PLUTONIUM AND ACTINIDE WASTE IMMOBILIZATION IN CERAMICS VIA MELTING

S.V. Stefanovsky[1], V.I. Vlasov[1], A.G. Ptashkin[1], O.I. Kirjanova[1], Y.M. Kulyako[2], S.A. Perevalov[2]
[1] SIA Radon, 7th Rostovskii per. 2/14, Moscow 119121 RUSSIA, itbstef@cityline.ru
[2] Vernadsky Institute of Geochemistry and Analytical Chemistry, Kosygin st. 19, Moscow 117975 RUSSIA, kulyako@glasnet.ru

ABSTRACT

Samples of zirconolite-, pyrochlore-, and murataite-based ceramics potentially suitable for immobilization of actinide waste and excess weapons plutonium have been prepared via melting in a resistive furnace and a cold crucible, and examined with X-ray diffraction. Melting temperature ranged between 1400 ^{0}C and 1700 ^{0}C. The samples with zirconolite, pyrochlore, and murataite as major phases were obtained after melting under oxidizing conditions. An extra phase in the most of the samples was perovskite. The highest perovskite content was found to be in the murataite-based ceramics produced under reducing conditions (in glassy carbon crucibles). The reason of this effect is formation of trivalent plutonium entering the perovskite phase. Pu leach rate from the mutataite ceramic measured by 7-day MCC-1 test at 90 ^{0}C was found to be ~10^{-6} g/(m^2·day).

Keywords: melting, murataite, perovskite, pyrochlore, zirconolite.

1. INTRODUCTION

Zirconolite and complex fluorite-structured oxides are considered as promising host phases for excess weapons plutonium immobilization [1]. Pyrochlore-based ceramic containing ~10 wt.% Pu is suggested to be produced at LLNL using a cold pressing and sintering method [2]. An alternative way developed in Russia is inductive melting in a cold crucible (IMCC) successfully applied earlier to produce waste glasses and ceramics in Russia and France [3-6]. Advantages of the cold crucible over Joule-heated ceramic melter are higher specific productivity, higher temperature availability, lower sensitivity to batch quality, longer lifetime, smaller overall dimensions and weight, and easier remote dismantling and disposal.
Various ceramics (zirconolite-, pyrochlore-, murataite-based) appropriate for the IMCC were designed and tested at SIA Radon in cooperation with Institute of Geology of Ore Deposits and Institute of Geochemistry RAS [7,8]. This work briefly describes recent results.

2. LAB-SCALE EXPERIMENTAL PROCEDURE

Zirconolite $Ca_{0.88}Gd_{0.12}Zr_{0.88}Pu_{0.12}Ti_{1.78}Al_{0.22}O_{7.00}$ (Z) and pyrochlore $Ca_{0.89}Gd_{0.22}Hf_{0.23}U_{0.44}Pu_{0.22}Ti_{2.00}O_{7.00}$ (P1) formulations were taken from reference data [1]. One more pyrochlore $Gd_{1.9}Pu_{0.1}Ti_{2.0}O_7$ (P2) had simplified composition in suggestion that all the plutonium enter the Gd-site in a trivalent form. Murataite compositions were specified as $Ca_{2.59}Fe_{0.37}Zr_{0.39}Pu_{0.36}Mn_{2.05}Ti_{6.67}Al_{0.57}O_{20.20}$ (Sample M1) and $Ca_{2.58}Gd_{0.75}Zr_{0.37}Pu_{0.33}Mn_{1.90}Ti_{6.20}Al_{0.53}Fe_{0.34}O_{20.54}$ (Sample M2). Exact murataite formula is not established yet. Suggested general formula is $A_4B_2C_7O_{22-x}$, where A = Na, Ca, Zr, Ln, An; B = Mn, Zn, Fe; C = Ti, Al, Fe.
Ceramic precursors were prepared by intermixing of non-radioactive additives (CaO, TiO_2, ZrO_2, Gd_2O_3, HfO_2, Al_2O_3, Fe_2O_3, MnO) followed by treatment with high mechanical energy using an activator with hydrostatic yokes AGO-2. High homogeneous mixtures were soaked with plutonium nitrate solution. Samples were melted at 1400-1600 ^{0}C in glassy carbon crucibles placed in a resistive furnace followed by crystallization in turned-off furnace. Synthetic melted zirconolite-, pyrochlore-, and murataite-based ceramics were studied with X-ray diffraction (XRD) using a DRON-4 diffractometer (Cu K_α-radiation). Pu leach rates from these ceramics were measured using a 90 ^{0}C MCC-1 test [9]. Relative leach resistance of Sample Z to deionized, model ground, and sea water was also studied using the same procedure.

