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PHASE DIAGRAM OF THE NEODYMIUM CHLORIDE–SODIUM CHLORIDE SYSTEM

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Abstract

Differential thermal analysis was used to study the phase diagram of $NdCl_3$–NaCl system. The peritectic reaction was found to occur at 540±7°C. The peritectic compound was confirmed to be $Na_3Nd_5Cl_{18}$ by means of X-ray diffraction analysis. The homogeneity range $Na_3Nd_5Cl_{18}$ could not be defined accurately, but appeared to be between 59 and 70 mol% of $NdCl_3$ at temperatures between 300 and 540°C.

Keywords: DTA, $Na_3Nd_5Cl_{18}$, neodymium chloride, phase diagram, sodium chloride

Introduction

Molten salts are being considered for use as fluid targets in the nuclear incineration of transuranium elements with proton accelerators. The molten salts are also used as the media in high-temperature chemical reprocessing of spent nuclear fuel of fast reactors. Sodium chloride is a candidate solvent in the nuclear incineration program at JAERI because of the high solubility of actinides.

The phase diagrams of alkali-actinide chloride systems are of prime importance for considering their application. For alkali-uranium and alkali-plutonium chloride systems, the following phase diagrams have been described in the literature: (Li, Na, Rb)Cl–UCl_3 [1], (Li, Na, K, Cs)Cl–UCl_4 [2], (Li, Na, K, Rb, Cs)Cl–$PuCl_3$ [3] and (K, Rb, Cs)Cl–$PuCl_4$ [4]. These phase diagrams show that the systems of (Li, Na)Cl–UCl_3 and (Li, Na)Cl–$PuCl_3$ have only eutectics, whereas the systems of RbCl–UCl_3 and (K, Rb, Cs)Cl–$PuCl_3$ have more than two double salts and display more complex phase diagrams.

Alkali-rare earth chloride systems, especially heavier alkali metal chlorides (K, Rb, Cs) with rare earth elements, have attracted interest owing to the presence of a great variety of double salts and their structural properties. On the other hand, sodium chloride-lighter rare earth element (lighter than samarium) chloride systems have attracted little attention, because of the apparently simple phase diagrams [5] with a single eutectic.

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Lighter rare earth elements account for about 50% of fission products in the spent nuclear fuel of light water reactors (LWR). Neodymium is a principal fission product among the rare earth elements and can also be regarded as a stand-in for transplutonium elements such as americium and curium on account of chemical similarities.

Recent studies reported by Sharma and Rogers [6] and Seifert *et al.* [7] on the NaCl–$NdCl_3$ system showed phase diagrams with a peritectic reaction. However, the identified peritectic compound was different in these studies, with NaCl·$3NdCl_3$ reported by Sharma and Rogers [6] and $Na_3Nd_5Cl_{18}$ by Seifert *et al.* [7].

Therefore, the present study reexamines the phase diagram of the NaCl–$NdCl_3$ system by means of differential thermal analysis and powder X-ray diffraction measurements.

Experimental

Reagents

Neodymium chloride hexahydrate ($NdCl_3 \cdot 6\ H_2O$, 99.5% purity) was first dehydrated at 200°C in vacuum (10^{-2} torr), and was sublimed in vacuum (10^{-5} torr) at 1000°C. Sodium chloride was dried at 500°C in vacuum (10^{-5} torr). The materials thus prepared were treated and stored in an argon-filled dry box which was controlled at a water content of <2 ppm and oxygen content <10 ppm. Argon was circulated through a column of copper-bearing alumina, and a molecular sieve column to remove oxygen and water, respectively.

Procedure

Differential thermal analysis

Sample preparation and DTA measurements were performed in an argon-filled dry box. The thermocouple was Pt–Pt10%Rh welded to platinum stages. Mixtures of ~0.3 g by weight were prepared by homogenizing neodymium trichloride and sodium chloride in an agate mortar. In order to better define the liquidus for future thermodynamic modelling of the phase diagram, more than thirty mixtures of various compositions were prepared. About 10 to 20 mg of each mixture was hermetically encapsulated in a gold crucible.

