Phase Diagrams of LiCl-NdCl₃, NaCl-NdCl₃, and CaCl₂-NdCl₃, Systems

Kazuo IGARASHI*, Mineo KOSAKA, Yasuhiro IWADATE†, Takeo HATTORI†, and Junichi MOCHINAGA†

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1 INTRODUCTION

Phase diagram is very important in studying the mixture melts. The phase diagram of binary LiCl-NdCl₃ system is not yet reported. The phase diagrams of NaCl-NdCl₃ and CaCl₂-NdCl₃ systems reported by Morozov et al. are eutectic type without any intermediate compounds or solid solutions. While studying the phase diagrams of ternary PrCl₃-CaCl₂-NaCl₂ and LaCl₃-CaCl₂-NaCl₃ systems by DTA and DSC, we found that peritectic compounds with a composition of 3LaCl₃NaCl were formed in the binary NaCl-LnCl₃ (Ln= Pr and La) systems. Since NdCl₃ has the same crystal structure, P6₃/m, as LaCl₃ and PrCl₃⁴,⁵) and the cationic radius of Nd³⁺ is also nearly equal to those of La³⁺ and Pr³⁺,⁶) the formation of analogous peritectic compound is expected in the NaCl-NdCl₃ system. We report the phase diagrams of binary LiCl-NdCl₃, NaCl-NdCl₃, and CaCl₂-NdCl₃ systems.

2 EXPERIMENTAL

NdCl₃ used was synthesized by the reaction of Nd₂O₃ (99.9% purity) with reagent grade NH₄Cl at 350°C. The product was purified by the sublimation under a reduced pressure. Impurity contents in the NdCl₃ crystal are almost equal to those reported previously.⁷) Chemicals LiCl, NaCl, and CaCl₂ of analytical reagent grade were dried by a conventional procedure.⁸) Then the salts were melted and solidified. All chemicals were handled in a glove box filled with dry argon. DTA was used for the measurements of transition temperatures. The measurements were carried out under the purified argon, using α-Al₂O₃ as reference material and a chromel-alumel thermocouple, with a cooling rate of 4-14°C/min. If necessary, measurements were repeated with slower cooling rates (2 or 3 °C/min) and newly prepared samples. The DTA apparatus was calibrated with the melting points of pure Al, Zn, and Pb.

3 RESULTS AND DISCUSSION

The melting point of NdCl₃ determined is 756°C, being slightly lower than the literature value.⁹,¹⁰) The melting points of LiCl(610°C), NaCl(802), and CaCl₂(772) are in good agreement with the literature values. The eutectic and peritectic temperatures were determined by averaging the observed temperatures.

Figure 1 shows the phase diagram of LiCl-NdCl₃ system. As expected from many binary systems including LiCl, this phase diagram is the simple eutectic type with the eutectic point at 451°C, 30.1mol% NdCl₃.

The phase diagram of CaCl₂-NdCl₃ system is shown in Fig. 2. It is also the simple eutectic type with the eutectic point at 587°C, 41.0 mol% NdCl₃. The phase diagram of this system reported by Morozov et al. is essentially the same as our result, although there are small differences in the eutectic temperature and composition.

The phase diagram of NaCl-NdCl₃ system is shown in Fig. 2, in which the eutectic point was observed at 436°C, 39.0 mol% NdCl₃. In this system, the small peaks in DTA besides the liquidus and eutectic temperatures were observed at 538°C over the composition more than 53.8 mol% NdCl₃. The appearance of such transition temperatures suggests the formation of peritectic compound.

Seifert et al. have recently investigated the phase diagrams of ACl-LnCl₃ (Ln=La₁₂, Ce₁₃), Pr₁₄, and Nd₁₅); A=Na, K, Rb, and Cs) systems by means of DTA, and have found the formation of new compounds in all the systems. For the NaCl-LnCl₃ systems, they reported the peritectic compounds with the composition, NaLn₁₁.₆₇Cl₁₄. In their phase diagrams, however, the depicted peritectic temperatures do not appear at constant temperatures.

Key words: Phase diagram, NdCl₃, LiCl, NaCl, CaCl₂
As mentioned before\textsuperscript{2,3}, we found the peritectic compounds, \(3\mathrm{LaCl}_3\mathrm{NaCl}\) and \(3\mathrm{PrCl}_3\mathrm{NaCl}\), in the binary \(\mathrm{NaCl}-\mathrm{LaCl}_3\) and \(\mathrm{NaCl}-\mathrm{PrCl}_3\) systems, although the systems were reported as the simple eutectic type without intermediate compounds in literatures.\textsuperscript{1,11} By considering the similarities of the crystal structure\textsuperscript{4,5} and the cationic radius\textsuperscript{6} of \(\mathrm{NdCl}_3\) to \(\mathrm{LaCl}_3\) and \(\mathrm{PrCl}_3\) in addition to the composition of \(3\mathrm{NdCl}_3\mathrm{NaCl}\) similar to the former two systems. However, the confirmation of the compound by an X-ray diffraction is not yet done because of strong hygroscopicity of the sample.

References