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Characterization of $Na_x(Ca/Sr)_{1\text{-}2x}Nd_xWO_4$ complex tungstates fine-grained ceramics obtained by Spark Plasma Sintering

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ABSTRACT

Mineral-like matrix $Na_x(Ca/Sr)_{1\text{-}2x}Nd_xWO_4$ (x = 0, 0.1 and 0.2) for radwaste is proposed. Powder samples of complex tungstates have been synthesized by coprecipitation from aqueous solutions of Na, Ca, Sr, Nd salts. Crystallographic characteristics of compounds have been calculated and a monotonous change observed in them along with some x value changes. Monophasic ceramics with high relative density (97–100%) from these powders have been obtained through Spark Plasma Sintering (SPS). SPS of tungstates has been shown to occur in multiple stages, with the sintering kinetics at the final stage of sealing controlled by diffusion both in the crystal lattice and along grain boundaries. Activation energies have been determined for sintering of tungstates at different x values. The reduced activation energy of sintering at the third heating stage (at high temperatures) could be ascribed to the grain growth.

1. Introduction

One of the key challenges in modern materials science is to develop new compounds and materials based thereon to immobilize radioactive waste (RAW), including radioactive waste produced by the pyroelectrochemical fuel regeneration technology in a new generation of fast nuclear reactors, as well as for other applications.

Mineral-like materials are considered promising for RAW immobilization [1–5]. They have high chemical, thermal, hydrolytic stability and are characterized by wide isomorphism in the cationic and/or anionic parts of the crystalline structure. It is therefore possible to produce solid solutions of different compositions and complexity, plan and manage variations in their properties: create "materials on a plan".

In trying to solve the issue of managing RAW generated by nuclear technologies, experts focus on frame compounds, including such natural minerals as monazite [6–9], kosnarite [10–18], langbeinite [7,14,19], whitlockite [20], etc. In this context, crystalline materials, including ceramics with scheelite structure, are understudied.

It is known that isostructural scheelite-like compounds and solid solutions may contain many elements the isotopes of which are present in radioactive wastes [21,22]. Among them are solid solutions of tungstates and molybdates of cerium [23], thorium, uranium and plutonium [24–26]. Moreover, tungstates and isostructural molybdates with scheelite structure can be formed during precipitation in NaCl-KCl alkali chloride melts and other lithium-free chloride melts and they have relatively high chemical resistance [27–32]. This is especially important when developing methods to immobilize RAW resulting from pyrochemical MOX fuel regeneration. Our recent experiments show however, that such compounds are also resistant to chloride melts, which contain lithium chloride (in LiCl-KCl melts [33] that can potentially advance pyroelectrochemical technologies of fuel recycling for a new generation of fast nuclear reactors). During precipitation of tungstates as double salts, alkaline earth elements are almost completely removed from LiCl-KCl melt.

At the same time when applying the phosphate precipitation technology, the authors of [34,35] have found that among such melts only $LnPO_4$ and Li_3PO_4 precipitate. Divalent cations were not detected in the solid phase. Another LiCl-KCl melt treatment technology based on zeolite ion exchange that is described in [35–37] showed extraction of strontium and lanthanides reaching up to 85 wt% and 96 wt%. Therefore, it is highly relevant to study tungstates with scheelite structure in order to ensure their further application to remove radionuclides of strontium, barium and other fission products from LiCl-KCl melt during regeneration.

Besides, it shall be noted that tungsten might be present in RAW because together with rhenium they form the basic part of alloys for fuel element cladding. The scheelite structure has a frame structure, tetragonal syngony, sp.gr. $I4_1/a$. Ca atoms are surrounded by eight O atoms forming a dodecahedron, while W atoms are surrounded by O atoms forming a tetrahedron. CaO_8 are linked to each other by edges,

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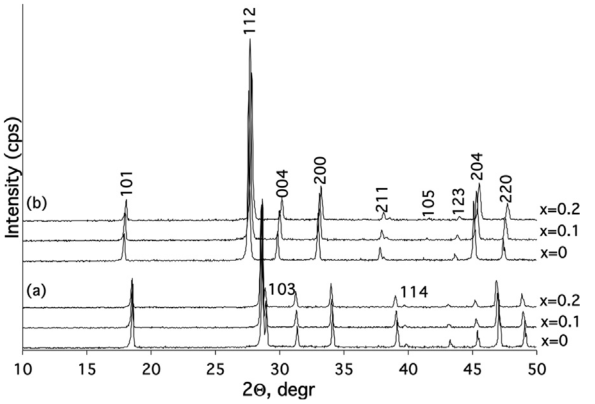

Fig. 1. XRD data. (a) $Na_xCa_{1-2x}Nd_xWO_4$ and (b) $Na_xSr_{1-2x}Nd_xWO_4$. T = 1000 °C.

and every polyhedron is conjugated to four neighboring CaO_8 [38]. Iso- and heterovalent isomorphism is typical of the tungstates with scheelite structure. In calcium tungstate Ca^{2+} cation can be fully or partly replaced with Sr^{2+}, Ba^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, Fe^{3+}, REE, Nb^{5+} and Ta^{5+}; whereas W^{6+} cation also can be fully or partly replaced with Ge^{4+}, V^{5+}, Mo^{6+}, I^{7+} and Re^{7+} [22,38].

