On possibility of the murataite fusion temperature lowering for radioactive waste immobilisation

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Abstract. The problem of radioactive waste management is extremely important for the nuclear energy development. The global strategy for safe handling of all types of radioactive waste consists in reducing volumes by concentrating and entering into radionuclides inside stable solid matrices. The most dangerous components of high-level radioactive waste are supposed to be immobilized in mineral-like matrices with their further safe disposal in geological formations. The solution can be glass-ceramic matrix materials, in particular, obtained by direct melting: resistant as crystal matrices and a simple method of preparation - like glass. The most promising from the point of view of the process of obtaining and the range of included nuclides is murataite. Ceramics can be obtained by melting the initial composition of powders with HLW components at a temperature of 1350°C. The authors of this work previously showed the fundamental independence of the quality of the ceramics obtained from the exposure time in a liquid state. In this work, the possibility of obtaining fused murataite at a low synthesis temperature with the introduction of fluxing agents was experimentally shown. The decrease in temperature does not prevent the formation of murataite under the condition of the presence of a liquid phase. A significant influence of the quality of the preparation of powder and tablets on the resulting structure of ceramics has been established. Also demonstrated is the possibility of obtaining murataite without the addition of a fluxing agent with the introduction of fluorides MnF₂ and FeF₃ into the initial mixture of murataite instead of corresponding oxides.

1. Introduction

Nowadays, the radioactive waste management is a hot issue for the development of nuclear energy. The Federal Task Program “The New generation nuclear power technologies for the period 2010-2015 and for the future until 2020” is aimed at developing new efficient closed fuel cycles for fast reactors. The recycling of nuclear materials requires the creation of a new system for the efficient and safe radioactive waste management.

The global strategy for safe management of all RW types consists in reducing their volumes by concentrating and immobilizing radionuclides into stable solid matrices. The most dangerous components of HLW are supposed to be immobilized in mineral-like matrices and then safely
disposed in geological formations. The HLW safety must be ensured by multi-stage engineering barriers (matrix - container - buffer) and protective properties of the geological environment [1].

Currently, there are several reference approaches to the RAW immobilization: vitrification, embedding into either cement compounds or crystalline matrices. Despite their undeniable advantages, these methods have significant drawbacks. The cement compounds are used to embed only MLW and LLW that do not contain actinides.

From the viewpoint of long-term environmental safety, glass matrices cannot be used to immobilize wastes containing long-lived radionuclides that pose threat for tens and hundreds of thousands of years. It is impossible to guarantee the safety of glass with vitrified waste for a long period because of its insufficient chemical stability and tendency to spontaneous crystallization at elevated temperatures.

Crystal matrices based on artificial minerals, of which natural analogues have existed under changing natural conditions for long periods, have an undoubted advantage over glass, thus proving their long-term geological stability. However, most of these ceramic matrix materials have a complex multi-stage manufacturing technology, including preparation of charge, its pressing and sintering. All this affects negatively the economy of the process and the amount of secondary RW.

A response to this problem can be glass-ceramic matrices, in particular, produced by direct melting. These matrices are resistant like crystal ones and easy-to-produce like glass ones. Murataite is the most promising from the viewpoint of the production and the range of nuclides embedded.

Murataite is a rare natural mineral found in pegmatites in the Colorado state (USA) [2] and near Lake Baikal (Russia) [3]. Structural studies of Colorado murataite of chemical composition \((Y,Na)_{2}(Zn,Fe)_{2}Ti_{2}O_{29}(F,\text{O})_{10}F_{4}\) showed that its crystal-chemical structure can be presented as \(A_{1}B_{5}C_{i}TX_{40}\), where \(A=Y, Na\); \(B=Ti\); \(C=Fe\); \(T=Zn\); \(X=O, F\) \((a=14.89 \text{ Å}, Z = 4)\) [4, 5]. This structure has several cationic positions: distorted cube \(A\), octahedron \(B\), trigonal bipyramid \(C\), and regular tetrahedron \(T\). Octahedra are linked through common edges to form compact groups \(B_{3}X_{13}\), of which four groups are linked through vertices to form \([B_{2}T_{1}X_{6}]^{4}\) polyanion known as the Keggin unit. This polyanion has the form of Laves tetrahedron containing in its centre a small tetrahedron \(T\); trigonal bipyramid \(C\) is inside the tetrahedron hexagonal edges.

