

Fluoride addition effect on the EXAFS of neodymium cation in molten LiCl - KCl

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Introduction

Neodymium magnet has the strongest magnetism among the magnets currently industrialized, thus it has been used as motors in hybrid cars, electric vehicles, wind farms and medical instruments which are required with strong magnetism. However, over 90 % of the first resource of rare earths including neodymium is now produced in China. If the demand of the electric vehicles and wind farms rapidly increases in the world, it leads to special concern about the lacking of rare earth resource. Therefore, we have focused on nickel misch metal hydride batteries as a secondary resource of rare earths, and investigated applicability of molten salt electrolysis to extract neodymium from them. To find out much efficient electrochemical condition for the separation of neodymium, the electrochemical behaviour of neodymium in molten LiCl - KCl eutectic coexisting various amount of LiF has been examined. To elucidate the relationship between the variation of electro-reduction potential and local structure around neodymium cation depending on fluoride concentration in molten chloride, EXAFS experiments of neodymium cation in molten LiCl - KCl - LiF have been performed.

Experimental

EXAFS spectra of Nd L_{III}-edge (6.209 keV) were collected with a fixed time scan method by using Si (111) double crystal monochromator in transmission mode. Mixtures of NdCl₃ ($x = 5\text{mol}\%$) in eutectic LiCl - KCl with LiF in the amount of various times to the concentration of NdCl₃ (0 to 12), were melted once in a glassy carbon crucible at 873 K in a glove box filled with an argon atmosphere in high purity. Then, they were mixed with boron nitride powder, and pressed into pellets. To prevent from the chemical reaction during heating process in EXAFS measurements, these pellets were installed in a cell made with pyrolytic boron nitride and the electric furnace was filled with He gas under 30 kPa. EXAFS data were analysed by using the WinXAS ver.3.1.

Results and discussion

The inter-ionic distance between neodymium cation and anion of structural functions of molten NdCl₃ - LiCl - KCl - LiF (0 and 12 times of concentration of Nd) at 298 K and 1073 K are shown in Fig. 1. In both temperatures, with increasing fluoride concentration, inter-ionic distance between Nd³⁺ and anion decreases, that is corresponding to the fact that chloride anions in the

1st coordinated sphere around Nd³⁺ are exchanged by fluoride anions. The most striking feature derived from the figure is that the inter-ionic distance in molten state (at 1073 K) approaches to the value at pure fluoride at 8 - 10 times of LiF concentration while the one at solid state (at 298 K) rapidly reaches to the value at fluoride at 3 times of LiF concentration. It is considered that even larger anions coordinated structure with 8 or 10 anions can be expected in fluoride melts, while the 6 coordinated octahedron is well known to be predominantly existing in various chloride melts. It has been found that the electro-deposition potential depending on fluoride concentration is shifted positively once until the 3 times of concentration of LiF, and shifted negatively over the 3 times of concentration of LiF. Thus intermediately exchanged coordination by fluoride anion makes unstable local structure around neodymium cation in chloride melts, and this fact is caused to positive shift of electroreduction potential in electrochemical behaviour. The similar strategy can be applicable to compounds containing actinide and the profound discussion on the relationship between electrochemical behaviour and local structure will be expected.

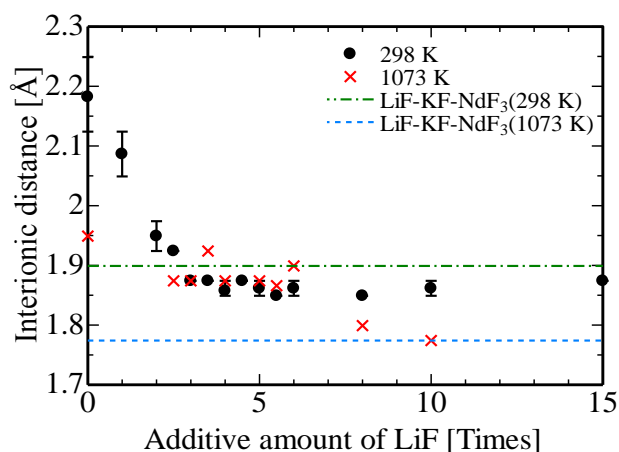


Fig. 1 The inter-ionic distance between Nd³⁺ and anion of structural functions of molten NdCl₃ - LiCl - KCl - LiF (0 and 12 times of concentration of Nd) at 298 and 1073 K.

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