Thermal Expansion of Scheelite-Like Molybdate Powders and Ceramics

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Abstract— $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ ($x = 0-0.5$, $\Delta x = 0.1$) solid solutions with the scheelite structure have been synthesized for the first time and their crystallographic parameters have been determined as functions of composition and temperature. Their thermal expansion coefficients have been determined in the temperature range 25–1000°C: $\alpha_a = (12.9-14.9) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $\alpha_c = (24.9-25.9) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. Using spark plasma sintering at $t_{\text{max}} \approx 872-985^\circ\text{C}$ and $\tau \approx 650-750$ s, we have prepared ceramics with relative densities in the range 97–99%.

Keywords: scheelite, strontium, neodymium, waste, spark plasma sintering

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INTRODUCTION

Improving radioactive waste (RAW) safety is a priority issue in the modern nuclear industry. Enhancing the performance of existing materials and designing novel materials with excellent service characteristics needed for high-level waste management should help to reduce the risk of radionuclides reaching the environment. In this context, it is promising to use crystalline mineral-like waste forms, implementing “nature-like” technologies.

Among such crystalline forms, structural analogs of scheelite (CaWO_4) group minerals, in particular, molybdates, warrant special attention.

Molybdenum has attracted research interest as a potential fuel rod cladding material capable of replacing zirconium [1], which is at present widely used for this purpose and suffers from the following drawbacks: (1) It can actively react with water to form hydrogen at temperatures above 700°C, which is extremely dangerous in the case of nuclear power plant accidents; (2) It reacts with overheated uranium dioxide in nuclear fuel, which leads to additional heat release and lowers the melting point of the fuel, thus contributing to the overheating and melting of the reactor core of the nuclear power plant [2, 3]. The use of Mo instead of Zr in the above-mentioned constructions will lead to the formation of a new type of Mo-containing waste.

Brinkman et al. [4] studied molybdates with the powellite structure, similar to the scheelite structure, for the immobilization of Mo-rich nuclear waste. Such crystalline waste forms can also include lanthanides and actinides [5].

In nature, scheelite crystallizes in tetragonal symmetry (sp. gr. $I4_1/a$). Its crystal structure is made up of CaO_8 and WO_4 polyhedra, which share oxygen vertices [6].

Characteristically, compounds with such structure exhibit broad isovalent and heterovalent isomorphism. According to Evdokimov et al. [7], the Ca cations can be partially or fully replaced by Sr, Cu, Mn, Fe, Ba, rare-earth (Nd, Pm, Sm, Eu), Cr, Nb, and Ta cations, and the W cations can be replaced by Mo, Ge, V, Ir, and Re. Extensive studies have been concerned with scheelite-structure compounds containing cations: K and La–Lu [8]; Ca, Sr, Ba, and REE [9]; alkaline-earth metals and Pm [10, 11]; Li, Na, and Np [12]; Na and U(IV) [13]; K, Rb, Cs, Nd, Pu, and Am [14]; Li, Na, and Pu [15]; Li, K, La, Nd, Dy, and Er [16]; Li, Rb, and REE [17]; Li, K, Rb, Tl, and Nd [18]; Li, Tl, and REE [19]; K, Cu, Ho, Gd, and Tb [20, 21]; and Li, Ba, Gd, and Tm [22]. All of the systems studied contain either individual compounds (Ca, Sr, Ba, and rare-earth tungstates and molybdates) or solid solutions with two types of cations: (1) alkali and alkaline-earth metals, (2) alkali metals and *f*-elements (rare

earths and uranium), and (3) alkaline-earth and rare-earth metals.

The behavior of substances with the scheelite structure on heating has been better studied for individual compounds. Thermal expansion coefficients in the range 25–1000°C were reported to be $\alpha_a = 13.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $\alpha_c = 22.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for CaWO_4 , $\alpha_a = 12.7 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_c = 21.4 \times 10^{-6} \text{ K}^{-1}$ for CaMoO_4 , $\alpha_a = 11.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for SrMoO_4 , and $\alpha_a = 9.38 \times 10^{-6} \text{ K}^{-1}$ for BaMoO_4 . The studied tungstates and molybdates are classified as materials with a large linear thermal expansion coefficients (LTECs).

It should be taken into account that powder samples are not reliable forms for radioactive waste disposal. In this work, we propose placing polycrystalline compounds into ceramic matrices. In such a case, the sintering method is an important issue. Pang et al. [25, 26] prepared ceramics with the compositions $\text{K}_{0.5}\text{La}_{0.5}\text{MoO}_4$ and $\text{Li}_{0.5}\text{Ln}_{0.5}\text{MoO}_4$ ($\text{Ln} = \text{Nd, Er, Gd, Y, Yb, Sm, Ce}$) by uniaxial cold pressing followed by firing in the range 560–720°C for 2 or 5 h, which ensured relative densities $\rho_{\text{rel}} = 93\text{--}95\%$.