Crystallographic positions of various sizes allow incorporating a large variety of chemical elements into the structure [6].

Further studies of murataites revealed the existence of its crystalline modifications with three- (as in natural murataite), five-, eight-, and seldom occurring sevenfold repetition of the cell relative to fluorite cell type (denoted as \(M_{3}\), \(M_{5}\), \(M_{8}\), and \(M_{7}\), respectively). It has been established that the presence of manganese in the system (along with titanium, actinides and REE) is necessary to form synthetic murataite phases. The chemical composition of the matrix has been patented by the FSUE RADON [7]; its chemical and radiation resistance has been studied. The matrix composition is 55% \(\text{TiO}_{2}\), 10% \(\text{MnO}_{2}\), 10% \(\text{CaO}\), 5% \(\text{Al}_{2}\text{O}_{3}\), 5% \(\text{Fe}_{2}\text{O}_{3}\), 5% \(\text{ZrO}_{2}\), and 10% of HLW (by mass) of various chemical compositions.

Ceramics can be produced by alloying the initial powder with HLW components at 1350°C. The authors previously showed the fundamental independence of the ceramics quality from the exposure time in the liquid state; however, they also showed the fundamental importance of the formation of a liquid phase [8]. To evaluate the effect of temperature on the samples alloying, murataite was synthesized at 900°C, 1000°C, 1100°C, 1200°C, 1300°C, and 1350°C. The research results show that the samples alloying occurs at 1350°C, and sintering occurs at a temperature less than 1350°C. Figure 1 show samples produced at different temperatures.

XRD data indicate that alloyed ceramics is more preferable from the viewpoint of phase purity. To evaluate the effect of exposure time, a series of experiments was carried out at \(t = 1350^\circ\text{C}\) for 5, 15, 30, 60 and 120 minutes. The XRD results show that all samples are composed of murataite \(\text{Ca}_{2.5}\text{Mn}_{2}\text{Ca}_{0.5}\text{Ti}_{2.5}\text{Zr}_{0.5}\text{FeAlO}_{2.5}\), rutile \((\text{TiO}_{2})\), \(\text{Fe}_{2}\text{MnO}_{4}\), \(\text{CaO}\) and crichtonite \((\text{CaTi}_{2}\text{O}_{3})\). The authors [8] conclude that the duration of exposure time does not affect the samples alloying, and the synthesis
can be carried out at a temperature of 1350°C for 5 minutes that significantly reduces the furnace operation time and the probability of fission products removal.

![Samples produced at different temperatures](image)

**Figure 1.** Samples produced at different temperatures

However, this temperature is high enough, especially considering a gradient that inevitably has to be created in the furnace, and requires specific heater materials and furnace design.

At the same time, work [9] proposes an original technique of low-temperature pyrochlore synthesis using a fluxing agent. Given that pyrochlore and murataite are extreme states of a continuous polysomatic series [10], it should be assumed that a similar technique can be used to reduce the temperature of murataite production.

The purpose of this work is to experimentally verify the method of reducing the temperature of glass-ceramic murataite matrix production for HLW immobilization by adding fluxing agents. Fluorides (NaF, AlF₃, TiF₄, YF₃) and chlorides are traditionally used as fluxing agents. The fluxing agent starts melting, destroys porosity and binds non-melted ceramic particles with each other thus creating a eutectic system. During sintering, the ceramic material does not melt, but the fluxing agent melts and binds the particles together.

