APPLICATION OF MECHANICAL ACTIVATION TO PRODUCTION OF PYROCHLORE CERAMIC CONTAINING SIMULATED RARE-EARTH – ACTINIDE FRACTION OF HLW

S.V. Stefanovsky, O.I. Kirjanova
SIA Radon, 7th Rostovskii per. 2/14, Moscow 119121 RUSSIA, profstef@radon.ru

S.V. Chizhevskaya
University of Chemical Engineering, Miusskaya 9, Moscow 125047 RUSSIA, chizh@rctu.ru

S.V. Yudintsev, B.S. Nikonov
Institute of Geology of Ore Deposits RAS, Staromonetnii 35, Moscow 109017 RUSSIA, syud@igem.ru

ABSTRACT

Samples of zirconate pyrochlore ceramic $(REE)_2(Zr,U)_2O_7$ (REE = La…Gd) containing simulated REE–An fraction of HLW were synthesized by two routes: 1) conventional cold compaction of oxide mixtures in pellets under pressure of 200 MPa and sintering of the pellets at 1550 ^{0}C for 24 hours; and 2) using preliminary mechanical activation of oxide powders in a linear inductive rotator (LIV-0.5E) and a planetary mill – activator with hydrostatic yokes (AGO-2U) for 5 or 10 min. All the samples sintered at 1550 ^{0}C were monolithic and dense with high mechanical integrity. As follows from X-ray diffraction (XRD) data, the ceramic sample produced without mechanical activation is composed of pyrochlore as major phase but contains also minor unreacted oxides. The samples prepared from pre-activated mixtures are composed of the pyrochlore structure phase only. Scanning electron microscopy (SEM) data also show higher structural and compositional homogeneity of the samples prepared from mechanically activated batches. The samples produced from oxide mixtures mechanically activated in the LIV for 10 min were slightly contaminated with iron resulting in formation of minor perovskite structure phase not detected by XRD but seen on SEM-images of the samples. Comparison of the samples prepared from non-activated and activated batches showed higher density, lower open porosity, water uptake, and elemental leaching for the samples fabricated from mechanically activated oxide mixtures.

INTRODUCTION

According to high level waste (HLW) partitioning concept, HLW is to be partitioned on short-lived Cs/Sr and long-lived rare earth (REE) – actinide (An) fractions to be conditioned separately [1]. The Cs/Sr fraction is supposed to be vitrified with borosilicate glass production, whereas REE-An fraction requiring storage for millions of years must be incorporated in durable crystalline host. One of the best ceramic waste forms with very high radiation and chemical stability is zirconate pyrochlore [2]. However, this phase is very high fusible and its formation rate is extremely low. Reaction in the mixture of Gd_2O_3 and ZrO_2 milled in an agate mortar has not been completed at 1550 ^{0}C for 40 hours [3].

To accelerate reactions in the system Gd_2O_3-ZrO_2 (generally REE_2O_3-ZrO_2) and to improve product quality a treatment of oxide mixtures with high mechanical energy may be applied. Such treatment may be performed in various units – planetary mills, impinging jets, apparatus with rotating magnetic field, etc. [4-6]. Absorption of high mechanical energy may cause activation of batch particles accompanied by formation of exitation states, free radicals, ions, fresh-cracked surfaces, and other physical and chemical effects. Activated particles interact with significantly higher rate. This allows to reduce process duration or temperature, for example, reactions in the ceramic mixtures with pyrochlore formulations in the systems CaO-UO_2-TiO_2 and CaO-ZrO_2-UO_2-TiO_2 pre-treated in an activator with hydrostatic yokes were completed within the temperature range of 1000-1100 ^{0}C that is lower than in non-activated mixtures by 200-300 ^{0}C [6].

In this work we have studied an effect of mechanical activation on phase formation in complex REE-zirconate system containing simulated REE-actinide fraction of HLW.

