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Polysomatism and structural complexity: structure model for murataite-8*C*, a complex crystalline matrix for the immobilization of high-level radioactive waste

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Abstract: Murataite-8*C*, a prospective synthetic material for the long-term immobilization of high-level radioactive waste and a member of the pyrochlore–murataite polysomatic series, was investigated by means of single-crystal X-ray diffraction. The crystal structure (cubic, F-43m, $a = 39.105(12)$ Å, $V = 59799(32)$ Å^3, $Z = 4$) is of outstanding complexity and contains forty symmetrically independent cation sites. Its crystal-chemical formula determined on the basis of the crystal-structure refinement, $Al_{25.44}Ca_{55.96}Ti_{282.20}Mn_{53.72}Fe_{17.24}Zr_{15.00}Ho_{36.64}O_{823}$, is in good agreement with the empirical formula calculated from electron-microprobe data, $Al_{23.02}Ca_{52.85}Ti_{284.10}Mn_{54.31}Fe_{17.59}Zr_{14.83}Ho_{38.04}O_{823}$. The crystal structure is based upon a three-dimensional octahedral framework that can be described as an alternation of murataite and pyrochlore modules immersed into a transitional substructure that combine elements of the crystal structures of murataite-3*C* and pyrochlore. The obtained structural model confirms the polysomatic nature of the pyrochlore–murataite series and illuminates the chemical and structural peculiarities of crystallization of the murataite-type titanate ceramic matrices. 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.

Key-words: murataite; pyrochlore; crystal structure; polysomatic series; radioactive waste immobilization; structural complexity.

Introduction

Murataite-(Y) is a complex titanate mineral first discovered in alkali pegmatites in St. Peters Dome area in Colorado, United States (Adams *et al.*, 1974) and later found in pegmatites in the Baikal region in Russia (Portnov *et al.*, 1981). Its crystal structure (cubic, space group F-43m, a = 14.886 Å) was determined by Ercit & 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 $^{[8]}R_6{}^{[6]}M1_{12}{}^{[5]}M2_4{}^{[4]}TX_{43}$, where R = Y, HREE, Na, Ca, Mn, $M1$ = Ti, Nb, Na, $M2$ = Zn, Fe, Ti, Na, T = Zn, Si and X = O, F, OH. The presence of α-Keggin clusters in the crystal structure of murataite-(Y) relates the mineral to the recently described natural polyoxometallates such as ophirite (Kampf *et al.*, 2014a), peterandresenite (Friis *et al.*, 2014) and kokinosite (Kampf *et al.*, 2014b).

The interest in murataite-(Y) was renewed in 1982, when its synthetic analogue was identified in Synroc-type (Ringwood *et al.*, 1988) titanate ceramics with imitators of high-level radioactive waste at the Savannah River nuclear power plant (Morgan & Ryerson, 1982). Laverov *et al.* (1998a) reported the formation of a 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 × 3 × 3, 5 × 5 × 5, 7 × 7 × 7 and 8 × 8 × 8 fluorite-like cubic supercells, referred in the following as murataite-3*C*, -5*C*, -7*C* and -8*C* phases (Laverov *et al.*, 1998b). It is necessary to note that only murataite-3*C* has a natural analogue while murataite-5*C*, -7*C* and -8*C* are unofficial designations used to

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