Differential thermal analysis measurements were performed with a thermal analyzer (model DT-50A, Shimadzu Corp., Tokyo, Japan) installed in the dry box described above. Heating and cooling rates of 5°C min^{-1} were used. Initially a temperature calibration was performed with In, Sn, Pb and Zn at the same heating and cooling rates. Alumina powder was used as the reference material. With the calibration curve thus obtained and its extrapolation to higher temperatures, the melting points of alkali chlorides measured under the same conditions as the

NaCl–$NdCl_3$ samples, were 604, 806, 771, 723 and 645°C for LiCl, NaCl, KCl, RbCl and CsCl, respectively. The standard deviation of the mean for each salt was less than 1°C. The melting points of alkali chlorides have been reported to be 610, 801, 771, 723 and 645°C for LiCl, NaCl, KCl, RbCl and CsCl, respectively [8]. Regression analysis of the measured transition temperatures against the literature data gives error limits of ±2.5°C. Considering the standard deviation of the mean of each set of measurements, transition temperatures measured in this study are considered to be accurate within ±4°C for a single salt.

Heating and cooling curves were taken at least four times continuously owing to the complex thermal behaviour of the sample, especially at compositions ranging from 59 to 70 mol% of $NdCl_3$. The transition temperatures were derived from extrapolated peak onsets for the eutectic and peritectic reactions and offsets for the liquidus. The temperatures thus determined were averaged for repeated runs except for the first heating curve where an insufficient homogeneity of the sample by powder mixing was suspected. Due to the large degree of supercooling and the complex thermal behaviour of the samples with compositions ranging from 59 to 70 mol% of $NdCl_3$, the transition and liquidus temperatures were taken only from the heating curves.

X-ray diffraction measurements

A mixture of $NdCl_3$ and NaCl (~3 g) was melted in a sealed quartz tube at 850°C and quenched in water. A piece of the solidified melt was annealed in a quartz tube at the desired temperature for 48 to 600 h and quenched. The annealed sample was powdered and mounted on a standard glass sample holder. The surface of the sample was covered with a Mylar film in order to prevent absorption of moisture. The X-ray diffraction pattern was taken at room temperature with a diffractometer (model Gigerflex, Rigaku Corp., Tokyo, Japan).

Results and discussion

Differential thermal analysis

The areas of the transition peaks in the DTA curve taken of the sample in an open platinum crucible decreased with repeated heating and cooling cycles.

A small quantity of residue was found when the solidified melt was dissolved in water. Therefore, it was judged that the use of a hermetic-type crucible was essential. It was considered that the $NdCl_3$ reacted with impurities in the atmosphere of the dry box resulting in neodymium oxychloride.

Typical DTA curves obtained with hermetic-type crucibles are shown in Figs 1 –2.

Figure 1 displays the DTA curves for the sample containing 10 mol% of $NdCl_3$ and for the sample containing 80 mol% of $NdCl_3$, respectively. In the DTA curve of the sample with 10 mol% of $NdCl_3$, a sharp endothermic peak at about

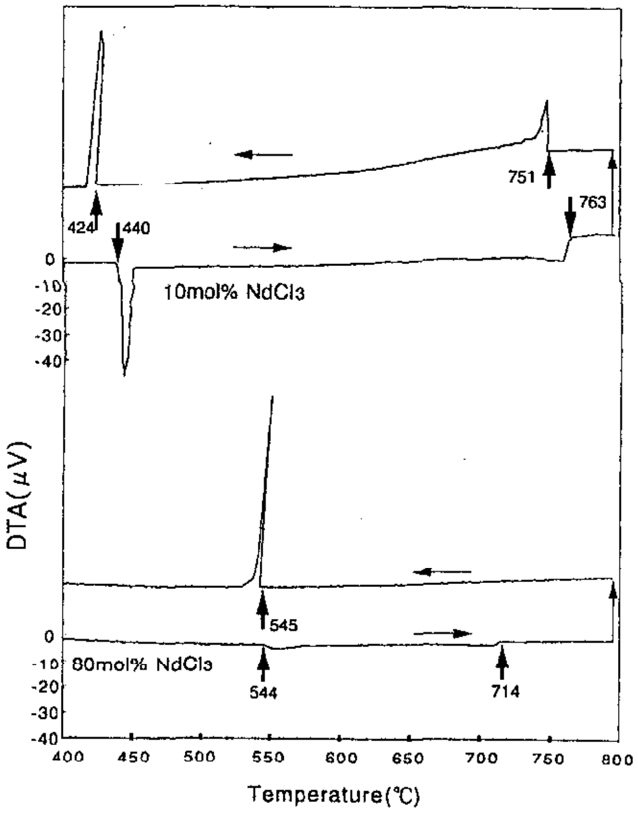

Fig. 1 DTA curves for the mixture of NaCl–10 mol% $NdCl_3$ and for the mixture of NaCl–80 mol% $NdCl_3$. Numbers in the figure are either onset or offset temperatures in degrees centigrade

440°C is ascribed to the eutectic reaction [5–7]. The liquidus temperature was found to be 763°C. The cooling curve with two sharp peaks also indicates the above two reactions. In the DTA curve for the sample with 80 mol% of $NdCl_3$, the small peak at about 545°C is ascribed to the peritectic reaction [6, 7]. Although the liquidus temperature was found to be 714°C in the heating curve, it is absent in the cooling curve. This fact indicates a large degree of supercooling during the cooling of the salt mixture at this composition.