3. PHASE COMPOSITION

As follows from XRD data, zirconolite is the major phase in the sample Z (Figure 1). It accounts for ~60-65% of total bulk of the sample. Major zirconolite peaks are (in Å): 2.917, 2.780, 2.498, 1.801, 1.796, 1.738, etc. Perovskite is observed as an extra phase (peaks at 2.706, 1.916, 1.554, 1.356 Å). Its content can be estimated as 30-35%.

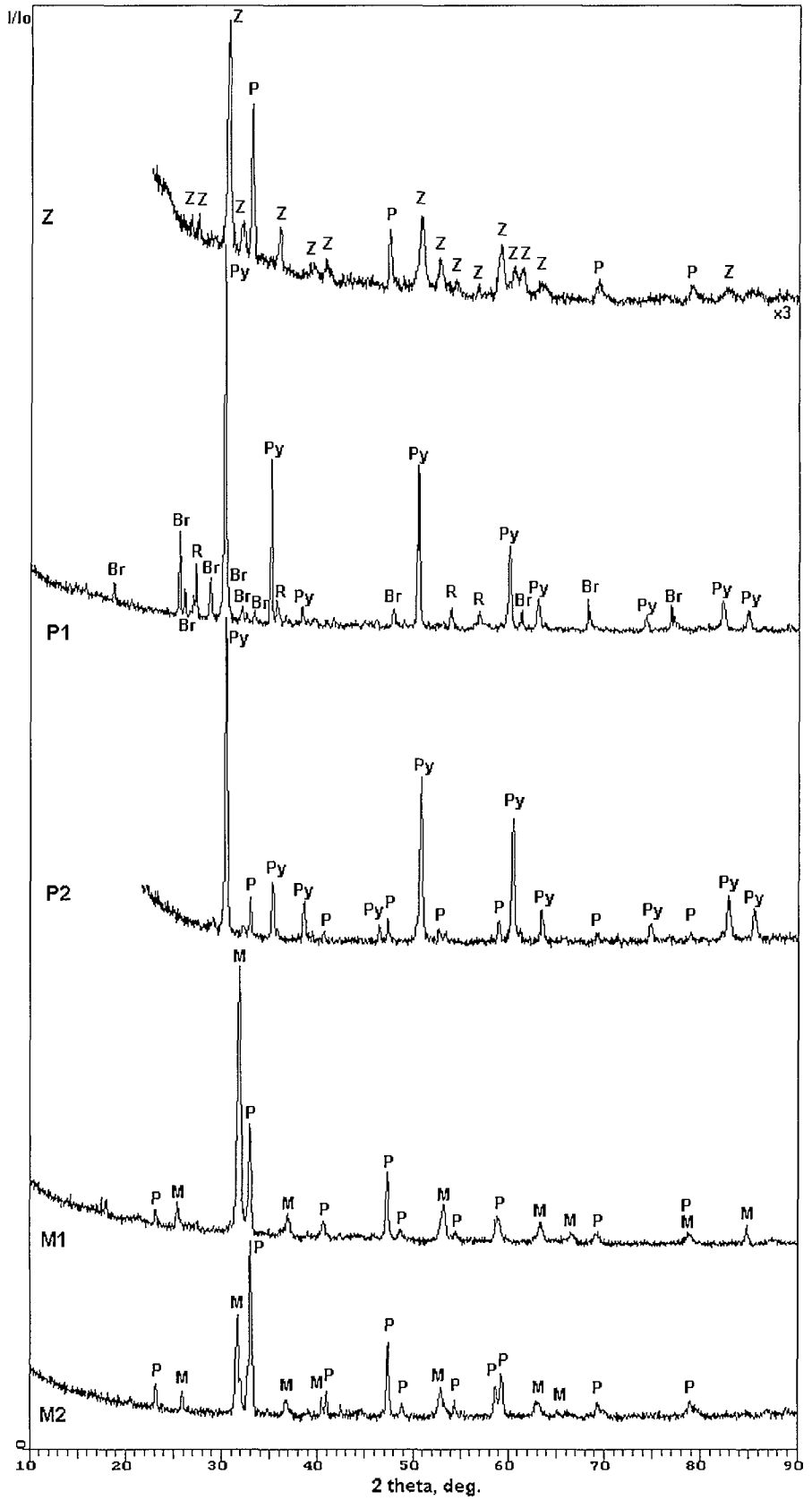

Figure 1. XRD patterns of the samples studied

Sample P1 consists of pyrochlore-type phase - 70-75% of total bulk (reflections at 2.93, 2.53, 2.34, 1.80, 1.54, 1.47, 1.27, 1.17, 1.13 Å) and brannerite - 25-30% of total (major reflections are 3.42, 3.35, 4.71, 3.02, 2.90, 2.74, 1.89 Å). Minor rutile (peaks at 3.24, 1.69 Å) is also present.
Sample P2 is composed of major pyrochlore (peaks at 2.936, 2.543, 2.332, 1.955, 1.797, 1.531, 1.467, 1.278, 1.173, and 1.131 Å) and minor perovskite (reflections 2.714, 2.217, 1.920, 1.738, 1.556 Å).
Major phase in Sample M1 is synthetic analog of murataite whose reflections are positioned at (in Å): 2.810 (the strongest), 8.51, 2.452, 1.720, 1.467, 1.406. Position of the strongest reflection at 2.810 Å points to formation of murataite with eight-fold fluorite cell (murataite-8C). The second in abundance phase in this sample is perovskite (major reflections at, Å: 2.718, 2.219, 1.922, 1.871, 1.866, 1.561, 1.557, 1.356) accounting for 25-30% of total bulk in the murataite-based ceramic M1. The M2 sample is markedly different in phase composition from the M1 sample. Major phase in this sample is perovskite (60-65% of total, major reflections are, Å: 2.714, 3.84, 1.918, 1.560, 1.551, 1.357) and murataite is second in abundance phase (30-35% of total). Major murataite diffraction peak is positioned at 2.827 Å. This is close to murataite with five-fold fluorite cell (murataite-5C). As seen from Figure 1 this peak has weaker component at ~2.81 Å pointing to possible formation of the murataite-8C as well.