EXPERIMENTAL

Ceramic composition with zirconate pyrochlore formulation was as follows (in wt.%): La_2O_3 – 7.1, Ce_2O_3 – 14.0, Pr_6O_{11} – 6.8, Nd_2O_3 – 22.2, Sm_2O_3 – 4.1, EuO – 2.0, Gd_2O_3 – 0.9, UO_2 – 3.1, ZrO_2 – 39.8. This composition corresponds to formula $(La_{0.26}Ce_{0.51}Pr_{0.24}Nd_{0.79}Sm_{0.14}Eu_{0.04}Gd_{0.03})(U_{0.07}Zr_{1.93})O_7$ [generally $(REE)_2(Zr,U)_2O_7$ (REE = La…Gd)]. Gd was used as Am and Cm surrogate. One sample was synthesized by sintering at 1550 ^{0}C of oxide mixture milled in an agate mortar. Product of heat-treatment for 6 hours was re-milled and sintered again for 6 hours. This operation was repeated two times. The mixture was compacted in pellets under pressure of 200 MPa before sintering. Total sintering duration was 24 hours. The other ceramic samples were prepared from oxide powders pre-mechanically activated in a linear inductive rotator (LIV-0.5E) and a planetary mill – activator with hydrostatic yokes (AGO-2U) for 5 or 10 min. Activated samples were cold pressed at 200 MPa, heated to 1550 ^{0}C and kept at this temperature for 3 or 6 hours. A list of the samples studied is given in Table I.

The samples were examined with X-ray diffraction (XRD) using a DRON-4 diffractometer (Cu K_α - radiation), scanning (SEM/EDS) and transmission electron microscopy (TEM) using a JSM-5300 + Link ISIS and a JEM100c + KEVEX-5100 units, respectively. Apparent density, open porosity and water uptake were measured using Russian standard tests [7]. Elemental leaching was determined using a 7-day MCC-1 test at 90 ^{0}C [8].

RESULTS AND DISCUSSION

As follows from XRD data, all the samples are predominantly composed of pyrochlore structure phase (Figure 1). XRD pattern of the pyrochlore phase in the ceramic samples studied is very similar to $Nd_2Zr_2O_7$ (JCPDS 17-458). Major reflections within the range $5 \leq 2\Theta \leq 75$ degrees are (Å): 6.083…6.151 (111), 3.187…3.200 (311), 3.060…3.075 (222), 2.649…2.663 (400), 2.428…2.442 (331), 2.037…2.048 (511), 1.875…1.882 (440), ~1.795 (531), 1.598…1.606 (622), 1.530-1.539 (444), ~1.386 (731), 1.326…1.331 (800). Reactions in the oxide mixture have not been completed as it is seen from complex structure of diffraction peaks (peaks splitting) due to variation in pyrochlore composition (Figure 2). As it has been confirmed by SEM/EDS data (Figure 3, a) pyrochlore phase composition in the sample M/24 prepared from non-activated oxide mixture is markedly varied especially in Ce and Nd contents:

Table I. Ceramic samples with pyrochlore formulation sintered at 1550 ^{0}C.

Sample	Mechanical activator	Treatment duration, min.	Sintering duration, hours	Phases	Averaged value of pyrochlore reflection (222)	a, Å
M/24	No	- (Milling in mortar)	24	Pyrochlore (predominant), cubic zirconia-based solid solution, Nd-oxide (traces)	3.058	10.593
A/5/3	AGO-2U	5	3	Pyrochlore	3.064	10.614
A/5/6	-"-	5	6	Pyrochlore	3.062	10.607
A/10/3	-"-	10	3	Pyrochlore	3.060	10.600
A/10/6	-"-	10	6	Pyrochlore	3.062	10.607
L/5/3	LIV-0,5E	5	3	Pyrochlore (predominant), baddeleyite (minor)	3.069	10.631
L/5/6	-"-	5	6	Pyrochlore (predominant), baddeleyite (traces)	3.073	10.645
L/10/3	-"-	10	3	Pyrochlore	3.060	10.600
L/10/6	-"-	10	6	Pyrochlore	3.062	10.607

