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Synthesis and properties of some insoluble high-temperature neodymium ceramic compounds

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Abstract

Compounds in the double oxide systems of Nd_2O_3–BeO, Nd_2O_3–ZrO_2, Nd_2O_3–ThO_2, Nd_2O_3–Al_2O_3, Nd_2O_3–Cr_2O_3 Nd_2O_3–Nb_2O_5 have been synthesized by mixing the starting components nearly at the molecular level. Among the physical and chemical properties of these double oxides that have been determined are the melting points, the phase diagrams. The mechanism of syntheses of neodymium monoaluminate, chromite, and niobite have been elucidated. Based upon the results of this study, the technique of compound synthesis from molecular mixtures, followed by calcining at about 900°C, is recommended.

Keywords: Double oxides; Rare earth elements; Neodymium compounds

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1. Introduction

Separation of the highly radioactive components of nuclear wastes continues to be an important technology in the nuclear power industry. When the most toxic and long-lived radionuclides contained in the rare earth element (REE) fractions, actinide fractions, cesium fraction, and strontium fraction are separated and isolated, the residual short-lived radioisotopes do not present a significant hazard. Currently, the radioactive waste immobilization is carried out by immobilizing the toxic and long-lived radioisotopes in crystalline phosphates or borosilicate glasses. However, Synroc-type ceramic materials such as aluminates, titanates, zirconates, and chromates could serve as a safer materials for radioactive waste disposal. Efficient syntheses of these ceramic materials, and some of their physical and chemical properties, are the subject of this paper.

Using literature data [1–5], we have selected and analyzed a number of neodymium compounds which are promising from our standpoint as the REE representing ones. Their basic properties are given in Table 1.

According to the data given in Table 1, one can see that the niobates, chromites, and aluminates of Nd (as well as other REE) are the most promising for investigation. All of these compounds are similar in properties, namely, the melting point — 1900–2400°C; specific gravity — 6–7 g/cm^3; percentage of neodymium — 50–60 mass%. They are insoluble in water, making them potentially suitable for application as the matrix material for immobilizing radioactive REE, and for other purposes as well.

In this work we have developed techniques for synthesis of these compounds, and characterized melting behavior (phase diagrams) of the mixtures. Classical solid-state methods for synthesis of those compounds starting from oxide powder are very complicated and labor consuming, require high temperatures, and are next to impossible to implement in radioactive waste management technology. The need of improved synthesis technology is particularly important for immobilization of radioactive waste REE and for fabrication of the radiation sources. We selected for study solution phase techniques of synthesis that allow mixing of the starting components at the molecular level, avoiding the kinetic difficulties inherent in the solid state methods, and considerably reducing the temperature of synthesis. These goals were achieved by means of either drying mixed solutions of starting components or by co-precipitating hydroxides from the mixed solutions followed by drying and calcining.

Synthesis of neodymium chromites was performed by mixing nitrate solutions of neodymium and chromium(III) at the ratio of neodymium to chromium of 1/1 followed by drying and calcining at different temperatures. Completion of neodymium chromite synthesis substantially depends on the calcination temperature of the dried mix. For example, at 600°C the synthesis was about 50% complete, whereas

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Table 1
Some physicochemical properties of neodymium-based refractory compounds

Compound	Chemical formula	T_{melt}, °C	Specific gravity, g/cm^3	Content of neodymium, % by mass	Solubility in water
Neodymium oxide	Nd_2O_3	1900	7.24	85.75	hydrolyzed
Neodymium orthoniobate	$NdNbO_4$			47.9	not soluble
Neodymium niobate	$3Nd_2O_3{\cdot}Nb_2O_3$			67.86	not soluble
Neodymium monoaluminate	$NdAlO_3$	1947	6.99	65.81	not soluble
Neodymium chromite	$NdCrO_3$	2417	6.91	59.06	not soluble

at 700°C it occurred almost completely in about 20 min of calcination. The final completion of synthesis of 95–98% was attained at 850–880°C. Completion of synthesis was determined by means of chemical analysis and powder X-ray diffraction phase identification. However, for fabrication of compacted items (pellets, blocks), production of the incompletely synthesized compounds may be even beneficial on account of higher chemical activity of the powder and, hence, lower sintering temperature thereof. Complete synthesis could be achieved by further sintering. Synthesis was conducted in two ways: (1) drying and calcining of mixed solutions of neodymium and chromium nitrate; (2) co-precipitation of neodymium and chromium hydroxides, rinsing the precipitate, and finally drying and calcining of the precipitate.