### 2. Experimental part

The following materials were used: zirconium oxide (IV) “Pur.” TU 6-09-2486-77, Novosibirsk plant of rare-earth metals; iron oxide (III) “P.A.” GOST 4173-77, Labtech; calcium oxide (II) " P.A." GOST 245-76, OOOPo "UfaHimProekt"; magnesium perchlorate " P.A." TU 6-09-3880-75, G.S. Vereshchagin Plant, Slavgorod; titanium oxide (IV) GOST 13463-67-7, Germany; manganese oxide "Pur." GOST 4470-79, "Vekton"; sodium fluoride "Pur." TU 6-09 3322-78 "NevaReaktiv"; iron fluoride "Pur." TU 6-09-01-357-76 "Vekton"; manganese fluoride "Pur." TU 6-09-01-367-76 "Vekton".

Before the experiment, the initial components with simulators of HLW oxide precipitates were dehydrated in a drying oven at a temperature of 150°C. The dehydrated reagents were stored in a desiccator filled with calcined anhydrous calcium chloride. Before the experiment, the calculated amounts of the required reagents were weighed on the Sartorius analytical balance with an accuracy of 0.001 g, and homogenized by grinding in a porcelain or agate mortar. The resulting mixture was put into either alumina crucible or beryllium oxide crucible and sintered in a furnace, in air, at temperature 1050°C. The desired operation mode was set using the thermo controller Thermomat™ menu:

- heating from room temperature to 1050°C at a rate of 500°C/h, and to 1200°C at a rate of 350°C/h;
- cooling from 1050°C to room temperature was in a natural way;
- exposure for the required period of time (1- 4 hours).
To prepare samples a manual hydraulic press PLG-20 was used. Before pressing, the mold was lubricated with a 3% solution of stearic acid in ethyl alcohol. Pressing was done with a force of 2 MPa.

The samples phase composition was identified by XRD using a photo method. Samples were prepared on glass rods. To do this, the test sample was ground in an agate mortar and applied onto a thin glass rod (diameter 10 μm) lubricated with epoxy resin. The glass rod was placed into the Debye-Scherrer camera holder to adjust the sample in the centre position. X-ray diffraction of the samples was performed on an X-ray film, with copper radiation with a Ni filter using an URS-2.0 X-ray source. At the end of the shooting, the film was developed. Reflexes were displayed on the film. According to the reflexes, the phase composition was identified using the JCPSD X-ray diffraction data files [11] and the RENTGEN software package using the PICAR automatic X-ray image processing system [12, 13] taking into account the main systematic errors for the absorption and film shrinkage. Some samples were X-rayed on a diffractometer DRON-3M. For this purpose, the sample under study was added with diamond powder as an internal standard.

3. Results and discussion
The method for reducing the murataite synthesis temperature was experimentally verified. Sodium fluoride was used as a fluxing agent (melting point 993°C). The synthesis temperature was 1050°C.

Table 1 presents the composition of charge with different contents of the NaF fluxing agent; the appearance of produced samples is presented in figure 2.

| Matrix composition, %wt. | TiO₂ | MnO₂ | CaO | Al₂O₃ | Fe₂O₃ | ZrO₂ | Fluxing agent, NaF, % |
|--------------------------|------|------|-----|-------|-------|------|-----------------------|
| Sample A                 | 56,17| 11,17| 11,17| 6,17  | 6,17  | 6,17 | 3                     |
| Sample B                 | 55,83| 10,83| 10,83| 5,83  | 5,83  | 5,83 | 5                     |
| Sample C                 | 55   | 10   | 10   | 5     | 5     | 5    | 10                    |
| Sample D                 | 53,4 | 8,4  | 8,4  | 3,4   | 3,4   | 3,4  | 20                    |

Sample A, figure 2 (a), is brown in colour with white and brown inclusions of a granular structure; this suggests that the process was not fully completed. The sample is easily destroyed when pressed with tweezers; a single structure did not form.