Conditions for the fabrication of ceramics by spark plasma sintering (SPS), a method used in this study, can be varied widely. In particular, the sintering process can be run at high pressures and relatively low temperatures for a short time, which makes it possible to produce ceramics from materials with low decomposition temperatures and volatile compounds having high-temperature phase transitions [27, 28].

In designing materials for nuclear waste consolidation into crystalline matrices, an important issue is to have data on the formation of solid solutions with compositions more complex than those described above, their behavior on heating, and the feasibility of producing dense ceramics from such materials.

This work is a step in this direction. Our purpose was to prepare and characterize molybdate solid solutions with the scheelite structure in which alkali, alkaline-earth, and rare-earth metals (Na, Sr, and Nd) can be present together. In these materials, Sr and Nd imitate nuclear decay products. In addition, Nd imitates minor actinides.

In this paper, we report the synthesis of $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ ($x = 0\text{--}0.5$, $\Delta x = 0.1$) solid solutions, their composition stability limits, their behavior on heating, and the preparation and characterization of ceramics based on these solid solutions.

EXPERIMENTAL

Synthesis of powders. Powders were prepared via coprecipitation in aqueous systems. Stoichiometric amounts of the starting chemicals NaNO_3 , $\text{Sr}(\text{NO}_3)_2$, and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in water and then an $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ precipitant solution was added with constant stirring, leading to instantaneous precipitation. Stirring was continued for an additional 30 min. The resultant suspension was held at 90°C for 10 h. The dry residue was ground in an agate mortar for 20 min and then held at 500, 600, 700, 800, 900, and 1000°C for 15 h at each temperature. After each heat treatment step, we determined the phase composition of the materials and reground them in the agate mortar.

Preparation of ceramics. Ceramics were produced by SPS. The synthesized powders were placed in a graphite press die 10.8 mm in inner diameter and heated by high-power millisecond DC pulses (up to 3 kA). The temperature was monitored with a Chino IR-AH pyrometer focused on the surface of the graphite press die. The sintering process was run in vacuum (6 Pa) at an applied uniaxial pressure of ~ 70 MPa.

Methods and instruments. The elemental composition of the samples was determined by energy dispersive X-ray (EDX) spectroscopy on a JEOL JSM-6610LV scanning electron microscope (JEOL Ltd., Japan).

The phase composition of the powders and ceramics was determined by X-ray diffraction on a Shimadzu LabX XRD-6000 X-ray diffractometer in the angular range $2\theta = 10^\circ\text{--}50^\circ$ with filtered CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$).

High-temperature X-ray diffraction data were collected in the temperature range 25–1000°C and angular range $2\theta = 15^\circ\text{--}60^\circ$ on a Panalytical X'Pert Pro X-ray diffractometer equipped with an Anton Paar HTK-1200N high-temperature chamber.

Ceramics were produced by sintering the powders in a Dr. SINTER Model SPS-625 spark plasma sintering system (SPS Syntex Inc. Ltd., Japan).

The density of the ceramics was determined by hydrostatic weighing in distilled water on a Sartorius CPA 225D balance.

RESULTS AND DISCUSSION

Powder samples. The synthesized samples had the form of microcrystalline powders lilac in color (except the $x = 0$ powder, which was colorless).

The intended and experimentally determined x values (Table 1) differed insignificantly.

Table 1. Intended and experimentally determined elemental compositions of the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ samples

x	Na, x	Sr, $1 - 2x$	Nd, x
calculation	experiment		
0	0	1	0
0.1	0.11	0.78	0.11
0.2	0.20	0.60	0.20
0.3	0.29	0.42	0.29
0.4	0.41	0.18	0.41
0.5	0.5	0	0.5

X-ray diffraction characterization after heat treatment showed that single-phase $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ ($x = 0-0.5$) products were obtained at 800°C and that their composition persisted after heat treatment at 1000°C for 15 h. Figure 1 shows X-ray diffraction patterns of the $\text{Na}_{0.1}\text{Sr}_{0.8}\text{Nd}_{0.1}\text{MoO}_4$ sample after all heat treatment steps. Similar results were obtained for the other compositions. Figure 2 shows X-ray diffraction patterns of the samples after heat treatment at 800°C.

Fig. 1. X-ray diffraction patterns of the $\text{Na}_{0.1}\text{Sr}_{0.8}\text{Nd}_{0.1}\text{MoO}_4$ powder after heat treatment at (1) 500, (2) 600, (3) 700, (4) 800, (5) 900, and (6) 1000°C.

