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Spectroscopic analysis of Ce^{3+} and Ho^{3+} ions in LiCl-KCl eutectic melt at high temperature

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1. Introduction

The pyrochemical reprocessing technique is a promising approach for the recycling nuclear spent fuel and reducing high radioactive waste. The chemical characteristics of lanthanides and actinides dissolved in molten salts at high temperature are critical issue to realize the pyrochemical reprocessing system. [1] The spectroscopic analysis was carried out with the aim of investigating the chemical behavior of Ce^{3+} and Ho^{3+} ions dissolved in a molten LiCl-KCl eutectic. Experimental details will be given in this presentation.

2. Experimental and Results

2.1 Experimental

Experimental setup for recording the laser-induced fluorescence spectra of lanthanide elements dissolved in a molten LiCl-KCl eutectic apparatus is shown in Fig. 1. A furnace system placed in lower part of the glove box contains a rectangular quartz cell (diameter: 10 mm; length 50mm) linked with a circular quartz channel (diameter: 10 mm, length: 350 mm). A high temperature up to 390 ℃ was introduced to drive a molten LiCl-KCl in the rectangular cell. A frequency-doubled, Q-switched, Nd:YAG laser (Quantel, Brilliant) was operated at 10 Hz. The 355-nm laser light (pulse duration: ~6 ns) was delivered to the molten salt with a pulse laser energy of 10 mJ. The fluorescence signal collected through an optical fiber (2 × 8 mm^2, 345 fibers) was fed to a monochromator (grating: 1200 lines/mm). A photomultiplier tube (PMT - Hamamatsu, R928) mounted on the exit slit of the monochromator allows a successive fluorescence signal to convert an electric signal. The electric signal of PMT is digitalized by a computer-controlled detector (Acton SpectraHub) in conjunction with SpectraSense software. The digital oscilloscope (Agilent, Infiniium 8000) interfaced to a computer was synchronized with laser beam and PMT via. preamplifier (SR445A, SRS) to record time-resolved fluorescence emission.

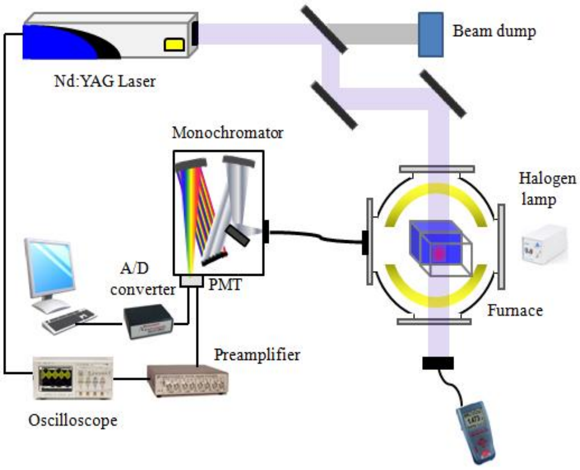

Fig. 1. Schematic diagram of experimental setup

2.2 Results and Discussion

Electronic absorption and fluorescence spectra, a spectral signature indicating the presence of excited elements, were recorded in a LiCl-KCl eutectic melt at 390℃. Figure 2(a) presents absorption and fluorescence spectra of Ce^{3+} measured at 0.5 wt.% of $CeCl_3$ in eutectic melt. The electronic structure of Ce^{3+} ions is susceptible to being excited due to the overlap with absorption band of Ce^{3+} ions and 355nm excitation wavelength. A heavily broadened fluorescence emission attributable to 5d-4f transition appears. Ce^{3+} ions are populated into an upper 5d level by 355-nm laser pulse, after which, non-radiatively decays to the lowest 5d level. [2-3] The ions then undergo radiative relaxation to 4f level, producing broad band emission. We recorded the fluorescence emission as a function of $HoCl_3$ concentration in a eutectic melt. (See. Fig. 2(b)) None of the Ho^{3+} fluorescence emission was observed. However, the fluorescence emission of Ho^{3+} ions appeared in the presence of Ce^{3+} ions. (See. Fig. 2(c)) It may be attributed to the fact that the broadened fluorescence of Ce^{3+} serves the excitation source of Ho^{3+} ions. The fluorescence intensity of Ho^{3+} increases up to 0.02 wt.% of $HoCl_3$ and then subsequently decreases over 0.07 wt.% of $HoCl_3$. This is due to the concentration quenching effect. [4-5]