Figure 2 shows the DTA curves for the sample containing 67 mol% of $NdCl_3$ for each heating and cooling cycle measured continuously four times. Around this composition, the behaviour is very complex in comparison with the above two samples. In the first heating and cooling cycle in Fig. 2, there are three endothermic peaks on the heating and three exothermic peaks on the cooling curve, corresponding to the eutectic and peritectic reactions and liquidus, respectively. In the second heating and cooling cycle, there are also three endothermic peaks

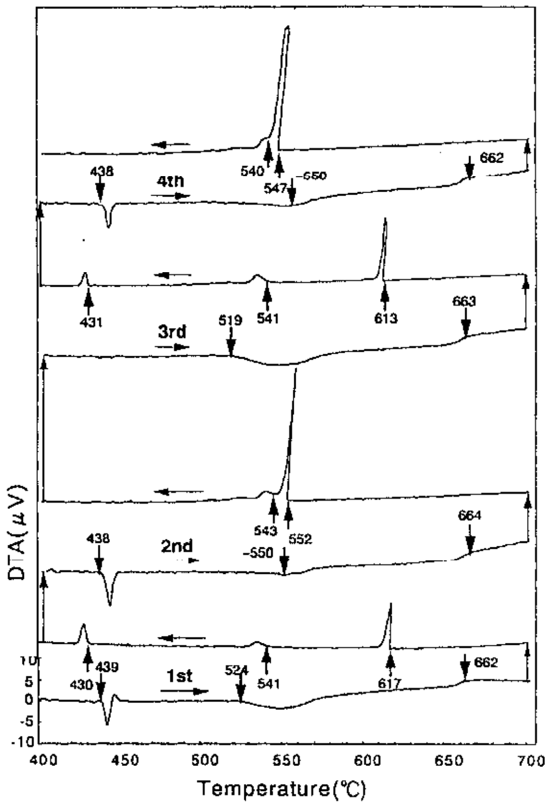

Fig. 2 Heating and cooling curves for the mixture of NaCl–67 mol% $NdCl_3$ measured continuously four times. Numbers in the figure are either onset or offset temperatures in degrees centigrade

in the heating, but there are apparently two exothermic peaks in the cooling curve. The exothermic peak corresponding to the eutectic reaction disappears in the cooling curve. In this cooling curve, the liquidus temperature is lowered from 617°C at the first cooling curve to 552°C, and nearly overlaps with the peak corresponding to the peritectic reaction. In the third heating and cooling cycle, there are only two endothermic peaks at about 520 and 660°C corresponding to the peritectic reaction and liquidus, respectively, in the heating curve, whereas in the cooling curve, there are three exothermic peaks. The liquidus temperature is observed at 613°C in the cooling curve. On the other hand, the DTA curve obtained in the fourth cycle essentially reproduced that of the second cycle. Similar complexity existed for all samples with compositions of 59–70 mol% of $NdCl_3$. This was also the case at a slower rate of heating, 2°C min^{-1}. Although each pattern seemed to appear randomly, the heating curve with two endothermic peaks always appeared after the cooling curve with two exothermic peaks.

This complex behaviour is considered to be due to the preferential segregation of $NdCl_3$ and a marginal stability of the peritectic compound, which would have resulted in inhomogeneous mixtures on cooling. From these observations, the peritectic compound is assumed to contain less than 70 mol% of $NdCl_3$. This supports the assignment of the intermediate phase as $Na_3Nd_5Cl_{18}$ by Seifert *et al.* [7] rather than $NaCl \cdot 3NdCl_3$ by Sharma and Rogers [6]. Further evidence was obtained from the results of X-ray diffraction analysis discussed below.

