_{0.25}\text{O}_{0.5}$) compaction in pellets, sintering at $1300\text{ }^\circ\text{C}$
5a	$\text{CaZr}_{0.75}\text{U}_{0.25}\text{Ti}_2\text{O}_7$	Grinding of $\text{CaO-TiO}_2\text{-ZrO}_2\text{-UO}_2$ mixture in the mortar, compaction in pellets, sintering at $1000\text{ }^\circ\text{C}$
5b	--	Grinding of $\text{CaO-TiO}_2\text{-ZrO}_2\text{-UO}_2$ mixture in the mortar, compaction in pellets, sintering at $1200\text{ }^\circ\text{C}$
5c	--	Grinding of $\text{CaO-TiO}_2\text{-ZrO}_2\text{-UO}_2$ mixture in the mortar, compaction in pellets, sintering at $1300\text{ }^\circ\text{C}$
5d	--	Grinding of $\text{CaO-TiO}_2\text{-ZrO}_2\text{-UO}_2$ mixture in the mortar, compaction in pellets, sintering at $1400\text{ }^\circ\text{C}$
5e	--	Grinding of $\text{CaO-TiO}_2\text{-ZrO}_2\text{-UO}_2$ mixture in the mortar, compaction in pellets, sintering (melting) at $1550\text{ }^\circ\text{C}$
6a	--	Treatment of part of $\text{CaO-TiO}_2\text{-ZrO}_2$ mixture ($\text{CaZr}_{0.75}\text{Ti}_2\text{O}_{6.5}$) in the apparatus with rotating magnetic field for 10 min, blending with non-treated UO_2 ($\text{U}_{0.25}\text{O}_{0.5}$) compaction in pellets, sintering at $1300\text{ }^\circ\text{C}$
6b	--	Treatment of part of $\text{CaO-TiO}_2\text{-ZrO}_2$ mixture ($\text{CaZr}_{0.75}\text{Ti}_2\text{O}_{6.5}$) in the apparatus with rotating magnetic field for 15 min, blending with non-treated UO_2 ($\text{U}_{0.25}\text{O}_{0.5}$) compaction in pellets, sintering at $1300\text{ }^\circ\text{C}$
7	--	Treatment of part of $\text{CaO-TiO}_2\text{-ZrO}_2\text{UO}_2$ mixture in the apparatus with rotating magnetic field for 15 min, compaction in pellets, sintering at $1300\text{ }^\circ\text{C}$

RESULTS

XRD data are shown on Figures 1-3. The sample #1 is composed of a mixture of initial oxides and product of their reaction – zirconolite (Figure 1, 1). XRD patterns of the samples ## 2-4 are quite similar (Figure 1, 2-4). They consist of major zirconolite and minor rutile reflections. Zirconolite is present as monoclinic variety (2M) [7]. Appearance of the samples ## 5d, 5e, 6a, 6b, and 7 is rather similar. They are dense fine crystalline materials with dark uniform color. Unless these samples, the samples ## 5a, 5b, and 5c have brown color, low mechanical integrity and contain white-colored inclusions.

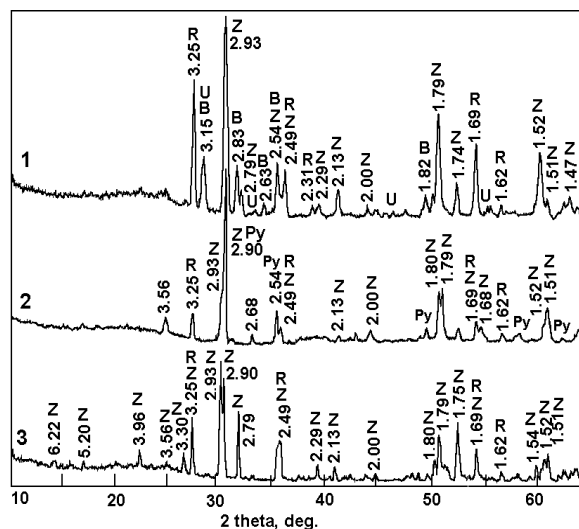


Figure 3. XRD patterns of the sintered ceramic samples ## 6a (1), 6b (2), and 7 (3).
 B – baddeleyite, Py – pyrochlore, R – rutile, U – uraninite, Z – zirconolite.