Formation of perovskite in the samples is mainly due to slightly reducing melting conditions (melting in glassy carbon crucibles). This resulted in reduction of Pu(IV) to Pu(III). Samples with similar compositions but doped with UO_2 rather than PuO_2 didn't contain any perovskite phase being prepared under oxidizing conditions and only traces of perovskite phase occurred after melting under slightly reducing conditions [10].
Perovskite phase in Sample Z is probably solid solution on the basis of $(Ca,Gd,Pu^{3+})(Ti,Al)O_3$. Sample P2 doesn't contain neither Ca nor Al, and general perovskite formula is obviously $(Gd,Pu^{3+})Ti^{3+}O_3$. Predominance of perovskite in the sample M2 is due to significant Gd content stimulating formation of the phase with general formula $(Ca,Gd,Pu^{3+})(Ti^{4+}Ti^{3+}Al)O_3$ with perovskite structure. It should be noted that formation of perovskite phase was established in the Ce-containing sample produced at LLNL by cold pressing and sintering [11].

4. LEACH RESISTANCE

Pu leach rate from zirconolite and pyrochlore ceramics in deionized water at 90 ^{0}C was found to be ~$5.9\cdot10^{-5}$-$1.3\cdot10^{-4}$ g/(m^2·day). Murataite demonstrates lower Pu leach rate - ~10^{-6} g/(m^2·day). We were able to measure only an order of magnitude due to appreciable error in measurement of surface area of the samples M1 and M2. From reference data Pu leach rates from zirconolite and pyrochlore ceramics measured in 7-day MCC-1 test are 10^{-4}-10^{-5} g/(m^2·day) [12]. So, leach resistance of melted and cold pressed and sintered or hot-pressed ceramics is very similar. Lower Pu leach rate from murataite ceramic as compared to zirconolite and pyrochlore ceramics is due to zoned structure of murataite grains with maximum actinide concentration in the core creating an additional barrier against leaching [7,8,13]. Perovskite formation doesn't affect negatively because perovskite also can retain Pu strongly and ^{238}Pu leach rate from perovskite ceramics are between $5\cdot10^{-5}$ and $1\cdot10^{-4}$ g/(m^2·day) [14].
We also compared leach resistance of the melted zirconolite ceramic Z in deionized water, model groundwater, and model seawater. Results are shown in Table I.