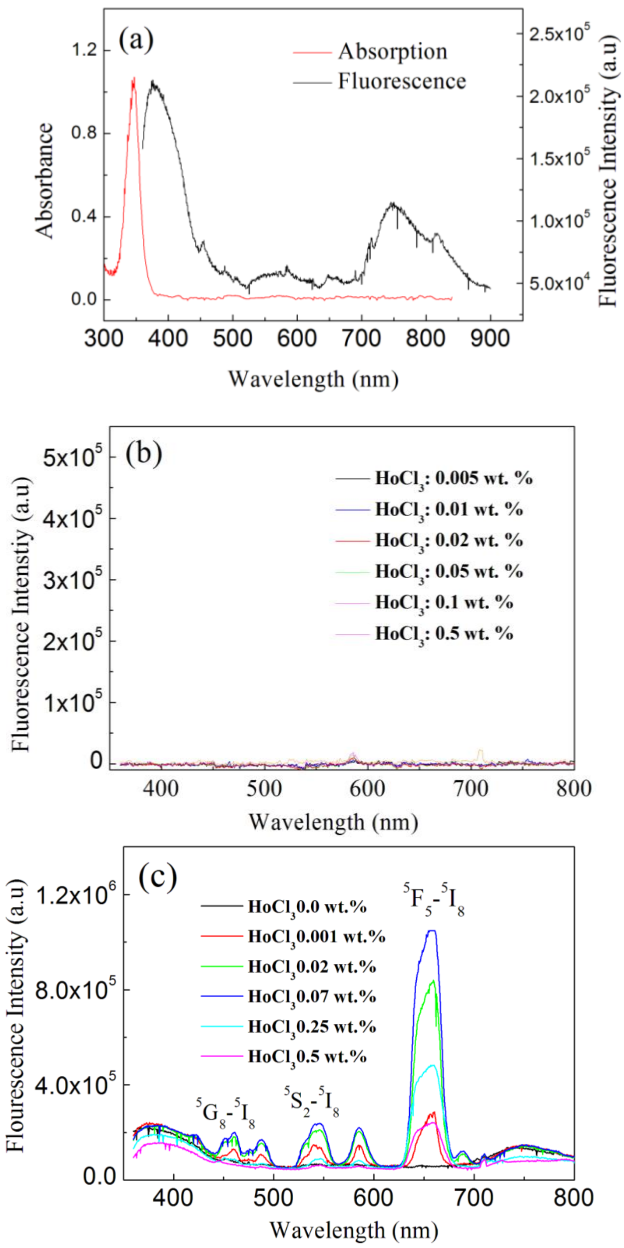

Fig. 2. (a) Absorption and fluorescence spectra of Ce^{3+} dissolved in a LiCl-KCl eutectic melt containing 0.5 wt.% of $CeCl_3$ (b) Fluorescence spectra of Ho^{3+} as a function of HoCl3 in a LiCl-KCl eutectic melt (c) Fluorescence spectra of Ho^{3+} as a function of $HoCl_3$ in a LiCl-KCl eutectic melt containing 0.5 wt.% of $CeCl_3$.

3. Conclusions

Optical emission spectroscopy was used as a diagnostic tool for investigating the chemical behavior of Ce^{3+} and Ho^{3+} in eutectic melt. We observed the sensitization of Ho^{3+} fluorescence emission due to broad band emission of Ce^{3+}. Furthermore, concentration quenching effect of Ho^{3+} was observed under high concentration of $HoCl_3$.

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