Zirconolite (probably with minor pyrochlore) becomes major phase only in samples prepared from untreated batches after sintering at temperatures 1400 °C and higher (the samples ## 5d and 5e). If in the sample #5d sintered at 1400 °C significant rutile fraction (in rough approximation, from comparison of peak intensities on XRD patterns in amount of 35-40 %) and minor perovskite are still present, after heat-treatment at 1550 °C (the sample #5e) rutile almost disappears but minor perovskite (about 15-20 %) occurs.

The samples ## 6a, 6b, and 7 prepared with the use of mechanical treatment in the apparatus with rotating magnetic field are composed of zirconolite and “pyrochlore” and minor rutile (Figure 3, 2,3). As follows from relative peak intensities on XRD patterns of the samples ## 5c, 6a, 6b, and 7 sintered at the same temperature (1300 °C), in the sample #6b rutile content is the lowest (Figure 3, 1-3). It should be noted, that relative intensities of XRD peaks at 2.93 and 2.90 Å change in favor of the latter and reflection at 2.79 Å (*hkl* 004, 313, 312) disappears on XRD pattern of the sample #6b. Thus, XRD pattern of the sample #6a differs noticeably from XRD patterns of the samples #5c and #6b with the same chemical composition and becomes similar to Ca-betafitite (pyrochlore-type) pattern [8]. Therefore, in the sample #6a major phase is pyrochlore-type phase.

It is seen from comparison of Figures 2 and 3, that target phases (zirconolite + pyrochlore) content reaches about 80 % in the sample prepared from mechanically activated batch and sintered at 1300 °C, whereas to get the same result using untreated batch temperature over 1400 °C is required. Thus, application of the mechanical activation in the apparatus with rotating magnetic field reduces temperature range of zirconolite/pyrochlore formation by 100-200 °C.

The samples ## 5c, 6a, 6b, and 7 sintered at the same temperature (1300 °C) were investigated in more details using SEM/EDS and TEM (Table II).

The sample # 5c is poorly sintered and composed of fine crystals with significant porosity. SEM image (Figure 4) demonstrates crumbly texture of the sample with individual rather coarse white-colored grains. These grains are Ca-U-Ti-Zr oxide with high uranium and low zirconium contents. Their composition is quite the same in different parts of the sample and recalculated well to “pyrochlore” formulation with sum of cations equal 4 and minor oxygen shortfall: $\text{Ca}_{1.00}(\text{Ca}_{0.35}\text{U}_{0.65})(\text{Ti}_{1.80}\text{Zr}_{0.20})_{2.00}\text{O}_{6.64}$. At the same time bulk composition demonstrates significant excess of calcium cations. It is possible these grains are aggregates of calcium oxide and newly formed pyrochlore grains as products of incomplete reactions in the batch. In the other samples Ca

excess in the pyrochlore-type phase is lower. Smaller fine gray-colored grains with round shape are rutile containing minor zirconium and uranium.

The samples #6a and #7 have the same phase composition. As in the previous sample, they contain pyrochlore-structured complex Ca-Zr-U-Ti oxide (Figure 3) as well as zirconium titanate and rutile (Figure 4). Zirconium titanate is not discernible on XRD patterns due to relatively low content and superposition of major peak (2.92 Å) with more intensive major zirconolite/pyrochlore peak. However, zirconium titanate is observed on SEM images (Figure 4). In both the samples one more complex Ca-Zr-U-Ti oxide with low uranium (Table II) content has been also found. As follows from chemical composition ($\text{CaZr}_{0.8}\text{U}_{0.2}\text{Ti}_2\text{O}_7$), shape of crystals (fine extended grains), and TEM pattern, this phase is monoclinic zirconolite-2M.