$(La_{0.12...0.20}Ce_{0.32...0.72}Pr_{0.12...0.16}Nd_{0.60...0.84}Sm_{0.08...0.12}Eu_{0.04...0.12}Gd_{0.01...0.03})(Zr_{2.18...2.22}U_{0.03...0.04})$ $O_{7.115...7.125}$. Average phase formula over scanning area is $(La_{0.20}Ce_{0.52}Pr_{0.13}Nd_{0.73}Sm_{0.09}Eu_{0.07}$ $Gd_{0.02})(Zr_{2.20}U_{0.04})O_{7.12}$. Therefore, grains of the given phase are formed by aggregates of pyrochlore with average formula (calculated): $(La_{0.23}Ce_{0.59}Pr_{0.15}Nd_{0.83}Sm_{0.10}Eu_{0.08}Gd_{0.02})(Zr_{1.95}$ $U_{0.05})O_7$ (in suggestion that all REEs, including Ce and Eu, exist in a trivalent form) and cubic zirconia-based solid solution. Formation of the pyrochlore structure phase has been confirmed by TEM (Figure 4). Selected area electron diffraction (SAED) patterns demonstrate typical pyrochlore structure. SEM/EDS examination also shows occurrence of traces of residual unreacted phases. For example, formula of partially reacted neodymium oxide grain (Figure 3, b) was found to be $(La_{0.04}Ce_{0.08}Pr_{0.04}Nd_{1.18}Sm_{0.04}Eu_{0.02}Gd_{0.01})(Zr_{0.40}U_{0.14})O_{3.28}$.

The sample A/5/3 prepared from oxide mixture mechanically activated in the AGO-2U unit for 5 min and sintered at 1550 ^{0}C for 3 hours is composed of pyrochlore structure phase only. But pyrochlore composition is slightly varied (Figure 2). Longer sintering results in formation of pyrochlore with fixed composition close to specified. As seen from Figure 2 the major pyrochlore peak becomes narrower and more symmetric at longer activation and sintering duration. This proposition holds true for mechanical activation in the LIV-0,5E, too (Figure.2, right).

