



Murataite-Pyrochlore Ceramics as Complex Matrices for Radioactive Waste Immobilization: Structural and Microstructural Mechanisms of Crystallization

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Abstract. Murataite-pyrochlore titanate ceramics are attractive waste forms capable to immobilize radioactive waste streams of complex compositions, thus eliminating the need for further chemical separation. We have investigated structures of three types of murataite: 3C, -5C, and -8C phases and demonstrate their polysomatic nature and structural complexity. Structurally simple pyrochlore crystallizes first, followed by crystallization of murataite-5C containing pyrochlore cells surrounded by fragments of Keggin clusters. This phase is overgrown by murataite-8C containing both murataite and pyrochlore cells. The crystallization finishes with the formation of murataite-3C, which is the most stable and less actinide-rich. The microstructure formed via this mechanism reminds a Russian doll, which creates additional barrier for the actinide leaching from the pyrochlore core. The high chemical and structural complexity of the pyrochlore-murataite series is unparalleled in the world of crystalline materials proposed for the HLRW immobilization, which makes it unique and promising for further exploration.

Keywords: Murataite · Pyrochlore · Crystal structure · Crystallization · Microstructure · Radioactive waste · Actinides

1 Introduction

One of the most important tasks for the advanced nuclear cycle is the elaboration of waste forms capable to immobilize waste streams of complex compositions, thus eliminating the need for further chemical separation. In this regard, the murataite-pyrochlore titanate

ceramics attract considerable attention due to their ability to immobilize radioactive wastes with different and complex chemical compositions, including actinides such as Pu-238. Over last few years, there has been a renewed interest in their synthesis and investigations (Maki et al. 2017; Lizin et al. 2018, etc.).

Murataite-(Y) is a complex titanate mineral first discovered in alkali pegmatites in St. Peters Dome area in Colorado, United States and later found in pegmatites in the Baikal region in Russia. Its crystal structure (cubic, space group $F\bar{4}3m$, $a = 14.886 \text{ \AA}$) was determined by Ercit and Hawthorne (1995) as based upon a framework of corner-linked α -Keggin clusters hosting a complex metal-oxide substructure. The simplified formula of natural murataite-(Y) can be written as $^{[8]}R_6^{[6]}MI_{12}^{[5]}M2_4^{[4]}TX_{43}$, where $R = Y$, HREE, Na, Ca, Mn, $MI = Ti, Nb, Na$, $M2 = Zn, Fe, Ti, Na$, $T = Zn, Si$ and $X = O, F, OH$. The interest in murataite-(Y) was renewed in 1982, when its synthetic analogue was identified in Synroc-type titanate ceramics with imitators of high-level radioactive waste at the Savannah River nuclear power plant (Morgan and Ryerson 1982). Laverov et al. (1998) reported the formation of murataite-type titanate phase in the uranium-bearing Synroc matrix from the Mayak factory, a radiochemical facility for the reprocessing of nuclear fuel located in Southern Ural, Russian Federation. It was found that five volume percent of synthetic murataite accumulate about 40% of the total amount of uranium present in the sample, which led to follow-up detailed studies of chemistry and properties of this material. Transmission electron studies allowed identification of synthetic varieties of murataite with $3 \times 3 \times 3$, $5 \times 5 \times 5$, $7 \times 7 \times 7$ and $8 \times 8 \times 8$ fluorite-like cubic supercells, referred in the following as murataite-3C, -5C, -7C and -8C phases (Laverov et al. 2011).

2 Methods and Approaches

We have studied crystal structures of murataite-3C, -5C and -8C using single-crystal X-ray diffraction analysis on the samples obtained by melting the mixture of oxides in an electric furnace at 1500 °C with subsequent cooling to the room temperature as described by Laverov et al. (1998). The details of the experimental procedures used to obtain structure models have been described in detail in (Krivovichev et al. 2010; Pakhomova et al. 2013, 2016).

3 Results and Discussion

Urusov et al. (2005) proposed that synthetic murataites can be considered as members of murataite-pyrochlore polysomatic series consisting of different combinations of 2D modules. The structural determination of murataite-5C reported by Krivovichev et al. (2010) confirmed the assumption about the modular nature of the polysomatic series and demonstrated that the murataite- and pyrochlore-type modules are not layers but zero-dimensional blocks (nanoscale clusters), combination of which in a 3-dimensional space generates at least two different derivative structures, which combine structural features of both murataite and pyrochlore. In particular, the crystal structure of murataite-5C can be described as an ordered arrangement of pyrochlore unit cells

immersed into the recombined murataite matrix, i.e. a substructure consisting of murataite structure elements.