Table II. Chemical compositions and formulae of co-existing phases in the U-containing samples

	5c		6a				6b			7				
	Py	R	Py	Z	ZT	R	Py	ZT	R	Py	Z	ZT	R	
Oxides	Oxide contents, wt.%													
CaO	18.0	0.3	16.5	14.6	1.3	1.2	15.7	0.7	0.2	15.9	15.0	0.6	0.5	
TiO ₂	33.4	91.7	35.2	40.9	40.6	81.6	35.2	37.0	80.6	36.4	41.0	39.3	82.8	
ZrO ₂	4.6	4.1	17.7	31.3	52.7	8.9	18.0	57.3	12.3	17.6	31.9	55.4	12.9	
UO ₂	42.9	0.7	31.8	13.4	6.0	2.5	31.1	6.8	1.2	30.1	11.2	5.1	0.6	
Σ	98.9	96.8	101.2	100.2	100.6	94.2	100.0	101.8	94.3	100.0	99.1	100.4	96.8	
Ions	Formula units													
Ca ²⁺	1.45	0.00	1.20	0.95	0.04	0.04	1.16	0.02	0.00	1.16	1.00	0.02	0.01	
Ti ⁴⁺	1.90	0.97	1.81	1.91	1.05	0.92	1.83	0.96	0.91	1.88	1.90	1.02	0.90	
Zr ⁴⁺	0.14	0.03	0.60	0.95	0.89	0.06	0.61	0.97	0.09	0.59	0.96	0.92	0.09	
U ⁴⁺	0.72	0.00	0.49	0.20	0.04	0.01	0.48	0.06	0.00	0.47	0.16	0.04	0.00	
Σ	4.21	1.00	4.10	4.01	2.02	1.03	4.08	2.01	1.00	4.10	4.02	2.00	1.99	
O ²⁻	7.00	2.00	7.00	7.00	4.00	2.00	7.00	4.00	2.00	7.00	7.00	4.00	2.00	

Py – “pyrochlore”, R – rutile, Z – zirconolite, ZT – zirconium titanate.

The major difference between the samples # 6a and #7 is pyrochlore-type phase content, which is ≥ 40 vol.% in the sample #6a and ≤ 30 vol.% in the sample #7. Major phase in the latter is zirconolite as well as zirconium titanate. Their ratio is approximately 2.5:1. In the whole, approximate phase compositions may be estimated from XRD and SEM/EDS data (in vol.%) as: pyrochlore – 50, zirconium titanate – 10, zirconolite – 25, rutile – 15 (the sample #6a) and pyrochlore – 25, zirconium titanate – 20, zirconolite – 50, rutile – 5 (the sample #7).

The sample #6b is composed of three phases. Major bulk of the sample (70-80 vol.%) consists of white-colored phase with high uranium content (up to 32 wt.%) and atomic ratio Zr:U \approx 1. We observed this phase in sintered zirconolite ceramic and marked it as zirconolite-2 [4]. TEM data demonstrate pyrochlore-type structure (Figure 4) that is in a good agreement with XRD (Figure 3, 2), optical and SEM data (isometric form of grains).

Two other phases are present in approximately equal amounts (10-15 vol.% each). These are zirconium titanate and rutile. Zirconium titanate grains have gray color and don't exceed 10 μm in size. Their compositions are recalculated well to $(\text{Zr,U})\text{TiO}_4$ formula where U content reaches 6-7 wt.% UO₂ or 0.06 formula units (f.u.). Rutile grains have black color and size similar to zirconium titanate grains but their content in the sample is lower. Rutile contains zirconium (up to 12 wt.% ZrO₂) and minor uranium (~1 wt.% UO₂). High zirconium content is due to higher miscibility in the system: TiO₂-ZrO₂ at high temperatures.

Grains of minerals have irregular shape as a result of their formation during solid phase synthesis process, because grains of the same phases crystallized from melt had more regular shape [9] corresponding to features of structure of the given compounds. Note also inhomogeneous distribution of the phases in the ceramics and relative high porosity (5-10 vol.%). Average size of pores is few microns.