The mechanical treatment in both activators following by sintering at 1550 ^{0}C for 6 hours results in formation of the pyrochlore structure with the same unit cell parameter $a = 10.607$ Å. Similar pyrochlore lattice parameter ($a = 10.593$ Å) is reached after sintering of manually milled (non-activated) oxide mixture at the same temperature for 24 hours. Table I demonstrates that equilibrium state in the REE_2O_3-ZrO_2-UO_2 system was achieved in the sample A/5/6 mechanically activated in the AGO-2U for 5 min. and sintered at 1550 ^{0}C for 3 hours, whereas to get the same result using LIV-0,5E mechanical treatment for 10 min. and sintering for at least 3 hours is required. At shorter mechanical treatment and sintering duration at first a phase with some expanded unit cell ($a = 10.614$ Å in the sample A/5/3, 10.631 Å in the sample L/5/3,
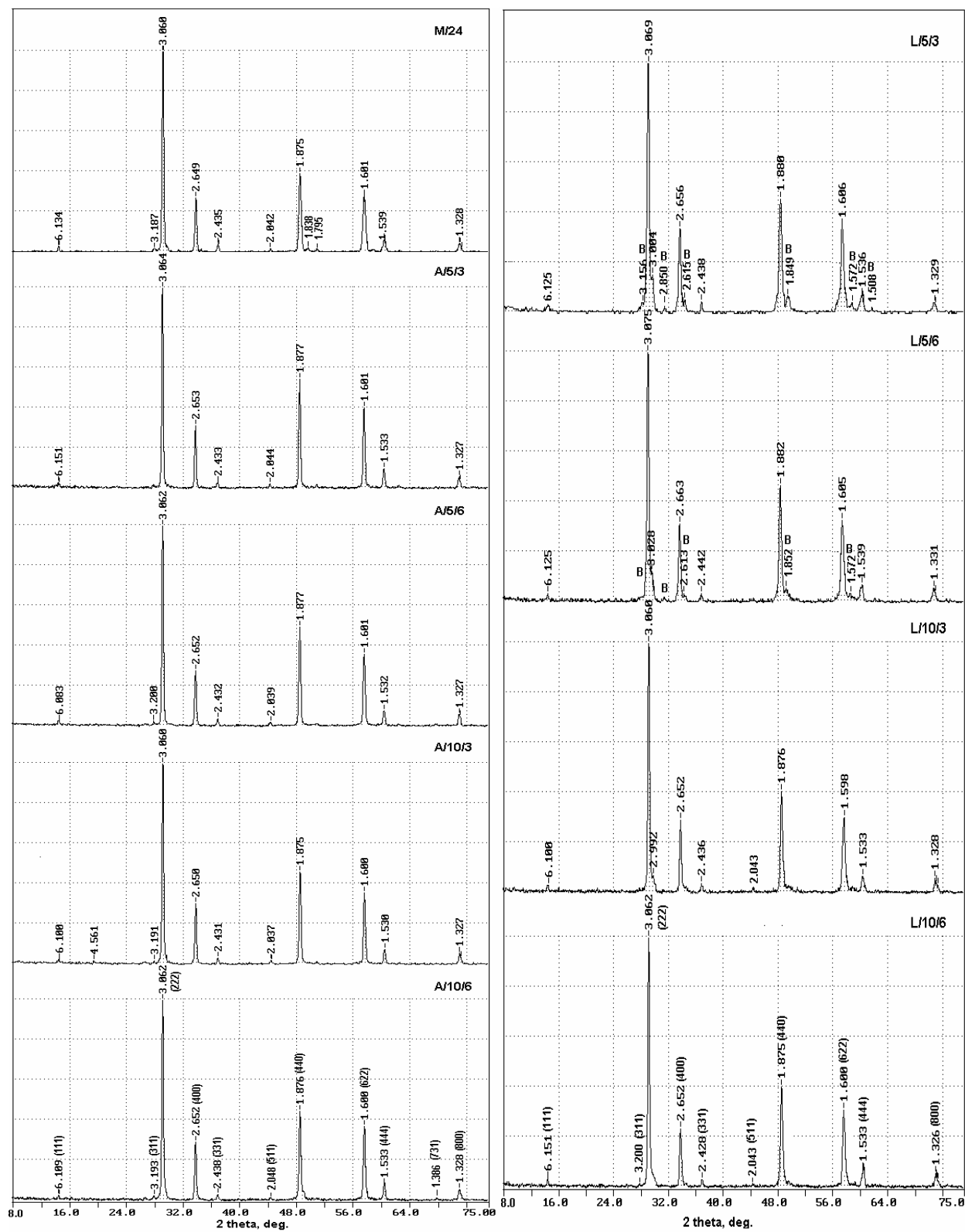
Figure 1. XRD patterns of the ceramic samples sintered at 1550 ^{0}C.
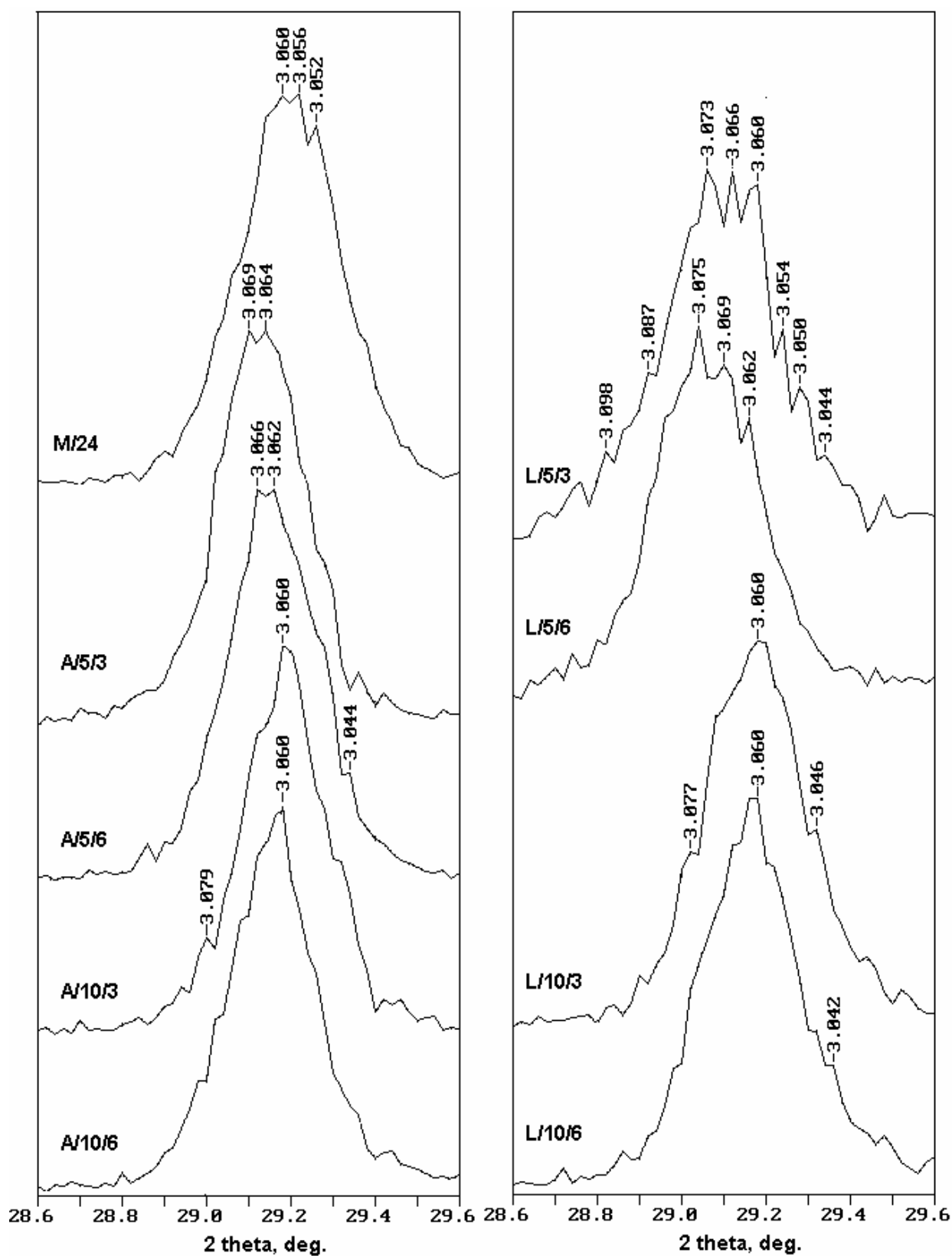B – baddeleyite, the rest of peaks are due to pyrochlore structure phase.