The crystal structure of murataite-3C was reported by Pakhomova *et al.* (2013), who demonstrated its general identity to natural murataite, with some important chemical and structural modifications. The modular nature of the murataite-pyrochlore polysomatic series was discussed by Laverov *et al.* (2011).

The crystal structure of murataite-8C was reported by Pakhomova *et al.* (2016) as based upon a three-dimensional octahedral framework that can be described as an alternation of murataite and pyrochlore modules immersed into transitional substructure that combine elements of the crystal structures of murataite-3C and pyrochlore. The obtained structural model confirmed the polysomatic nature of the pyrochlore-murataite series and illuminated the chemical and structural peculiarities of crystallization of the murataite-type titanate ceramic matrices.

Table 1. Information-based structural complexity parameters for the synthetic members of the pyrochlore-murataite polysomatic series

Material	v [atoms]	I_G [bits/at.]	$I_{G,\text{total}}$ [bits/cell]
Pyrochlore	22	1.686	37.088
Murataite-5C	336	4.892	1643.840
Murataite-8C	1387	6.558	9096.031
Murataite-3C	71	3.226	229.044

4 Conclusions

The information-based complexity parameters for the members of the pyrochlore-murataite are listed in Table 1. Both kinds of information-based complexity parameters (per atom and per cell) behave in a similar fashion: they are relatively small for the initial pyrochlore phase, then increase for murataite-5C, reach their maxima for murataite-8C and decrease for the final murataite-3C phase. This trend is also followed in the crystallization of murataite-pyrochlore ceramics: structurally simple and actinide-rich pyrochlore crystallizes first, creating conditions for the saturation of melt with Keggin clusters, which triggers crystallization of murataite-5C containing pyrochlore unit cells surrounded by fragments of Keggin clusters. This pyrochlore-rich phase is overgrown by murataite-8C containing both murataite and pyrochlore unit cells. The crystallization finishes with the formation of pure Keggin phase murataite-3C, which is the most stable and less actinide-rich. The microstructure formed during such a crystallization reminds a Russian doll ('matryoshka'), which creates additional barrier for the actinide leaching from the pyrochlore (or crichtonite) core. The high chemical and structural complexity of the members of the pyrochlore-murataite series is unparalleled in the world of crystalline materials proposed for the high-level radioactive waste immobilization, which makes it unique and promising for further technological and scientific exploration.

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References

- Ercit TS, Hawthorne FC (1995) Murataite, a UB_{12} derivative structure with condensed Keggin molecules. *Can Mineral* 33:1223–1229
- Krivovichev SV, Yudintsev SV, Stefanovsky SV, Organova NI, Karimova OV, Urusov VS (2010) Murataite-pyrochlore series: a family of complex oxides with nanoscale pyrochlore clusters. *Angew Chem Int Ed* 49:9982–9984
- Laverov NP, Sobolev IA, Stefanovskii SV, Yudintsev SV, Omel'yanenko BI, Nikonov BS (1998) Synthetic murataite: a new mineral for actinide immobilization. *Dokl Earth Sci* 363:1104–1106
- Laverov NP, Urusov VS, Krivovichev SV, Pakhomova AS, Stefanovsky SV, Yudintsev SV (2011) Modular nature of the polysomatic pyrochlore-murataite series. *Geol Ore Dep* 53:273–294
- Lizin AA, Tomilin SV, Poglyad SS, Pryzhevskaya EA, Yudintsev SV, Stefanovsky SV (2018) Murataite: a matrix for immobilizing waste generated in radiochemical reprocessing of spent nuclear fuel. *J Radioanal Nucl Chem* 318:2363–2372
- Maki RSS, Morgan PED, Suzuki Y (2017) Synthesis and characterization of a simpler Mn-free, Fe-rich M3-type murataite. *J Alloys Compd* 698:99–102
- Morgan PED, Ryerson FJ (1982) A “cubic” crystal compound. *J Mater Sci Lett* 1:351–352
- Pakhomova AS, Krivovichev SV, Yudintsev SV, Stefanovsky SV (2013) Synthetic murataite-3C, a complex form for long-term immobilization of nuclear waste: Crystal structure and its comparison with natural analogues. *Z Kristallogr* 228:151–156
- Pakhomova AS, Krivovichev SV, Yudintsev SV, Stefanovsky SV (2016) Polysomatism and structural complexity: Structure model for Murataite-8C, a complex crystalline matrix for the immobilization of high-level radioactive waste. *Eur J Mineral* 28:205–214
- Urusov VS, Organova NI, Karimova OV, Yudintsev SV, Stefanovskii SV (2005) Synthetic “murataites” as modular members of a pyrochlore-murataite polysomatic series. *Dokl Earth Sci* 401:319–325

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