Sample B, figure 2 (b), has a granular structure; it destroys under a slight mechanical effect, no alloying occurred; in the lower part of the sample there are crystalline white-yellow drips; this indicates that the fluxing agent left the sample due to its insufficient density and this reduced the time of contact between particles and liquid phase and did not allow the process to go in full.

Sample C, figure 2 (c), was split to examine its structure. The split sample is shown in figure 3. The cleavage face is brown in colour and has particles with metallic luster.
According to the XRD results, $\text{Fe}_{0.88}\text{Ti}_{1.11}\text{Zr}_{0.94}\text{O}_5$ cubic oxide phase and cubic $\text{MnAl}_2\text{O}_4$ are likely to be present. The presence of tetragonal $\text{TiO}_2$ phase is definite.

Figure 3 (b) shows clearly that the sample has brown and black inclusions; the inclusions boundaries are not clear; there are also inclusions with metallic luster that indicates the beginning of molten phase; the structure of the material produced is porous.

Sample D presented in more detail in figure 4 (a) is dense, solid; it has metallic luster. Also, a gradient of black to brown is seen on the sample surface, possibly due to leakage of fluxing agent. Figure 4 (b) shows white inclusions that evidences about outflow of fluxing agent to the crucible bottom.

Also, figure 4 (c, d) shows that the sample has a uniform gray-black colour, visible porous structure typical for the liquid phase solidification; there are metallic luster particles.
According to the XRD results, there are phases of cubic $\text{Fe}_{0.88}\text{Ti}_{1.11}\text{Zr}_{0.94}\text{O}_5$; more likely there is cubic $\text{CaF}_2$, an impurity of NaF. The presence of monoclinic $\text{Na}_{0.23}\text{TiO}_2$ and orthorhombic $\text{NaMnO}_2$ isn’t clearly confirmed.

As it can be seen, the obtained samples are close to murataite, but they do not form it. To achieve the target result, experiments on the murataite synthesis were performed followed by annealing at a temperature of 1050°C.

To ensure the similarity of cationic composition, a search was made for fluxing agents containing cations that are part of the murataite basic charge: having compared the melting temperatures, we decided to replace a part of charge oxides with fluorides, which have a low melting point. The composition of the adjusted charge is presented in table 2.

**Table 2.** Composition of charge with fluxing agents

| Matrix components | TiO$_2$ | CaO | Al$_2$O$_3$ | ZrO$_2$ | MnF$_2$ | FeF$_3$ | NaF |
|-------------------|---------|-----|-------------|---------|---------|---------|-----|
| Composition, %wt. | 45      | 10  | 5           | 5       | 15      | 10      | 10  |

Since the melting points of MnF$_2$, FeF$_3$, and NaF are 930°C, 1027°C, 993°C, respectively, it was decided to conduct the experiment on producing alloyed murataite at a temperature of 1050°C in air with a 2-hour exposure in an alumina boat. The charge was prepared according to the above-said method.

Figure 5 shows the produced sample that has a porous structure and is easily destroyed by mechanical effect. A microscopic examination showed molten zones and metallic luster.

![Sample produced by manual agitation](image)

**Figure 5.** Sample produced by manual agitation

According to the XRD results, there are two dominant phases: $\text{CaF}_2$, cubic (fluorite) and TiO$_2$, tetragonal (rutile). There are also additional phases, approximately in equal volume ratios:

- murataite, cubic. The interplanar distance of the strongest reflection of this phase $d=2.842\text{Å}$ shows a crystalline modification of 5C that is the most valuable in terms of the actinides immobilisation;
- $\text{CaTi}_{19}\text{O}_{38}$ hex. (crichtonite type);
- possible traces of a $\text{Na}_2\text{Ti}_3\text{O}_7$-like phase.