Figure 2. Splitting of the major pyrochlore reflection (222) on XRD patterns of the ceramic samples.
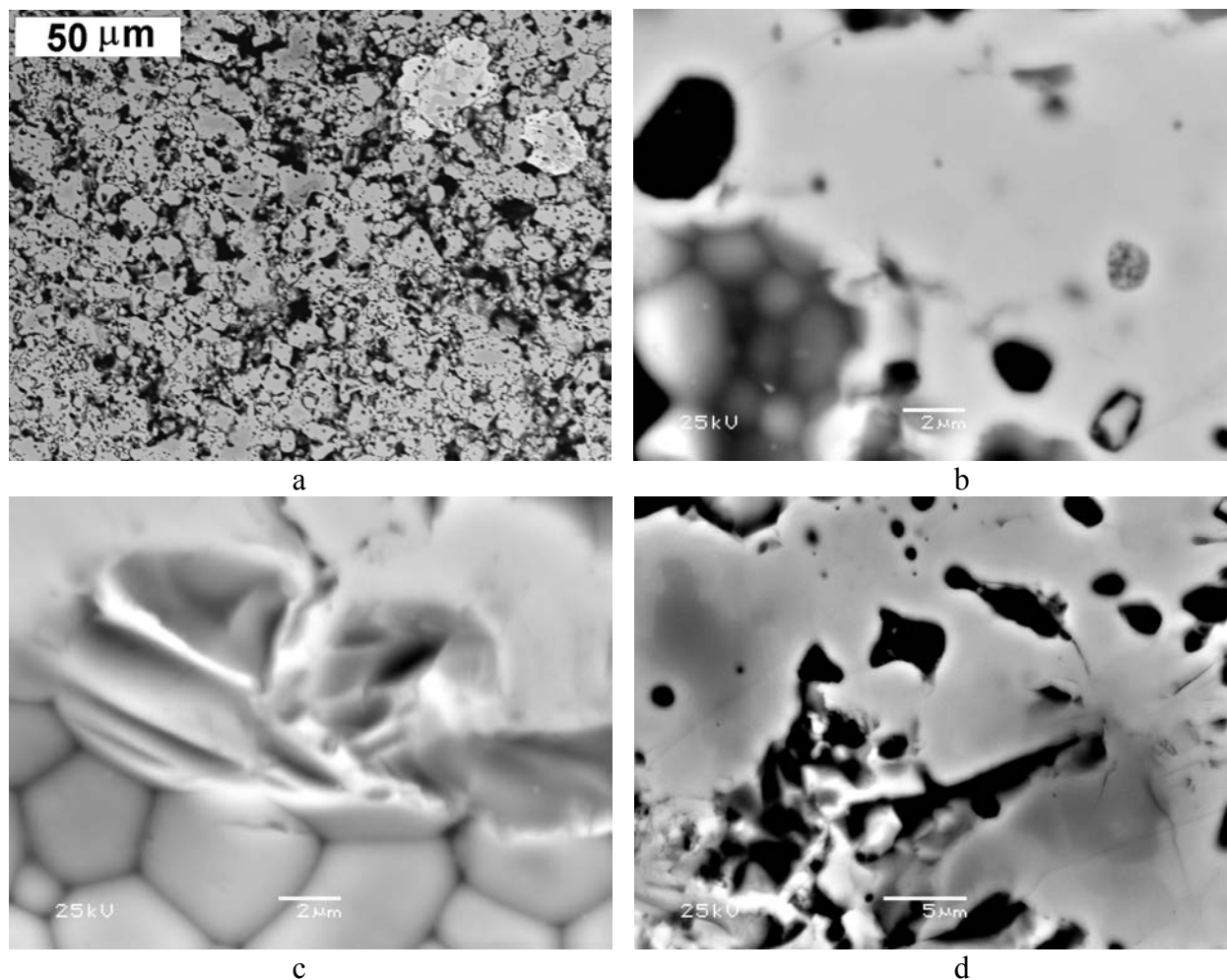
Figure 3. SEM images of the samples M/24 (a), A/5/3 (b), A/10/6 (c), and L/10/6 (d).
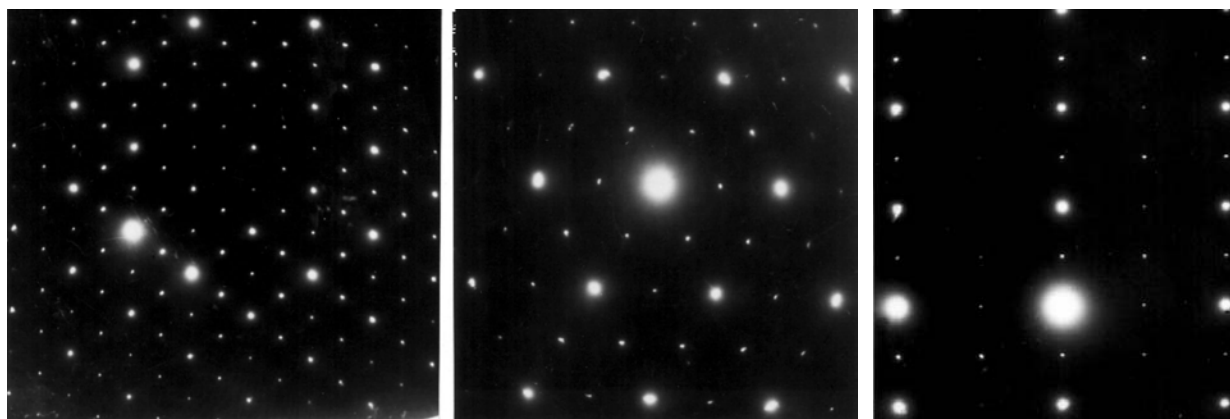