The powders had the scheelite structure, space group $I4_1/a$ (analogues in the ICDD database: SrMoO_4 , no. 08-0482; $\text{Na}_{0.5}\text{Nd}_{0.5}\text{MoO}_4$, no. 25-0852).

Figure 3 shows composition dependences of the a and c cell parameters for the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ samples. The unit-cell parameters vary linearly over the entire x range studied. With increasing x , both a and c decrease.

Thus, the system under study contains a solid solution series due to $2\text{Sr}^{2+} \rightleftharpoons \text{Na}^+ + \text{Nd}^{3+}$ heterovalent isomorphous substitutions.

The behavior of the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) samples on heating was studied by high-temperature X-ray diffraction in the temperature range from 25 to 1000°C. The temperature dependences of the calculated unit-cell parameters, $a(t)$ and $c(t)$, in Fig. 4 demonstrate that they increase monotonically with temperature.

The axial (α_a and α_c) and average (α_{av}) LTECs of the molybdates and thermal expansion anisotropy ($\Delta\alpha$) in them are presented in Table 2.

These data demonstrate that the molybdates under study have high LTEC values, approaching those reported for the SrMoO_4 molybdate [24].

Ceramic samples. Using the SPS of the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) powders, we

Fig. 2. X-ray diffraction patterns of the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ powders with $x = (1) 0, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.4,$ and $(6) 0.5$ after heat treatment at 800°C for 15 h.

Fig. 3. Composition dependences of the a and c cell parameters for the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ samples.

prepared ceramic samples. The corresponding sintering diagrams are presented in Fig. 5. The sintering conditions and the measured and relative densities of the ceramics are summarized in Table 3: $t_{\text{max}} \approx 872$ – 985°C , $\tau \approx 650$ – 750 s, $\rho_{\text{rel}} \approx 97$ – 99% .

Table 2. Thermal expansion coefficients and anisotropy of the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ molybdates

x	$\alpha \times 10^6, ^\circ\text{C}^{-1}$			
	α_a	α_c	α_{av}	$\Delta\alpha$
0	12.9	24.9	18.9	12.0
0.1	13.0	25.1	19.1	12.1
0.2	13.0	25.2	19.1	12.2
0.3	14.9	25.4	20.2	10.5
0.4	13.1	25.5	19.3	12.4
0.5	13.2	25.9	19.6	12.7

Fig. 4. Temperature dependences of the a and c cell parameters for the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ samples with $x =$ (1) 0, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.4, and (6) 0.5.

The X-ray diffraction patterns in Fig. 6 demonstrate that the ceramic samples are identical in phase composition to the starting powders.

Thus, we have extended knowledge of the family of Mo-containing phases with the scheelite structure and obtained new data on the behavior of molybdates with a complex cation composition on heating. SPS has been shown to be a promising process for sintering Mo-containing materials.

CONCLUSIONS

$\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ solid solutions exist over the entire composition range studied: $x = 0$ – 0.5 . Their unit-cell parameters vary monotonically with x . Evaluation of their thermal stability has shown that the synthesized powder samples retain their phase composition after heat treatment at 1000°C . Their thermal expansion coefficients have been determined in the temperature range 25 – 1000°C : $\alpha_a = (12.9$ – $14.9) \times 10^{-6} ^\circ\text{C}^{-1}$ and $\alpha_c = (24.9$ – $25.9) \times 10^{-6} ^\circ\text{C}^{-1}$. We have obtained ceramics with $\rho_{\text{rel}} \approx 97$ – 99% .

The present results demonstrate that molybdenum-containing scheelite-like crystalline materials can be used as matrices for the immobilization of RAW components.

Fig. 5. Shrinkage rate S and sintering temperature t as functions of heating/sintering time for the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ samples with $x =$ (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, and (f) 0.5: (1) sintering temperature, (2) shrinkage rate.

Table 3. Sintering conditions and characteristics of the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ ceramic samples

x	$P_{\max}$, MPa	$t_{\max}$, °C	$S_{\max} \times 10^3$, mm/s	τ_{sint} , s	ρ_{meas} , g/cm ³	ρ_{rel} , %
0	67.5	872	2.74	650	4.582 ± 0.008	97.08
0.1	67.3	985	6.99	750	4.675 ± 0.015	97.72
0.2	68.4	941	6.66	750	4.771 ± 0.009	99.29
0.3	69.1	942	7.28	750	4.783 ± 0.025	98.24
0.4	69	942	7.10	750	4.901 ± 0.009	98.93
0.5	68.5	942	7.16	750	4.987 ± 0.012	98.81

Fig. 6. X-ray diffraction patterns of the $\text{Na}_x\text{Sr}_{1-2x}\text{Nd}_x\text{MoO}_4$ powders (lower profiles) and ceramics (upper profiles) with $x = (1) 0, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.4$, and $(6) 0.5$.

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