Compounds with the scheelite structure have been studied as immobilization matrices for alkaline earth elements (AEE), including chloride melts used to recycle irradiated nuclear fuels [31,32]. Their representatives exhibit high stability in NaCl-KCl molten salts [33] and in aqueous systems [39]. Neodymium in compounds is acting as a fission product and as americium analog.

At the first stage, crystalline compounds with RAW components are usually produced as powders. Such waste immobilization form is not reliable enough, because the product obtained has a large surface area, including a phase boundary area in heterogeneous systems and therefore a widely developed reaction surface in heterogeneous processes involving solid phases. This affects the chemical and radiation stability of the products obtained and the possible release of radionuclides from the matrix.

It is therefore proposed to group powder samples in ceramics as the next step to solve this problem. This approach enables a safer method of RAW disposal.

Among various options to sinter ceramics from powders, Spark Plasma Sintering (SPS) has recently become more attractive as it is considered to hold promise for obtaining ceramic samples with high relative density (low porosity and therefore low surface area), including for potential nuclear technology applications [40,41]. The idea underlying this method is high-rate heating of powder materials in vacuum by passing direct current through the sintered material and the graphite mold with simultaneous application of pressure [42–44]. This method allows to change sintering parameters (heating rate, applied pressure, temperature and isothermal holding time) over a wide range and to adjust these parameters during the sintering process. This allows efficient control over density, porosity, microstructure parameters and phase composition of sintered materials. Papers [9,45,46] provide data on obtaining dense ceramics from complex salt, oxide and phosphate compounds.

Based on the above, the goal of this research was to study the compounds with scheelite structure (natural analog $CaWO_4$) in order to evaluate their applicability as a matrix for HLW immobilization, including pyroelectrochemical reprocessing of irradiated MOX fuel from fast nuclear reactors.

The first stage of this research was focused on obtaining powder compounds that contain neodymium and alkaline earth elements. The second stage of research involved SPS for sintering these compounds and characterizing the powders and ceramics.

2. Materials and methods

Targets of research: tungstates containing Na, Ca, Sr and Nd in such compositions as $Na_xCa_{(1-2x)}Nd_xWO_4$ and $Na_xSr_{(1-2x)}Nd_xWO_4$, where x = 0, 0.1 and 0.2.

Powder samples were synthesized by coprecipitation from aqueous solutions. Weighed portions of $Ca(NO_3)_2·4H_2O$ or $Sr(NO_3)_2·4H_2O$ nitrates and $Nd(NO_3)_3·6H_2O$ neodymium nitrate, were dissolved in distilled water if necessary, sodium tungstate solution was added as a precipitant and sodium source. Addition of the precipitant caused immediate precipitation. The suspension obtained was stirred for 30 min in a magnetic stirrer, and then filtered down through a paper filter. Filtration residue was washed with distilled water. Solid residue was dried at room temperature and then subjected to high-temperature treatment at T = 800, 900, 1000, 1100 and 1200 °C for 6 h at each stage. X-Ray diffraction (XRD) was used after each stage of isothermal holding to characterize phase appurtenance of powders.

Ceramic samples were obtained through SPS with Dr. Sinter Model-625 produced by SPS Syntex Inc. Ltd. (Japan). Samples were placed in a graphite mold and heated in a vacuum. The heating rate during sintering was V_h = 30–100 °C/min. After attaining the desired temperature, heating was switched off (holding time at sintering temperature t = 0 min), thus, the sample and the mold were allowed to gradually cool down. Sintering was performed in a vacuum (6 Pa) under uniaxial pressure of 75 MPa. The temperature was measured using a Chino IR-AH pyrometer focused on the surface of a graphite mold with outer diameter of 30 mm and inner diameter of 12 mm. The temperature accuracy was ± 10 °C, the shrinkage accuracy was 0.01 mm.

A dilatometer was used during sintering to register the value of effective shrinkage (L_{eff}). To calculate the dependence of effective shrinkage value on heating temperature, additional studies were performed into thermal expansion of the system with an empty mold. The effective shrinkage value (L) was calculated by subtracting thermal

Table 1
Crystallographic characteristics of $Na_x(Ca/Sr)_{1-2x}Nd_xWO_4$ compounds.

Compound	*a*, Å	±	*c*, Å	±	*V*, Å^3	α = β = γ°
$CaWO_4$	5.24072	0.00005	11.37374	0.00017	312.38143	90
$Na_{0.1}Ca_{0.8}Nd_{0.1}WO_4$	5.26087	0.00006	11.41582	0.00023	315.95283	90
$Na_{0.2}Ca_{0.6}Nd_{0.2}WO_4$	5.27036	0.00007	11.43941	0.00027	317.74899	90
$SrWO_4$	5.4293	0.00005	11,9781	0.00017	353.0820	90
$Na_{0.1}Sr_{0.8}Nd_{0.1}WO_4$	5.4104	0.00006	11,9076	0.00019	348.5644	90
$Na_{0.2}Sr_{0.6}Nd_{0.2}WO_4$	5.4000	0.00007	11,8447	0.00025	345.3915	90