Figure 4. SAED patterns of the pyrochlore structure phase from the planes of inverse lattice [(110)* – left, (111)* – middle, (211)* - right] in the samples M24 (left and middle) and A/3/6 (right).

and 10.645 Å in the sample L/5/6) is formed. The reason of this effect is probably formation of Nd- (and also Sm, Eu, and Gd)-enriched pyrochlore phase due to mechanical activation effects and insufficient sintering duration not allowing to reach equilibrium state. Longer treatment and sintering duration reduces the pyrochlore unit cell dimension to equilibrium value when pyrochlore grains composition is averaged and pyrochlore composition itself seeks to target one.

Comparison of the texture of the samples shows that the ceramics prepared using the mechanical activation are more uniform, shape of pyrochlore grains is more regular and porosity is lower than in the sample M/24 prepared from non-activated mixture with longer sintering duration (Figure 3). Nevertheless, variations in color (and composition) as compared to pyrochlore bulk on SEM-images occurred in the last sample (Figure 3, d). Darker core of these grains is enriched with zirconia due to incomplete reaction between initial baddeleyite and lanthanide oxides. Lighter rim is formed by pyrochlore some depleted with zirconia and enriched with lanthanide oxides and possibly uranium. This effect demonstrates that AGO-2U is some more effective activator as compared to LIV-0.5E.

Data on physical properties and leach resistance of pyrochlore ceramics are given in Table II. As it has been expected, mechanical activation and longer sintering duration increase apparent density and reduce open porosity and water uptake of the ceramics. However the difference in elemental leach rates between the ceramics produced from activated and non-activated oxide mixtures is not so prominent. Leach rates of major elements from the samples are similar and as a rule have the same order of magnitude. The only exception is the sample A/10/6 composed of well-formed pyrochlore grains (Figure 3, c) having lowest porosity and minimum surface subjected to leaching.

Table II. Physical properties and leach resistance of the pyrochlore ceramic samples.

Sample		M/24	A/5/3	A/5/6	A/10/3	A/10/6	L/5/3	L/5/6	L/10/3	L/10/6
Apparent density	g/cm³	4.68	4.92	4.95	4.93	4.98	5.58	5.63	5.60	5.72
	% of theoretical*	72	76	76	76	77	86	87	86	88
Open porosity, %		23.6	0.5	1.8	1.5	0.5	3.6	1.0	1.5	0.6
Water uptake, wt.%		5.0	0.4	<0.1	0.4	<0.1	2.4	1.0	2.0	0.5
Leach rate, g/(m² day)	La	$\sim10^{-5}$								
	Ce		$\sim10^{-5}$			$\sim10^{-6}$	$\sim10^{-6}$		$\sim10^{-5}$	$\sim10^{-6}$
	Pr	$\sim10^{-5}$	$\sim10^{-6}$							
	Nd	$\sim10^{-6}$								
	Sm	$\sim10^{-6}$								
	U	$\sim10^{-7}$								
	Zr	$\sim10^{-7}$								

* calculated theoretical density of the pyrochlore with specified composition is 6.49 g/cm³.