Table I. Pu leaching in various media at 90 ^{0}C

Period, days	Pu leach rate, 10^{-5} g/(m^2·day)		
	Deionized water	Model groundwater	Model sea water
0 to 7	13.4	7.1	10.7
7 to 14	9.4	7.4	17.0
14 to 21	8.5	9.1	6.9
21 to 28	10.8	9.6	5.5
28 to 43	5.9	4.1	3.2
43 to 50	12.7	7.6	8.7

As follows from Table I, initial (0 to 7 day) Pu release of Sample Z measured at 90 ^{0}C in deionized water is ~$1.3\cdot10^{-4}$ g/(m^2·day) that is within the range known from reference data [12]. It varies insignificantly with time. Pu release of the same sample in model groundwater is slightly lower (by about two times for a 0 to 7 day period).

5. IMCC

The IMCC is one of the most promising methods for waste forms production. It was successfully tested to obtain zirconolite- [4,6,7], pyrochlore- [7,13], and murataite-based [15] ceramics. Process equipment involves a high frequency (HF) generator operated at 1.76 or 5.28 MHz (Russian standard), an induction furnace (cold crucible with inductor placed within a process box), batch preparation and feeding units, and off-gas system. HF generators with vibrating power of 60, 160 and 250 kW are commercially available in Russia.

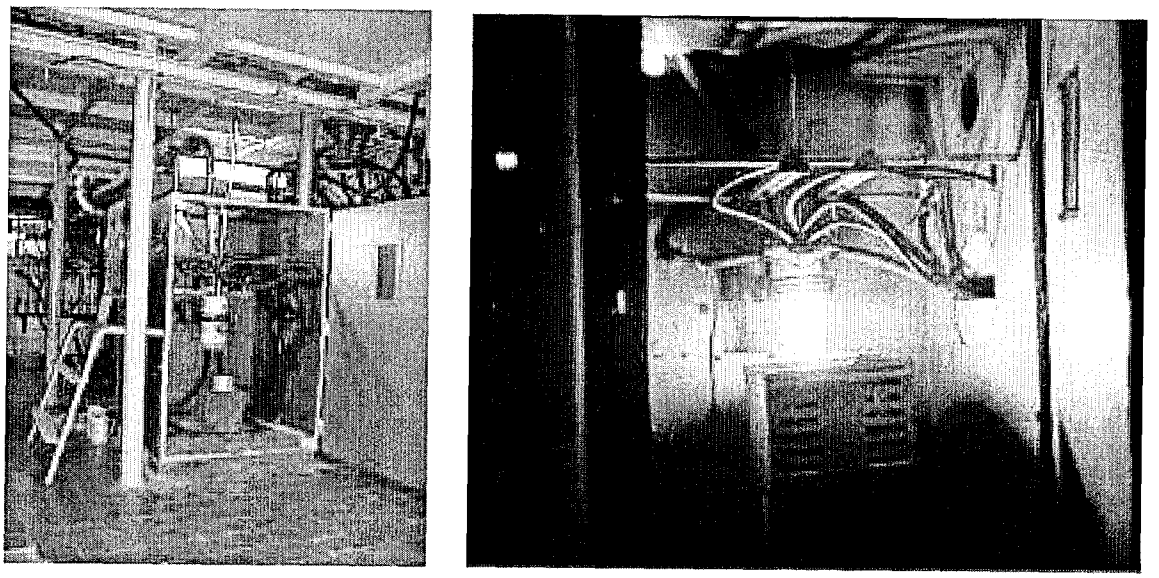

Figure 2. The cold crucible based bench-scale unit

Currently melting tests are performed at the Radon bench-scale facility (Figure 2) supplied with the cold crucibles with melt productivity ranging between ~1 and 50 kg/h (Figure 3). There are designs of the cold crucibles for periodical, semi-continuous and continuous modes of operation.