For development of synthesis technology, the knowledge of the reaction mechanism and optimum conditions of synthesis for neodymium chromite are very important. The mechanism of the solid-state reaction was studied in two ways. First, the differential thermal analysis (DTA) of calcining neodymium and chromium hydroxides (rinsed so as to be free of ammonium nitrate) showed that all the processes occurring with either release or absorption of heat were completed at 760–780°C. It could be assumed that at that temperature the formation of crystalline neodymium chromite is completed. Second, the DTA data are supported by the results of chemical analysis of the materials obtained at 600–800°C and by the X-ray diffraction patterns as well.

Thermogravimetric analysis of the co-precipitated hydroxides did not show any evidence of peaks inherent to the individual hydroxides at least up to the temperature of 600°C. In the co-precipitation of hydroxides followed by drying and calcining the hydrated form of neodymium chromite was formed and no separate hydroxide was formed.

The second process of synthesis by drying and calcining the nitrate mixture proceeded differently. During drying and calcining of the mixed nitrate solution and decomposition of nitrates, chromium was oxidized to the hexavalent state at about 260°C. Upon further heating to 600–700°C chromium reverted to the trivalent state and neodymium chromite is formed. The process of neodymium chromite formation was completed at 850–880°C. This temperature is slightly higher than that for synthesis from hydroxides.

Neodymium chromite (as well as chromites of some other REE) is potentially suitable as a matrix material for incorporation of radioactive REE. Synthesis either by the joint calcining of co-precipitated hydroxides or by drying and calcining of the chromium (or chromium acid) and neodymium nitrate mix is recommended. A calcining temperature of 900°C is recommended.

The synthesis of neodymium aluminate, $NdAlO_3$, was also studied. The recommended technique for synthesis of neodymium aluminate is drying of mixed Al and Nd nitrate solutions followed by calcining the powder at 900°C.

From the literature two compounds in the Nd_2O_3–Nb_2O_5 system are known to exist, namely, the neodymium orthoniobate $NdNbO_4$ and a compound of composition $3Nd_2O_3{\cdot}Nb_2O_5$. Synthesis of neodymium niobates was studied by the solid state technique from oxide powders. In Fig. 1 the dependence of the completeness of synthesis for neodymium niobate on the synthesis temperature from oxide powders is shown. From Fig. 1 one can see that up to 1500°C the synthesis of Nd_3NbO_7 is complete, whereas the compound of the $NdNbO_4$ formula is completely synthesized at that temperature.

Classic solid-state techniques for synthesizing ceramic materials from oxides are not very suitable for radiochemical engineering. Therefore, we attempted to find a suitable way of combining neodymium and niobium in the solution. Combination of neodymium and niobium solu-

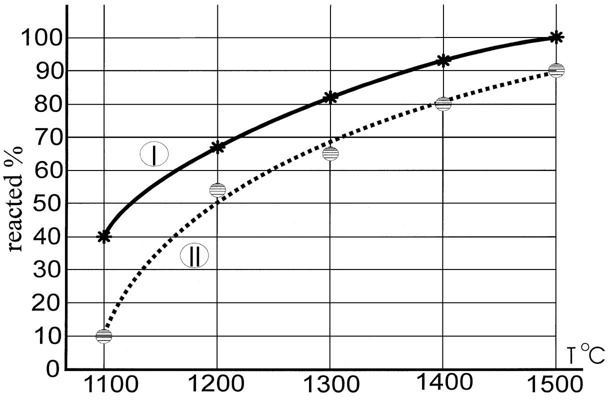


Fig. 1. Completion of synthesis for neodymium niobates from the oxide mixture versus synthesis temperature, $t=4$ h. Curve I: $Nd_2O_3/Nb_2O_5=1/1$; curve II: $Nd_2O_3/Nb_2O_5=3/1$.

tions is a complicated task, as the majority of niobium compounds is stable in alkaline media and is hydrolyzed in acidic media, and neodymium compounds behave conversely. Complex compounds of niobium with trioxyglutaric and malic acids appeared to resolve this difficulty. To prevent precipitating of neodymium hydroxide when introducing neodymium nitrate solution into the solution of niobium complex, the solution was acidified with nitric acid up to pH 2–3. The niobium complex was not decomposed under the conditions. An acidified solution of the niobium complex was well mixed with a solution of neodymium nitrate and remained stable for a long period of time. Synthesis was performed by two procedures: drying combined nitrate complexed solution followed by calcining, or co-precipitation of slightly soluble niobium and neodymium compounds followed by drying and calcining as well. The next step was drying and calcining of the slurry consisting of the neodymium nitrate solution and Nb_2O_5 powder. In Fig. 2 the dependence of the completion of synthesis upon temperature is shown.