Features of phase compositions in the samples ## 6a, 6b, and 7 are similarity in pyrochlore and difference in zirconium titanate and rutile compositions. Two latter phases in the sample #7 contain by 30 wt.% UO_2 lower than the same phases in the samples ## 6a and 6b. However, this may be due to variation of the phase compositions over the sample.

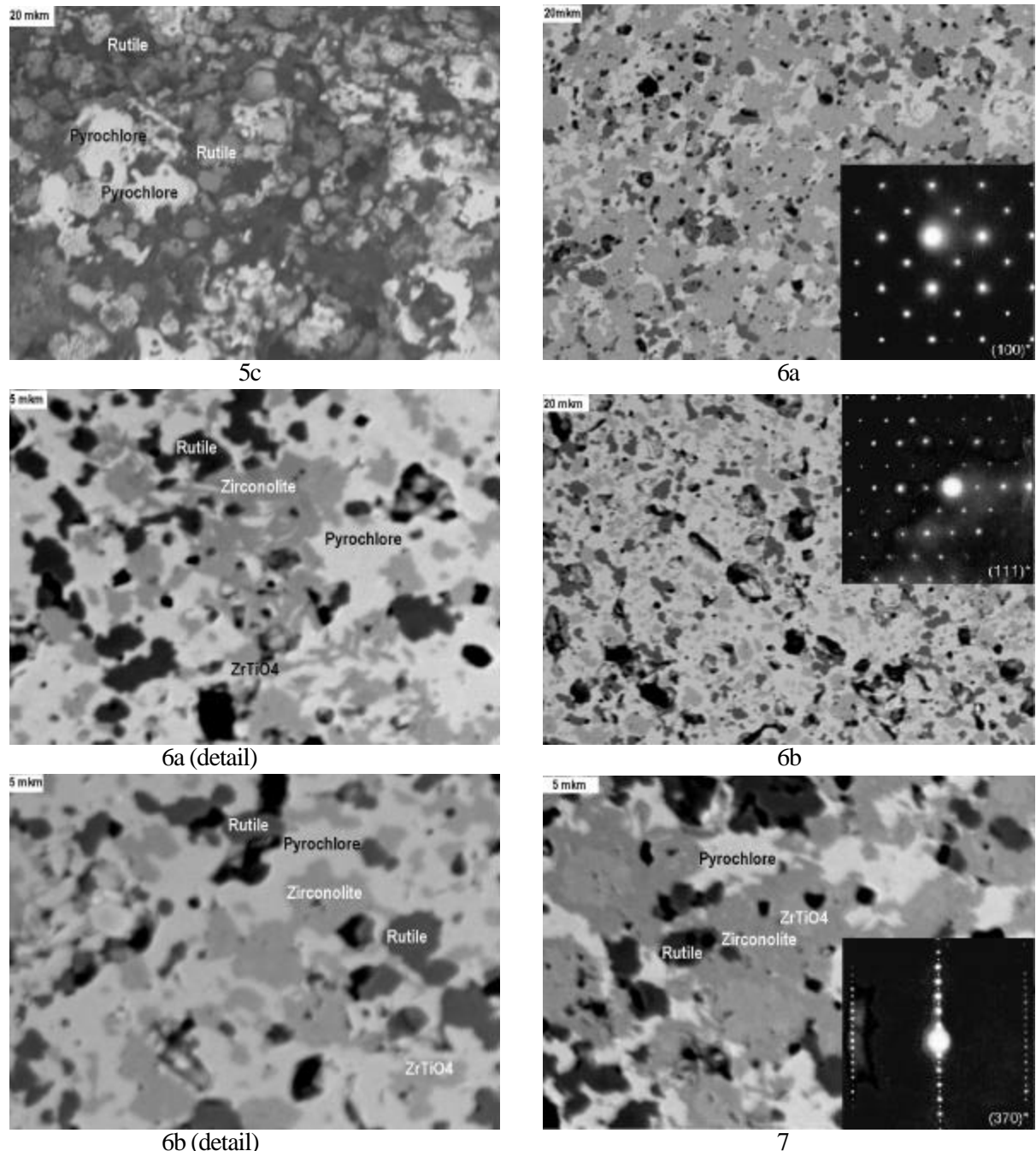


Figure 4. SEM images of the ceramic samples. Inserts are TEM patterns of pyrochlore in the samples ## 6a and 6b, and zirconolite in the sample #7 (mkm = μm).