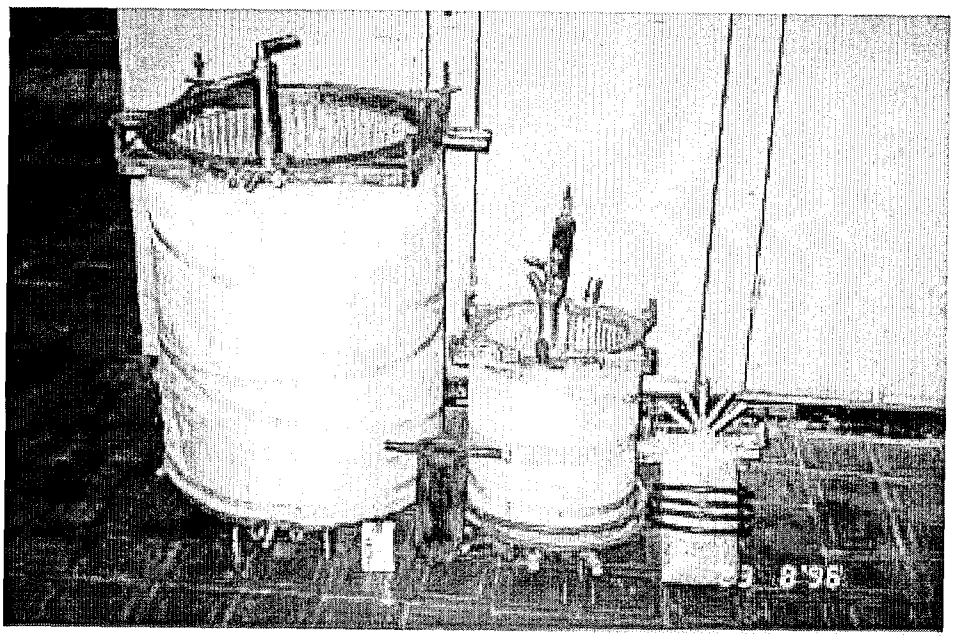

Figure 3. Cold crucibles

Up to date the IMCC process is tested at production of uranium- and thorium-bearing ceramics. The next step is design and installation of an experimental unit for production of plutonium-bearing samples. This unit is planned to install at the hot-cells location of the Vernadsky Institute of Geochemistry and Analytical Chemistry. It will be equipped with 5.28 MHz 20 kW HF generator, feed preparation, and off-gas systems.

6. CONCLUSION

Pu-bearing ceramics composed of major zirconolite, pyrochlore, and murataite and minor perovskite or brannerite were synthesized via melting under slightly reducing conditions (in glassy carbon crucibles) at 1400-1600 ^{0}C. One ceramic with major perovskite and murataite as secondary in abundance phase has been also obtained. Pu leach rate from zirconolite and pyrochlore ceramics in deionized water at 90 ^{0}C was found to be ~$5.9 \cdot 10^{-5}$-$1.3 \cdot 10^{-4}$ g/(m^2·day) whereas from murataite - ~10^{-6} g/(m^2·day). One of the most promising methods for Pu waste forms production is the IMCC. The experimental unit is under design now under cooperation of Radon and Vernadsky Institute of Geochemistry and Analytical Chemistry.

REFERENCES

[1] - A. JOSTSONS, L. VANCE, and B. EBBINGHAUS, "Immobilization of Surplus Plutonium in Titanate Ceramics", GLOBAL '99. Proc. Int. Conf. Jackson Hole, WY (1999) CD Rom.

[2] – W. BRUMMOND and G. ARMANTROUT, "Ceramic Process Equipment for the Immobilization of Plutonium", Waste Management '98. Proc. Int. Symp. Tucson, AZ, Rep. 65-05 (1998) CD Rom.

[3] – I. SOBOLEV, S. DMITRIEV, F. LIFANOV, S. STEFANOVSKY and M. OJOVAN, " Application of the Cold Crucible Technology for Raduiactive Waste Vitrification", XVIII International Congress on Glass. San Francisco, CA (1998) CD Rom.