From the data shown one can see that the synthesis of $NdNbO_4$ is for practical purposes complete at 1300°C, and 80% complete at 1200°C. Comparing the results obtained here with those for calcination of the oxide mixture, one may conclude that the assumption of the more rapid diffusion from molecular precursors is confirmed because the synthesis temperature for $NdNbO_4$ is reduced by about 200°C. The Nd_3NbO_7 is synthesized with much more difficulty, but the synthesis conditions for both techniques are for practical purposes the same. The difficulty of synthesis of Nd_3NbO_7 may be explained by the hypothesis that under the large excess of Nd_2O_3 in the reaction ratio of $Nd_2O_3/Nb_2O_5=3/1$ the phases $NdNbO_4$ and Nd_2O_3 are formed first, and the subsequent synthesis of Nd_3NbO_7 must proceed via the reaction of $NdNbO_4$ and Nd_2O_3 which is inhibited by slow diffusion.

Reduction of synthesis temperature for neodymium niobates was attained by the technique of synthesis based upon the drying and calcining of neodymium and niobium solution mixtures, where the starting components are mixed at a level close to the molecular one. In this case the diffusion difficulties in the synthesis process are completely eliminated. To create the mixture, the solutions of neodymium and niobium compounds were combined. This is difficult as in alkaline media neodymium hydroxide is precipitated, and in acidic media, as a rule, niobic acid is precipitated. Therefore, it was necessary to find a niobium complex soluble in acidic media. The most suitable of hydroxy-acids are the water soluble trioxyglutaric (TOGA) and malic acid.

In Fig. 3 the dependence of the completion of synthesis upon temperature for drying and calcining combined solutions of $Nd(NO_3)_3$ and malic niobium complex is shown. It is seen from Fig. 3 that the application of drying combined solutions of neodymium nitrate and malic niobium complex significantly reduces the temperature of synthesis for $NdNbO_4$ by 700°C and for Nd_3NbO_7 by approximately 600°C. It is worth mentioning that $NdNbO_4$ is synthesized much more easily and at a lower temperature. It could be explained by the fact that during synthesis of Nd_3NbO_7, $NdNbO_4$ is formed first, and the more complex reaction of $Nd_3NbO_7+Nd_2O_3$ resulting in the formation of Nd_3NbO_7 follows.

After the optimum conditions for synthesis of neodymium chromites, aluminates, and niobates were developed, the properties of some individual compounds and mixtures thereof were investigated.

One of the most important properties from the technological standpoint is the starting temperature of melting as the sintering temperature and conditions for fabrication of compacted items depend on that temperature. Therefore, we studied the melting diagrams for aluminate–niobate and chromite–niobate Nd-based systems.

Melting diagrams were studied by means of isothermal retaining according to the following technique. To eliminate the diffusion difficulties and facilitate reaching equilibrium, the samples were prepared by direct synthesis

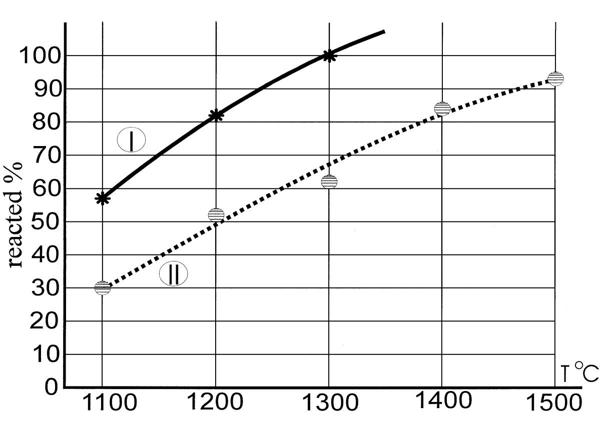


Fig. 2. Completion of synthesis for neodymium niobates from $Nd(NO_3)_3$ and Nb_2O_5 versus synthesis temperature, $t=4$ h. Curve I: $Nd_2O_3/Nb_2O_5=1/1$; curve II: $Nd_2O_3/Nb_2O_5=3/1$.