X-ray diffraction

Figure 3 compares the observed X-ray diffraction pattern of $NdCl_3$ with the Rietveld simulation [9]. The simulation was made with the program RIETAN [10]. The unit cell parameters are summarized in Table 1 [7, 11]. The broad peak at $2\Theta \sim 26^\circ$ is due to the diffraction from the Mylar film. Figure 4 shows the X-ray diffraction pattern for the mixture of $NdCl_3$ and NaCl with the composition of the peritectic compound. The sample was NaCl-63 mol% $NdCl_3$, which was melted at 850°C, and then annealed at 450°C for 240 h. After annealing the sample was quenched. The figure also shows the simulated pattern of $Na_3Nd_5Cl_{18}$ with the unit cell parameter in Table 1. The observed X-ray diffraction pattern for the salt mixture agrees with the simulated pattern of $Na_3Nd_5Cl_{18}$.

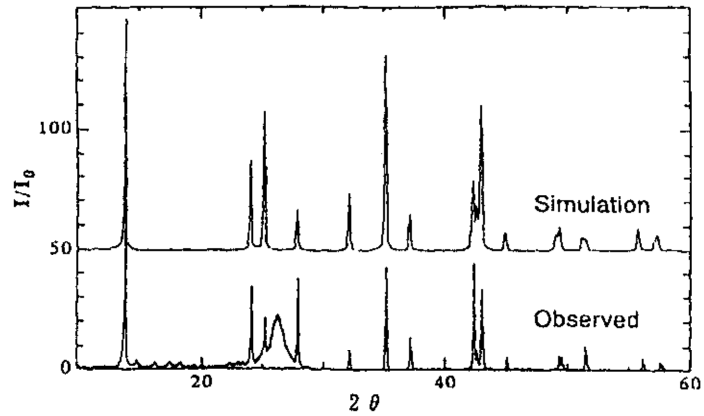

Fig. 3 Powder X-ray diffraction pattern and Rietveld simulation for $NdCl_3$

Table 1 Lattice parameters for neodymium and sodium double chlorides

Compound	Space group a/pm	a/pm	c/pm	Ref.
$NdCl_3$	$P6_3/m$	739.6	423.4	[11]
$Na_3Nd_5Cl_{18}$	$P6_3/m$	753.5	423.7	[7]

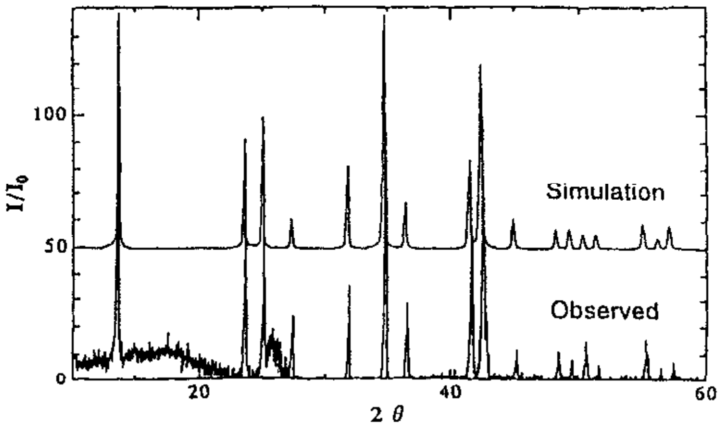

Fig. 4 Powder X-ray diffraction pattern for a mixture of NaCl–63 mol% $NdCl_3$, which was melted, annealed at 450°C for 240 h and quenched, and Rietveld simulation for $Na_3Nd_5Cl_{18}$

The results of X-ray diffraction measurements for the samples with various compositions and annealing temperatures are summarized in Fig. 5. The single-phase region of $Na_3Nd_5Cl_{18}$ could not be defined accurately, but single-phase pattern was found for the samples annealed at temperatures of 300 to 550°C, and compositions ranging from 59 to 70 mol% $NdCl_3$. The $Na_3Nd_5Cl_{18}$ single-phase region slightly differs from that reported by Seifert *et al.* [7] (temperature ranging from 350 to 550°C and compositions from 60 to 75 mol% $NdCl_3$ at 450°C).

