Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Feature article

Phase partitioning and uranium speciation in brannerite-based ceramics

S.V. Stefanovsky[a,*], S.V. Yudintsev[b], A.A. Shiryaev[a], V.Y. Murzin[c], A.L. Trigub[b,d]

[a] Frumkin Institute of Physical Chemistry, Electrochemistry of the Russian Academy of Sciences (IPCE RAS), Leninskii Av. 31, Bd. 4, Moscow 119071, Russia
[b] Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences (IGEM), Staromonetniy 35, Moscow 119017, Russia
[c] Deutsches Elektronen-Synchrotron (DESY), Notkestrasse 85, Hamburg 22607, Germany
[d] National Research Centre 'Kurchatov Institute', 1 Akademika Kurchatova pl., Moscow 123182, Russia

ARTICLE INFO

Article history:
Received 20 April 2016
Received in revised form 20 August 2016
Accepted 22 August 2016
Available online xxx

Keywords:
Brannerite
Ceramics
Cerium
Cold crucible
Uranium

ABSTRACT

Branneritecontaining ceramics were produced by cold pressing and sintering (CPS) and cold crucible inductive melting (CCIM) methods and examined by X-ray diffraction and absorption and by scanning electron microscopy. Brannerite content in the ceramics ranged between ~20 and 90 vol.%. Uranium is mainly partitioned between brannerite and minor mixed U/RE oxide but since brannerite is a dominant phase, it takes up to 90% of total U. Uranium in the ceramics is present as U(IV) and U(V). In the low-brannerite ceramics U occurs as U(IV) whereas in the ceramics with brannerite as major phase U(V) dominates over U(IV). Ce in the brannerite ceramics is mainly trivalent. The first coordination shell of U in ceramics produced by CPS is split into two sub-shells with U-O distances of 1.7–1.9 Å and ~2.1 Å while in the melted ceramics this interatomic distance is 2.1–2.2 Å. The next three atoms (Ti) are positioned at a distances of 3.1–3.2 Å.

1. Introduction

Actinides are the longest-lived and the most hazardous components of nuclear wastes. They require immobilization in chemically durable waste forms for long-term storage. A number of host phases were proposed for this goal such as titanates, zirconates, mixed titanozirconates with fluorite-derived structure (cubic zirconia, pyrochlore, murataite, zirconolite), phosphates and silicophosphates with monazite, apatite and kosnarite structures. They all possess high isomorphic capacity with respect to actinides and their rare earth (RE) analogs and good isolation characteristics (see, for example, [1–3]). Another titanate phase encountered in nuclear waste ceramics is a brannerite structure phase which was also suggested as a potential actinide form [4,5].

Brannerite with nominal formula ABB_2O_6–(U,Th,Ca,RE)(Ti,Fe)$_2O_6$ has a monoclinic lattice symmetry (space group C2/m, Z = 2). This is a typical accessory mineral of alkaline granites, pegmatites and metasomatic rocks. In deep geologic formations brannerite is resistant to underground water attack [6]. The brannerite structure allows broad range of substitutions in both *A* and *B* sites, oxidation state of incorporated uranium varies from U(IV) to U(VI) and on average is 4.4–4.7 [7].

Synthetic brannerite was found in some Synroc varieties proposed for immobilization of high-U wastes [5,8–12] and Actinide/RE fraction of high level waste (HLW) [13]. Both natural and synthetic brannerites as well as the brannerite-based ceramics are chemically quite durable [2,6,14–21] although their resistance against self-irradiation from ^{238}Pu dopant is somewhat lower than that of pyrochlore and zirconolite [22,23]. Nevertheless, isolating properties of brannerite are sufficient to consider it as a candidate actinide host phase.

In the present work, we perform a comparative study of phase composition and elemental partitioning in brannerite-based ceramics produced by the cold pressing and sintering (CPS) method (TCN1-1450, TCN2-1450, TCN1-1500, TCN2-1500) and brannerite-containing polyphase ceramic (LC2-CCIM, TCN2-CCIM) produced by cold crucible inductive melting (CCIM) [24] with a special goal to determine uranium speciation in these ceramics.

2. Experimental

The target chemical compositions of the ceramics and actual compositions of constituent phases as measured by energy-dispersive X-ray spectrometry (EDX) are given in Table 1. The TCN-1

* Corresponding author.
E-mail address: serge.stefanovsky@mail.ru (S.V. Stefanovsky).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.08.028
0955-2219/

Table 1
Chemical composition of starting powder mixtures (TCN1, TCN2 and LC2) and their constituent phases (B, T, O, S, R) after sintering, as measured by EDX, along with the calculated stoichiometry of the phases.