DISCUSSION

Fully single phase ceramics with target stoichiometry $\text{CaZrTi}_2\text{O}_7$ or $\text{CaZr}_{0.75}\text{U}_{0.25}\text{Ti}_2\text{O}_7$ have not been produced. As follows from comparison of XRD patterns (Figures 1-3), the mechanical treatment of oxide batches with the same composition increases target phase yield, currently zirconolite, probably due to better homogenization of fine-grade components, as compared to manual grinding in mortar, after sintering at the same temperatures. In the whole, mechanical treatment/activation of batch mixtures in the apparatus with rotating magnetic field reduces temperature range of zirconolite/pyrochlore formation by approximately 100-200 °C. From XRD patterns (Figure 1) difference in relative content of zirconolite and other phases, mainly rutile, between the samples mechanically treated in the planetary mill and the apparatus with rotating magnetic field is not seen. However, as it has been shown in ref. [10], ceramic samples prepared by sintering of batches activated in the apparatus with rotating magnetic field have better physical and mechanical properties than samples prepared using planetary mill.

Zirconolite reflections on XRD patterns are typical of zirconolite-2M, therefore, mechanical treatment/activation of initial batch doesn't result in formation of other zirconolite varieties. However, phase composition of ceramic samples with calculated formulation $\text{CaZr}_{0.75}\text{U}_{0.25}\text{Ti}_2\text{O}_7$ differs markedly from reference data [11] and phase composition of the samples prepared from non-activated batches (Figure 2) due to formation of noticeable pyrochlore content.

It should be noted, that in the samples #6a and #6b prepared by sintering of batches from mechanically activated precursor and non-activated UO_2 (calcine), pyrochlore dominates over zirconolite, whereas in the sample #7 produced from fully mechanically treated batch pyrochlore content is lower than zirconolite content, and in the sample #5d produced from initial oxide mixture at 1400 °C pyrochlore was not found, although it is present in the sample #5c sintered at 1300 °C. The reasons are as follows. Firstly, pyrochlore obviously is always intermediate product in the uranium-containing batches of the $\text{CaO-ZrO}_2\text{-UO}_2\text{-TiO}_2$ system. It may be unstable at high temperatures (=1400 °C) being subjected to decomposition with formation of zirconolite, uraninite, rutile, perovskite, etc. (Figures 2 and 3). Secondly, chemical mechanism of reactive sintering is different in non-activated or fully activated batches, and in partially treated batches. These mechanisms will be studied in details in future. Here, we can give only general discussion based on some suggestions.

In both non-activated and fully activated batches prepared from Ca, Zr, Ti, and U oxides formation of pyrochlore or U-bearing zirconolite goes through calcium uranates (mainly CaUO_4) following by interaction between calcium uranates and TiO_2 as well as ZrO_2 yielding minor amount of U-rich pyrochlore-type phase (Figure 2). Perovskite and possibly calcium zirconate as intermediate products also occur. At low uranium content intermediate pyrochlore-type phase reacting with ZrO_2 becomes enriched with zirconium and transforms to zirconolite although minor pyrochlore may remain (the samples #5c, #5d, and #7).

When fraction of the batch consisting of CaO, ZrO_2 , and TiO_2 is treated in the apparatus with rotating magnetic field, fine-grade very homogeneous activated mixture is formed. It can be suggested that some interaction between activated oxide grains occurs at ambient temperatures following by preferable reactions of zirconolite, zirconium titanate, and perovskite formation during heat-treatment to 1000-1200 °C. These intermediate products interact with UO_2 becoming enriched with uranium and yielding significant fraction of pyrochlore-type phase.