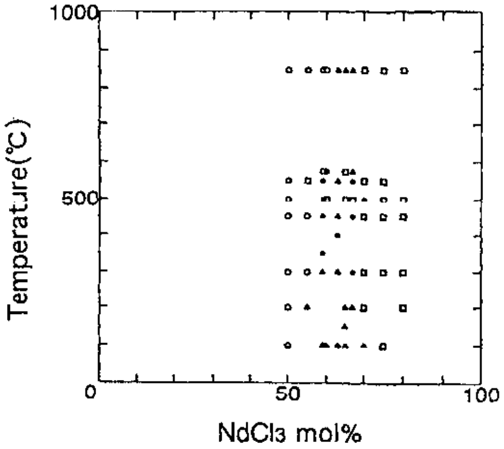

Fig. 5 Summary of X-ray diffraction measurements. • – $Na_3Nd_5Cl_{18}$; ○ – NaCl+$Na_3Nd_5Cl_{18}$; □ – $Na_3Nd_5Cl_{18}$+$NdCl_3$; △ – NaCl+$Na_3Nd_5Cl_{18}$+$NdCl_3$

Phase diagram

By combining the data from DTA and X-ray diffraction analyses, the phase diagram of $NdCl_3$–NaCl system was drawn as shown Fig. 6.

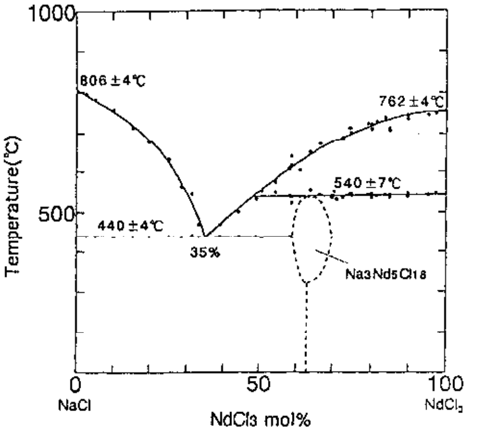

Fig. 6 Phase diagram of the NaCl–$NdCl_3$ system

The peritectic horizontal is at 540±7°C for $NdCl_2$ contents greater than 48%. This peritectic reaction temperature agrees with those reported by Sharma and Rogers [6] (545°C) and Seifert *et al.* [7] (540°C), though the latter could not draw the line clearly for the $NdCl_3$-rich end beyond the peritectic point due to a large scatter of their DTA data.

The eutectic temperature is 440±4°C. This temperature also agrees with that reported by Sharma and Rogers [6] (440°C), but 10°C higher than that reported by Seifert *et al.* [7] (430°C).

Although the eutectic and the peritectic temperatures agree with those reported by Sharma and Rogers [6], the present phase diagram differs from theirs in the composition of the peritectic compound; the peritectic compound proposed by them was $NaCl\cdot 3NdCl_3$, while this study supports the composition $Na_3Nd_5Cl_{18}$ which has been given by Seifert *et al.* [7].

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References

1 E. M. Levin, C. R. Robbins and H. F. McMurdie, 'Phase Diagrams for Ceramists, 1969, Supplement,'; Figs 1318–1337, compiled at the National Bureau of Standards, Edited by M. K. Reser, The American Ceramic Society, Columbus, Ohio, 1975.
2 E. M. Levin, C. R. Robbins and H. F. McMurdie, 'Phase Diagrams for Ceramists, 1969, Supplement,'; Figs 1240–1321, compiled at the National Bureau of Standards, Edited by M. K. Reser, The American Ceramic Society, Columbus, Ohio, 1975.

3 E. M. Levin, C. R. Robbins and H. F. McMurdie, 'Phase Diagrams for Ceramists, 1969, Supplement,'; Figs 1296–3036, compiled at the National Bureau of Standards, Edited by M. K. Reser, The American Ceramic Society, Columbus, Ohio, 1975.
4 R. S. Roth, T. Negas and L. P. Cook, 'Phase Diagrams for Ceramists, Volume V'; Figs 5638–5667, compiled at the National Bureau of Standards, edited and published by The American Ceramic Society, Columbus, Ohio, 1983.
5 Sun in'-Chzhu and I. S. Morozov, Z. Neorg. Khim., 3 (1958) 1914.
6 R. A. Sharma and R. A. Rogers, J. Am. Ceram. Soc., 75 (1992) 2484.
7 H. J. Seifert, H. Fink and J. Uebach, J. Thermal Anal., 33 (1988) 625.
8 I. Barin, Thermochemical Data of Pure Substances, VCH, Weinheim, Germany, 1995.
9 A. Albinati and B. T. M. Willis, J. Appl. Crystallogr., 15 (1982) 361.
10 F. Izumi, J. Crystallogr. Soc. Japan, 27 (1985) 23.
11 W. Zachariasen, J. Chem. Phys., 16 (1948) 254.