The diffraction pattern of the produced sample is shown in figure 6.
Figure 6. Diffraction pattern of the produced sample
F - fluorite; R - rutile; M - murataite; C - crichtonite; CA - diamond; □ - Na₂Ti₃O₇

Since the fluxing agent NaF can potentially deteriorate the mechanical properties of the produced matrix composition and its resistance to leaching, we adjusted the charge composition and conducted an experiment on producing murataite without adding sodium fluoride (table 3).

| Matrix components | TiO₂ | CaO | Al₂O₃ | ZrO₂ | MnF₂ | FeF₃ |
|-------------------|------|-----|-------|------|------|------|
| Composition, %wt. | 57   | 9,9 | 5,49  | 5,49 | 16,35| 5,7  |

The experiment was carried out according to the above method, at a temperature of 1050°C, 2-hour exposure, in the alumina crucible.

Figure 7 shows the produced sample. The sample has a porous structure, is easily destroyed by mechanical action; the microscope observation shows zones of different colours. It can be concluded that partial alloying has occurred. Due to the potential unsuitability of a heterogeneous matrix to incorporate HLW, the produced sample was not subject to the XRD.

Figure 7. Sample with no addition of fluxing agent to the charge of adjusted composition
The performed experiments did not result in the fused material; therefore we decided to increase the temperature up to 1200°C. This working temperature still allows using available structural materials in the furnace design.

Composition presented in Table 2 was used to make pellets 9 mm in diameter; the experiment was performed at a temperature of 1200°C, in air, 1-hour exposure, in BeO crucible. The charge was prepared according to the above method.

Figure 8 shows that the colour of the produced sample changed from white to black. The sample has metallic luster and large voids; no inclusions.

![Figure 8](image.png)

(a) before sintering  (b) after sintering  (c) cleavage face through the microscope

**Figure 8.** Sample produced at 1200°C

The XRD showed the following: as the main phase: - TiO$_2$, tetrag. (rutile), -b., CaF$_2$, cub. (fluoride), - CaTi$_2$O$_3$, hexag., (crichtonite), - Fe$_2$Ti$_3$O$_9$, hexag.; as minor phases: - murataite, cub., - ZrMn$_{0.8}$Ca$_{1.2}$Ti$_3$Fe$_{2.5}$Al$_{1.5}$O$_{16}$, cub.; Al$_2$O$_3$, hexag. is likely to present; Fe$_2$MnO$_4$, cub., - CaTiO$_3$, hexag. may present

The diffraction pattern of produced sample is shown in figure 9.

![Figure 9](image.png)

**Figure 9.** Diffraction pattern of produced sample

x- murataite; c- CaTi$_2$O$_3$; • - CaTiO$_3$; - TiO$_2$; Δ - CaF$_2$; O - Fe$_2$MnO$_4$; - Fe$_2$Ti$_3$O$_9$; © - ZrMn$_{0.8}$Ca$_{1.2}$Ti$_3$Fe$_{2.5}$Al$_{1.5}$O$_{16}$; A- diamond
4. Conclusion
Experiments have shown the possibility of producing fusion murataite at a low synthesis temperature, because of fluxing agents being added. The decrease in temperature does not prevent the murataite formation, provided by liquid phase formation. The influence of the following factors on the structure of the produced material are shown:

- fluxing agent content;
- temperature and exposure time.

A significant influence of the quality of powder and pellets preparation on the resulting ceramics structure is shown. In future, the effect of homogenization method will be studied: manual agitation, mechanochemical activation, obtaining a homogeneous charge from suspensions, etc.

A temperature elevation up to 1200°C is shown to result in better samples melting. At the same time, the target murataite phase is also detected at a low temperature, both as minor and main one.

If the content of fluxing agent is less than 5% wt., murataite is formed in trace amounts and minor phases; the fluxing agent content being in the range of 5-10%, the target phase is surely formed; a further increase in the fluxing agent does not lead to significant changes but probably decreases resistance to leaching due to a large amount of soluble sodium fluoride. The possibility is shown of obtaining murataite without adding a fluxing agent and with the murataite charge added with fluorides of its intrinsic elements MnF$_2$ and FeF$_3$; however, the optimal level of substitution of oxides for fluorides in the charge needs to be additionally studied.

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