Reference data on properties of REE-zirconates, except radiation stability [2], are very limited. It is known, that La and Zr leach rates from ceramic with nominal formula $La_2Zr_2O_7$ at 90 ^{0}C were found to be $\sim10^{-6}$ g/(m² day) [9]. For the ceramics designed for excess weapons plutonium immobilization [10] containing up to 95 wt.% pyrochlore with baseline composition

$Ca_{0.89}Gd_{0.22}Hf_{0.23}Pu_{0.22}U_{0.44}Zr_2O_7$, which were sintered at 1300-1500 ^{0}C for 4 hours in air or Ar leach rates for Gd, Pu, Hf and Zr by MCC-1 test at 90 ^{0}C were 10^{-6}-10^{-5} g/(m^2 day) after 7 days and 10^{-7}-10^{-6} g/(m^2 day) after 30 days [11]. To achieve densification (~93% of theoretical density for the given formulation) required for high leach resistance sintering temperature of zirconate formulations must be at least 1500 ^{0}C. In our work we sintered ceramics at 1550 ^{0}C. We have demonstrated that dense REE-zirconate ceramics requiring higher sintering temperature than Ca-bearing formulation can not be produced without additional mechanical treatment/activation of oxide mixtures.

CONCLUSION

Using mechanical treatment/activation of oxide mixtures containing simulated REE-actinide fraction of HLW the ceramics with zirconate pyrochlore formulation were produced. Mechanical activation reduces significantly sintering temperature or duration. Unlike ceramic produced from non-activated batch and contained source unreacted phases, the ceramics prepared from mechanically activated batches are almost single phase and have better physical properties than ceramics prepared from non-activated batch.

ACKNOWLEDGEMENTS

REFERENCES

1. Y.V. GLAGOLENKO, E.G. DZEKUN, E.G. DROZHKO, et. al., Quest. Rad. Safety ((Russ) [2] (1996) 3-10.
2. S.X. WANG, B.D. BEGG, L.M. WANG, R.C. EWING, W.J. WEBER, K.V. GOVIDAN KUTTY, J. Mat. Res. 14, [12] (1999) 4470.
3. S.V. YUDINTSEV, S.V. STEFANOVSKY, Y.N. JANG, S. CHAE, Glass and Ceramics (Russ.) [7] (2002) 18.
4. S.V. CHIZHEVSKAYA, S.V. STEFANOVSKY, Plutonium Futures – The Science. Conf. Trans. Santa Fe, NM, July 10-13, 2000, pp. 148-150.
5. S.V. CHIZHEVSKAYA, N.E. CHERNIAVSKAYA, A.V. OCHKIN, A.M. CHEKMAREV, S.V. STEFANOVSKY, Mat. Res. Soc. Symp. Proc. 663 (2001) 367.
6. S.V. STEFANOVSKY, S.V. CHIZHEVSKAYA, S.V. YUDINTSEV, "Waste Management '2002." Proc. Int. Symp., Tucson, CD-ROM, Rep. 310 (2002).
7. Laboratory Manual for Technology of Ceramics and Refractories (Russ.), edited by D.N. Poluboyarinov (Moscow, 1972).
8. Nuclear Waste Materials Handbook (Test Methods). DOE TIC, Washington, DC. Rep. DOE/TIC-11400 (1981).
9. I. HAYAKAWA, H. KAMIZONO, J. Mat. Sci. 28 (1993) 513.
10. B.B. EBBINGHAUS, R.A. VANKONYNENBURG, F.J. RYERSON et al., "Waste Management '98", Proc Int. Symp., Tuscon, CD-Rom. Rep. N65-04 (1998).
11. Y. ZHANG, K.P. HART, B.D. BEGG, et. al., Mat. Res. Soc. Symp. Proc. 713 ((2002) 389.