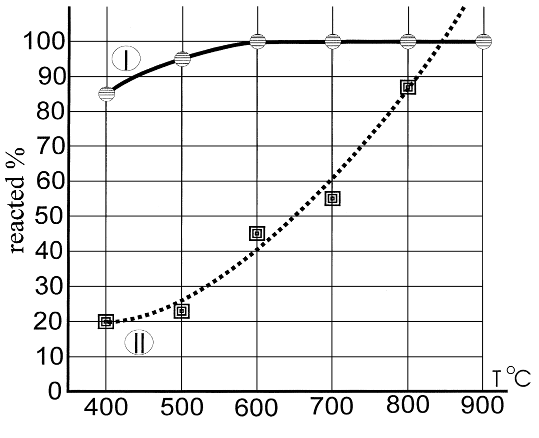
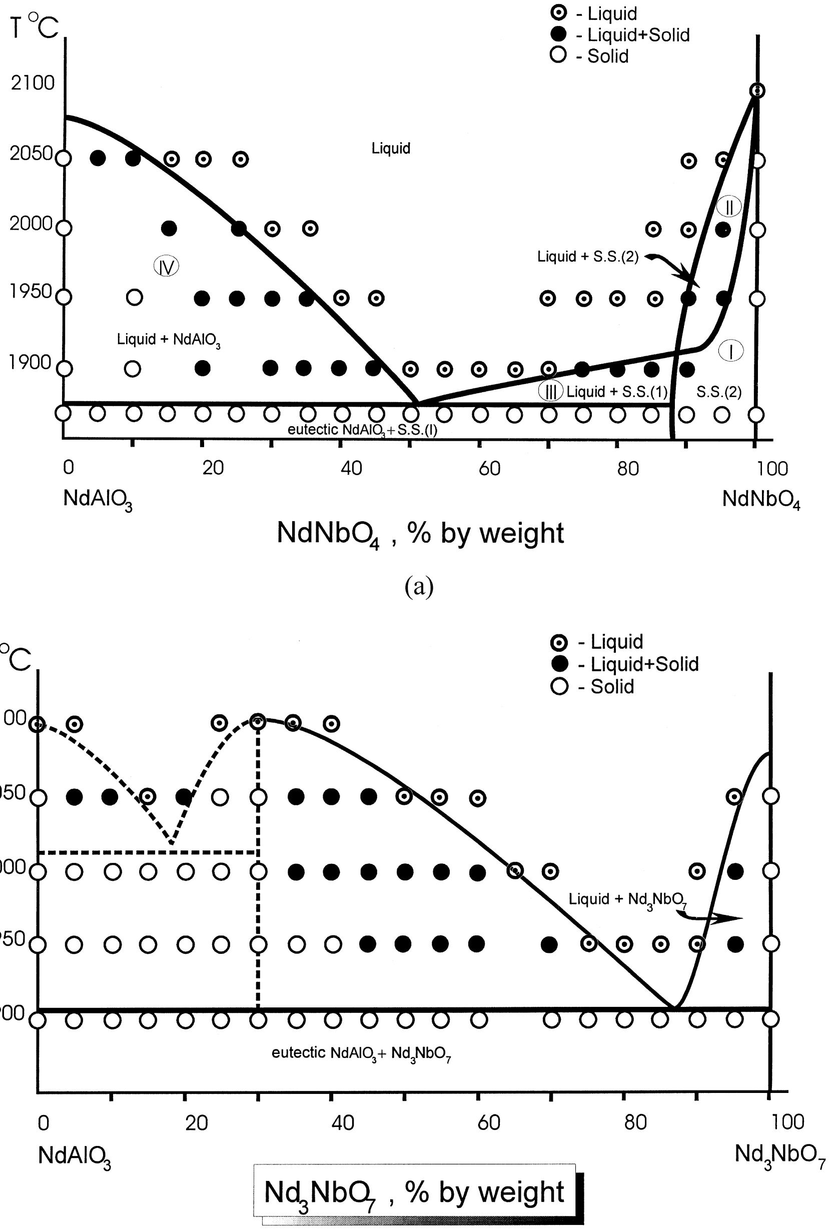


Fig. 3. Completion of synthesis for neodymium niobates by drying and calcining of combined solutions versus synthesis temperature, $t=4$ h. Curve I: $NdNbO_4$; curve II: Nd_3NbO_7.