In our previous works we investigated cold crucible melted Gd-containing ceramics with bulk compositions $\text{Ca}_{0.8}\text{Gd}_{0.2}\text{ZrTi}_{1.8}\text{Al}_{0.2}\text{O}_{7.0}$ and $\text{Ca}_{0.5}\text{Gd}_{0.5}\text{ZrTi}_{1.5}\text{Al}_{0.5}\text{O}_{7.0}$ [3,9] and sintered U-containing ceramics with bulk compositions $\text{Ca}_{0.71}\text{Zr}_{0.93}\text{U}_{0.16}\text{Ti}_{2.05}\text{Al}_{0.02}\text{O}_{7.00}$ and $\text{Ca}_{0.66}\text{Zr}_{0.86}\text{U}_{0.27}\text{Ti}_{2.27}\text{Al}_{0.01}\text{O}_{7.00}$ [4,12]. Two zirconolites, marked as zirconolite-1 and zirconolite-2, have been found. Monoclinic phase, marked as zirconolite-1, has been shown to be zirconolite-2M and its composition was close to nominal zirconolite stoichiometry [12]. The other phase, marked as zirconolite-2, had different from zirconolite-1 relationship between zirconium and titanium

(Zr:Ti ~ 0.2), and was markedly enriched with uranium (up to 0.52 f.u. U) in the uranium-containing and gadolinium (up to 0.74 f.u. Gd) in the gadolinium-containing samples. Averaged phase formulations in U- and Gd-containing samples were $\text{Ca}_{1.15}\text{Zr}_{0.40}\text{U}_{0.50}\text{Ti}_{2.02}\text{O}_{7.00}$ and $\text{Ca}_{0.30}\text{Gd}_{0.74}\text{Zr}_{0.33}\text{Ti}_{2.01}\text{Al}_{0.60}\text{Fe}_{0.02}\text{O}_{7.00}$, respectively. Taking into account this difference, it has been suggested that zirconolite-2 relates to cubic pyrochlore-structured phase. In the uranium-bearing samples about 80-90% of zirconolite-2 grains seemed to be monoclinic zirconolite-2M grains and about 10-20% of zirconolite-2 grains had cubic pyrochlore-structured lattice [12].

In the present work we have similar effect, but pyrochlore-structured phase dominates due to higher calcium content in the samples, features of preparation method (sintering of mixture from mechanically activated precursor and non-activated uranium dioxide) and higher sintering temperature.

Along with pyrochlore and zirconolite, rutile is also present in the ceramic samples. Its major reflection peaks on XRD patterns are 3.25 Å (100%), 2.49 Å (50%), and 1.69 Å (60%). They are observed on the most of XRD patterns of the samples studied (Figures 1-3). Occurrence of rutile is also confirmed by SEM/EDS (Figure 4). Because, zirconolite XRD pattern has the same reflection peaks but lower intensity (3.24 Å – 26%, 2.49-2.50 Å – 19%, and 1.70 Å – 5%), resulting peaks are superposition of individual peaks and reflection at 1.69 Å is characteristic of rutile. As follows from XRD patterns, rutile is occasionally present even in the samples sintered at high temperatures (Figures 1 and 3).

In the whole, zirconolite and pyrochlore takes up to 75-85 vol.% of total bulk of ceramics. The rest is composed of zirconium titanate and rutile incorporating about 6-7% and 1% of total uranium, respectively. It shows, that rutile as well as all other phases was formed during synthesis rather than remained as unreacted oxide.

CONCLUSIONS

Mechanical activation of the batches with zirconolite/pyrochlore formulations reduces temperature range of zirconolite and pyrochlore formation by approximately 100-200 °C, in particular, treatment of both whole batch and precursor only (CaO-TiO₂-ZrO₂ mixture not containing radioactive calcine – UO₂) in the apparatus with rotating magnetic field reduces sintering temperature from 1450-1550 °C to 1300-1400 °C. At that, ceramics with total content of zirconolite and pyrochlore up to 75-85% are formed. In the ceramics prepared from mechanically activated precursor and non-activated UO₂ pyrochlore content is higher as compared to non-activated and fully activated batches due to features of phase formation mechanism.

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