[4] – I.A. SOBOLEV, S.V. STEFANOVSKY, O.A. KNYAZEV, T.N. LASHTCHENOVA, V.I. VLASOV and D.B. LOPUKH, "Application of the Cold Crucible Melting for Production of Rock-Type Wasteforms", Proc. Sixth Int. Conf. Radioactive Waste Management and Environmental Remediation ICEM '97, ASME, 265 (1997).

[5] – A. JOUAN, R. DO QUANG and S. MERLIN, "Industrial Waste Vitrification Using the Cold Crucible Melter", Waste Management '98. Proc. Int. Symp. Tucson, AZ, Rep 57-03 (1998) CD Rom.

[6] – T. ADVOCAT, G. LETURCQ, J. LACOMBE, G. BERGER, R.A. DAY, K. HART, E. VERNAZ and A. BONNETIER, "Alteration of Cold Crucible Melter Titanate-Based Ceramics: Comparison with Hot-Pressed Titanate-Based Ceramic", Mat. Res. Soc. Symp. Proc., 465, 355 (1997).

[7] – N.P. LAVEROV, I.A. SOBOLEV, S.A. DMITRIEV, S.V. STEFANOVSKY, B.I. OMELIANENKO and S.V. IOUDINTSEV, "Collaborative Studies of High Level Waste Forms at SIA "Radon" and IGEM RAS", High-Level Radioactive Waste Management. Proc Eighth Int. Conf. ANS, 613 (1998).

[8] – I.A. SOBOLEV, S.V. STEFANOVSKY, B.F. MYASOEDOV, Y.M. KULIAKO and S.V. YUDINTSEV, "Phase Composition of Murataite Ceramics for Excess Weapons Plutonium Immobilization", Plutonium Futures – The Science. Conference Transactions. AIP Conf. Proc. 532, 122 (2000).

[9] – Nuclear Waste Materials Handbook (Test Methods). DOE Technical Information Center. Washington, DC, Report DOE/TIC-11400 (1981).

[10] – S.V. STEFANOVSKY, S.V. YUDINTSEV, B.S. NIKONOV, B.I. OMELIANENKO and A.G. PTASHKIN, "Murataite-Based Ceramics for Actinide Waste Immobilization", Mat. Res. Soc. Symp. Proc., 556, 121 (1999).

[11] - S.V. STEFANOVSKY, S.V. YUDINTSEV, B.S. NIKONOV, B.I. OMELIANENKO, A.I. GORSHKOV, A.V. SIVTSOV, M.I. LAPINA and R.C. EWING, "Pyrochlore-Type Phases for Actinides and Rare Earth Elements Immobilization", Mat. Res. Soc. Symp. Proc., 556, 27 (1999).

[12] – K.P. HART, Y. ZHANG, E. LOI, Z. ALY, M.W.A. STEWART, A. BROWNSCOMBE, B.B. EBBINGHAUS and W. BOURCIER, "Aqueous Durability of Titanate Ceramics Designed to Immobilise Excess Plutonium", Mat. Res. Soc. Symp. Proc., 608, 353 (2000).

[13] - S.V. STEFANOVSKY, O.A. KNYAZEV, D.B. LOPUKH and S.V. IOUDINTSEV, "The Cold Crucible Melting of Synroc", IT3 Int. Conf. On Incineration & Thermal Treatment Technologies. Proceedings. Salt Lake City, 155 (1998).

[14] – A.V. OCHKIN, S.V. CHIZHEVSKAYA, S.V. STEFANOVSKY, A.G. PTASHKIN and N.E. CHERNIAVSKAYA, "Leaching of Radionuclides from Cold Pressed and Sintered Perovskite and Zirconolite Ceramics", Proc. Int. Conf. On Decommissioning and Decontamination and on Nuclear and Hazardous Waste Management, Denver, ANS, 2, 796 (1998).

[15] – S.V. STEFANOVSKY, O.I. KIRJANOVA, S.V. YUDINTSEV and O.A. KNYAZEV, "Cold Crucible Melting of Murataite-Containing Ceramics", Waste Management '01. Proc. Int. Symp. Tucson, AZ (2001) CD Rom.