from solution and not by the mixing of powders of the starting materials. Solutions with the combined starting components were dried under an infrared lamp, calcined, kept at 1200°C for 1 h, and used for preparation of pellets with 3% by mass of paraffin binder additive under the compacting pressure of 4 t/cm^2. Pellets were sintered in air at 1400°C. The pellet densities were determined by hydrostatic weighing, by the pellet dimensions, and by the weight loss under sintering. To draw the melting diagram, the samples were subjected to isothermal retaining in a vacuum furnace at 1700–2150°C after each 50°C. As a supporting plate iridium or tantalum was used. The temperature was measured by the optical pyrometer with an accuracy of ±25°C. Results of experimental studies of melting diagrams with iridium supporting plate are given in Fig. 4.

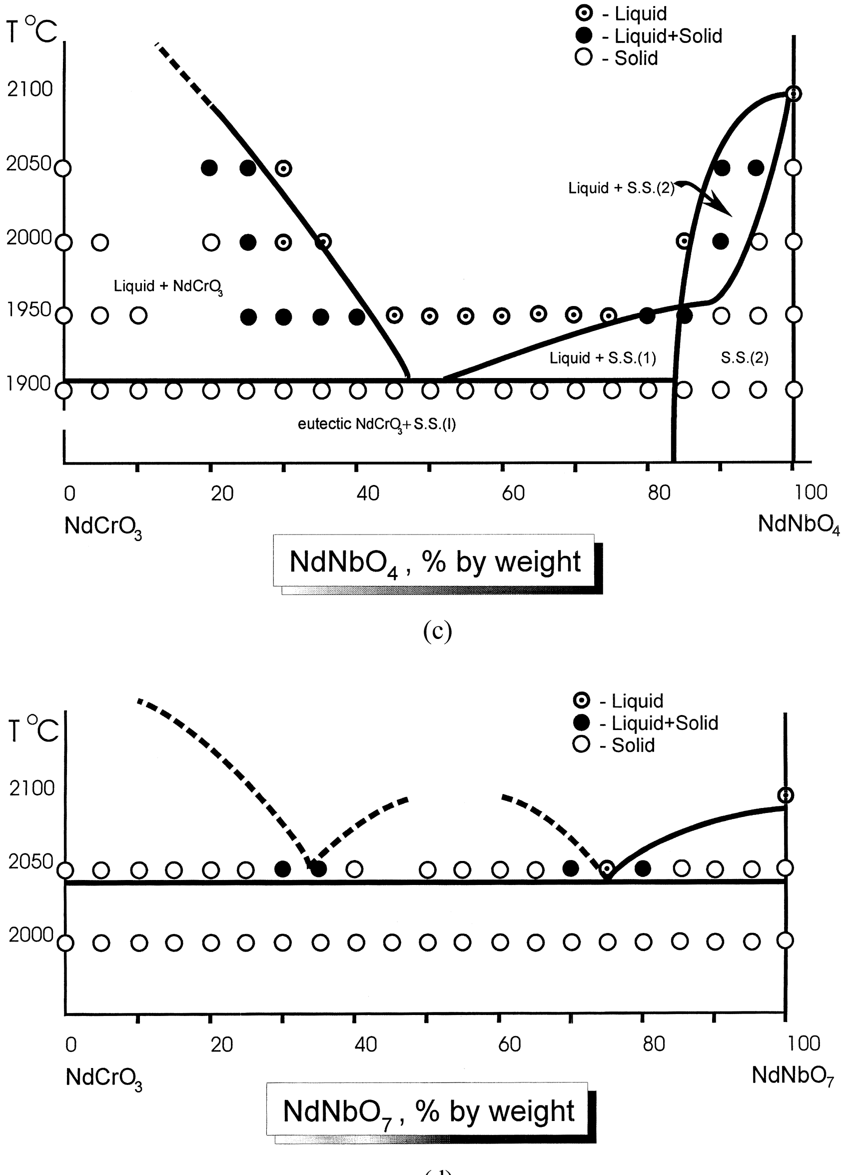
The systems in Fig. 4a and c are eutectic (eutectic point at 45 mass% $NdAlO_2$) with a peritectic (peritectic point at 15 mass% $NdAlO_3$). The presence of peritectic is witnessed by the sharp break of the liquidus curve and the curve of weight loss versus composition given in Fig. 5. The systems in Fig. 4b and d are eutectic with the presence of chemical compounds. In the $NdAlO_3$–Nd_3NbO_7 system the chemical compound corresponds to the content of



(a)

(b)

Fig. 4. Melting diagrams for the following systems on an iridium plate: (a) $NdAlO_3$–$NdNbO_4$; (b) $NdAlO_3$–Nd_3NbO_7; (c) $NdCrO_3$–$NdNbO_4$; (d) $NdCrO_3$–Nd_3NbO_7.