Oxide	TCN1	TCN1-1450		TCN1-1500				TCN2	TCN2-1450			TCN2-1500				TCN2-CCIM			LC2	LC2-CCIM			
	target	B	T	B	O	S1	S2	target	B	O	R	B	O	S	T	B	S	A	target	B	T	O	S
Al_2O_3		–	–	–	–	–	–	–	–	–	–	–	–	–	–	1.6	15.0	52.6	–	–	–	–	–
SiO_2		–	–	–	–	10.5	17.4	–	–	–	–	–	–	14.6	–	–	26.8	–	–	–	–	–	23.6
CaO		–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	1.4	–	0.8	–	0.7	0.6	5.3
TiO_2	45.0	43.7	52.1	42.4	0.0	29.4	27.4	42.0	41.8	–	99.5	41.5	–	12.0	51.6	36.0	13.4	47.4	51.9	44.5	52.8	0.9	15.7
La_2O_3		–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	5.9	2.1	5.9	3.1	10.1
Ce_2O_3	15.0	14.1	21.0	12.6	27.8	26.6	25.4	10.0	9.8	17.5	–	9.0	38.2	10.9	40.3	5.2	18.9	–	10.7	10.9	12.2	18.7	9.3
Pr_2O_3		–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	5.2	1.9	4.8	2.9	12.2
Nd_2O_3	15.0	11.1	25.9	10.7	17.3	31.5	29.8	10.0	8.7	15.7	0.5	7.7	13.7	52.1	6.3	6.2	19.3	–	17.0	17.2	17.2	11.4	4.6
Sm_2O_3	–	–	–	–	–	–	–	2.0	1.5	3.3	–	1.9	2.8	5.9	–	1.4	3.6	–	3.3	2.1	3.4	2.9	13.6
Eu_2O_3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.5	0.7	0.8	1.0	2.6
Gd_3O_3	–	–	–	–	–	–	–	2.0	2.0	4.5	–	2.4	3.4	4.5	1.8	2.0	1.6	–	0.8	1.0	0.9	1.5	0.4
UO_2	25.0	31.1	1.0	34.3	54.9	2.0	–	34.0	36.2	58.0	–	37.5	41.9	–	–	47.5	–	–	3.9	28.4	1.3	57.0	2.6
Ions	Formula units (fu)																						
Al^{3+}		–	–	–	–	–	–		–	–	–	–	–	–	–	0.12	3.11	1.89		–	–	–	–
Si^{4+}		–	–	–	–	2.37	3.61		–	–	–	–	–	3.72	–	–	4.72	–		–	–	–	4.89
Ca^{2+}		–	–	–	–	–	–		–	–	–	–	–	–	–	–	0.26	–		–	0.17	0.02	1.18
Ti^{4+}		2.01	9.00	2.00	–	4.98	4.28		1.99	–	1.00	1.99	–	2.30	8.95	1.71	1.76	1.08		2.00	9.00	0.02	2.46
La^{3+}																				0.05	0.50	0.04	0.77
Ce^{3+}		0.32	1.77	0.28	0.36	2.20	1.93		0.23	0.23	–	0.21	0.46	1.02	3.40	0.12	1.22	–		0.24	1.02	0.24	0.71
Pr^{3+}		–	–	–	–	–	–		–	–	–	–	–	–	–	–	–	–		0.04	0.40	0.04	0.92
Nd^{3+}		0.24	2.13	0.24	0.22	2.54	2.21		0.20	0.21	–	0.17	0.16	4.74	0.52	0.14	1.21	–		0.18	1.39	0.14	0.34
Sm^{3+}		–	–	–	–	–	–		0.03	0.04	–	0.04	0.03	0.52	–	0.03	0.21	–		0.04	0.26	0.03	0.97
Eu^{3+}		–	–	–	–	–	–		–	–	–	–	–	–	–	–	–	–		0.03	0.07	0.01	0.19
Gd^{3+}		–	–	–	–	–	–		0.04	0.05	–	0.05	0.04	0.38	0.14	0.04	0.09	–		0.03	0.06	0.02	0.19
U^{4+}		0.42	0.05	0.48	0.43	0.10	–		0.51	0.46	–	0.54	0.31	–	–	0.63	–	–		0.40	0.06	0.44	0.03
Σcations		3.00	12.97	3.00	1.00	12.18	12.04		3.00	1.00	1.00	3.00	1.00	12.66	13.02	2.80	12.59	2.97		3.01	13.02	1.00	12.57
O^{2-}		5.72	24.00	5.74	1.72	22.00	22.00		5.75	1.73	2.00	5.76	1.66	22.00	24.00	6.00	22.00	5.00		6.00	24.00	1.72	22.00

Please cite this article in press as: S.V. Stefanovsky, et al., Phase partitioning and uranium speciation in brannerite-based ceramics, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.08.028