(c)

(d)

Fig. 4. (*continued*)

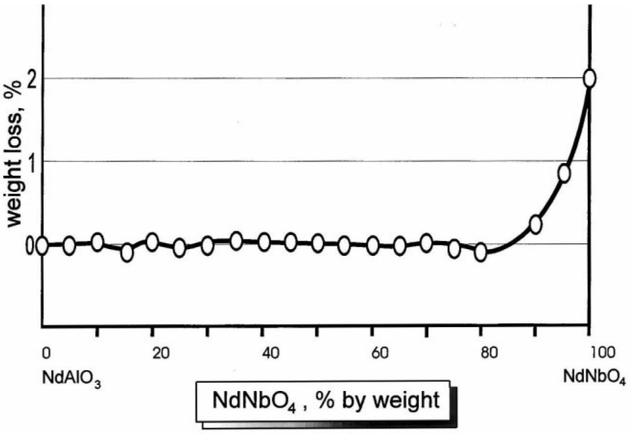


Fig. 5. Weight loss versus composition for $NdAlO_3$–$NdNbO_4$ system at the calcination temperature of 1450°C for 4 h.

Nd_3NbO_7 of 30 mass%, and the eutectics correspond to the content of Nd_3NbO_7 of 15 and 87 mass%. The eutectic line in that system is at 2050°C.

In addition, studies on the fabrication of compacted blocks by cold pressing and following sintering as well as by hot pressing were performed. A possible flowsheet for fabrication of ceramic blocks is given in Fig. 6.

2. Conclusions

This paper has shown that techniques of synthesis of refractory REE oxide compounds from mixtures of aqueous solutions are more efficient than synthesis from solid oxides. The technique allows neodymium mixed oxides to

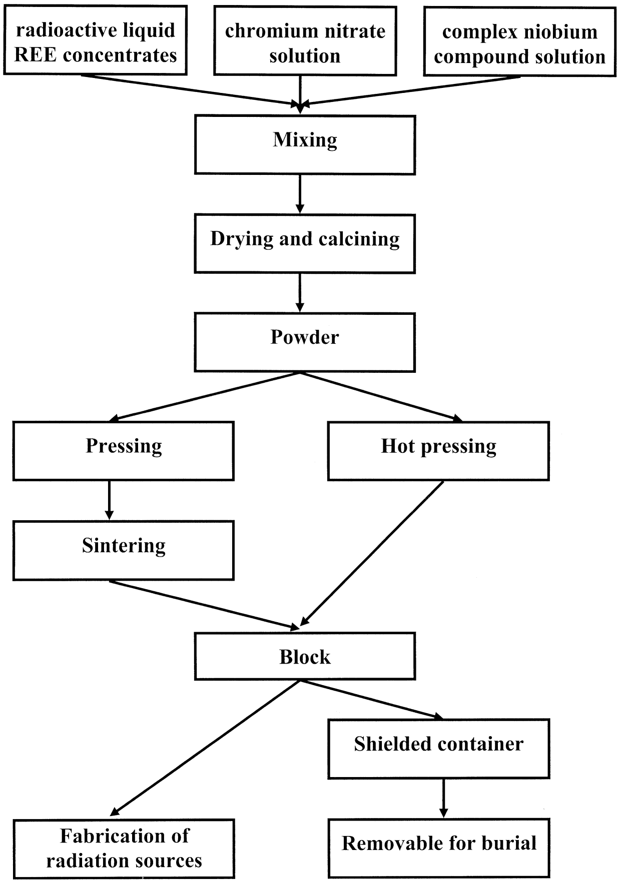


Fig. 6. Possible flowsheet for synthesis and fabrication of ceramic chromite and niobate REE blocks.

be synthesized at or below 800–900°C. Mechanisms of some reactions of these compounds have also been studied. Melting diagrams have been determined. These REE compounds may be used for immobilization of radioactive REE wastes.

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