DEVELOPMENT OF RAMAN SPECTROSCOPIC SENSORS FOR MAGNESIUM IN A MOLTEN SALT SYSTEM

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ABSTRACT

A study of the Raman spectra of the soluble magnesium(II) species in melts such as NaCl-KCl-CaCl$_2$ (41-41-18 mole %) has been carried out. Over the range of 0 to 25 mole % MgCl$_2$ in NaCl-KCl-CaCl$_2$ at 700 °C, the intensity of the MgCl$_4^{2-}$ Raman band near 250 cm$^{-1}$ was found to vary linearly with Mg(II) concentration. Such a correlation was made possible by normalizing the data to the Rayleigh scattering line from the melt. The precision of this determination is ±1.6 mole %. An all-quartz fiberoptic probe has been developed for measuring Raman spectra of the above melt system remotely.

INTRODUCTION

The light metal, magnesium, is produced today largely through the electrolysis of molten salt systems containing MgCl$_2$ (1,2). This electrolytic process is energy-consuming. Therefore, intensive research efforts have been initiated to reduce the energy consumption by studying the chemistry of related molten salt systems. Notably, Raman spectroscopic results have revealed the existence of MgCl$_4^{2-}$ species in several melt systems (3,4). No quantitative experiments have been carried out to demonstrate the direct correlation between the concentration of MgCl$_2$ and the intensity of the corresponding Raman band, and to our knowledge, no calibration curves have been determined. We want to report here the Raman spectral determination of soluble magnesium(II) in melts with compositions similar to those used in the electrolytic production of magnesium by the Dow Chemical Company (1). The establishment of the calibration curve in
melts of direct interest to the industry will be the first step toward the in-situ monitoring of the industrial electrolytic processes. The second part of this work is the development of a fiberoptic Raman probe for the remote measurement of the magnesium complex in these melts in order to apply this determination to industrial electrolytic process controls. The all-quartz fiberoptic probe developed by us previously (5) has been applied to such measurements.

**EXPERIMENTAL**

**REAGENTS:** Anhydrous magnesium chloride was synthesized by the decomposition of the corresponding carnallite salt (6), followed by distillation using a double bulb quartz vessel (7). No IR bands of hydroxide or magnesium oxide species were found in the magnesium chloride thus synthesized (8). The procedure for the purification of the other starting materials (NaCl and KCl) has been described previously (9). Anhydrous calcium chloride was supplied by T. Blanchard (University of Tennessee, Knoxville).

**INSTRUMENTATION:** Raman spectra were recorded with a Ramanor HG-2S spectrophotometer equipped with concave-aberration-corrected holographic gratings. This instrument, manufactured by Jobin Yvon (Instrument SA), employs a double monochromator. Excitation of the spectra was by means of the 514.5 nm-line from an argon-ion laser (Coherent). Spectral data were stored in a 4096 channel Nicolet model 1170 signal averager which permitted the averaging of spectra over repeated scans. The furnace used in the conventional high temperature Raman measurements has been described previously (10).

The fabrication of the all-quartz probe has been described in detail elsewhere (5). Briefly, the probe was constructed by the fusion of four 600 \( \mu \)m all-silica fibers into a quartz tube under vacuum. Vacuum was applied to make a seal and minimize bubbling of the quartz during the fusion process. This fusion method is very similar to those used in the fabrication of microelectrodes (11). Once fused, the probe tip was carefully cut and polished with successively finer grades of emery paper to a smooth finish.

**PROCEDURE:** For conventional Raman measurements, the sample was loaded into a quartz tube in a drybox under an argon atmosphere and sealed off by the use of a vacuum line. For fiberoptic Raman measurements, samples were loaded in a drybox into a quartz tube with a threaded glass connector as the probe port. The probe was inserted into the sample through the port. The whole assembly was then transferred
outside the drybox and put into a furnace. The laser light was focused into the excitation fiber through a microscope objective, and an xyz positioner was employed to optimize the laser input to the single fiber. About two-thirds of the laser power was lost during the laser-fiber coupling. Collection fibers were mounted side by side in another xyz positioner to increase collection efficiency and positioned at the focal point of the spectrometer input collecting lens.

RESULTS AND DISCUSSION

CALIBRATION CURVE: Figure 1 shows the Raman spectra of molten NaCl-KCl-CaCl₂(41-41-18 mole%) containing varying mole percent of MgCl₂ at 720 °C. This melt composition is similar to that used in the electrolytic production of magnesium (1,2). The Raman band near 246 cm⁻¹ is assigned to the totally symmetric stretching mode (A₁) of MgCl₄²⁻ (3,4). A calibration curve showing the variation in intensity of this Raman band as a function of MgCl₂ mole percent in this series of melts (NaCl-KCl-CaCl₂-MgCl₂) is shown in Figure 2. This calibration was obtained by normalizing the spectra to the intensity of the Rayleigh scattering observed in the sample melts at 100 cm⁻¹. This normalization technique requires the assumption that the intensities of the Rayleigh scattering for the above melts are independent of the concentration of magnesium chloride. We have also shown that the Rayleigh internal standard is insensitive to laser power. This novel use of Rayleigh scattering as an internal standard has not been reported before. With this calibration, one can currently determine the soluble MgCl₄²⁻ with a relative standard deviation of ±1.6 mole percent. This calibration curve will be used in future studies involving the determination of MgCl₄²⁻ in industrial melts.

PROBE: Figure 3a shows the Raman spectrum of MgCl₄²⁻ in a 4-component melt made from NaCl-KCl-CaCl₂-MgCl₂ (35-35-15-15 mole %) recorded by the use of the fiberoptic probe, while the corresponding Raman spectrum recorded by the traditional method is given in Figure 3b. As can be seen in Figure 3a, there is a broad shoulder around 500 cm⁻¹ in addition to the totally symmetric band due to MgCl₄²⁻. This shoulder is caused by the quartz Raman scattering in the optical fibers (12). The signal can be easily removed by baseline subtraction. The base-line subtracted Raman spectrum of Figure 3a is shown in Figure 4. As expected, Figure 4 can be superimposed on Figure 3b. This demonstrates that the calibration curve shown in Figure 2 can be used with remote Raman sensors. A similar Raman spectrum was recorded by the probe for the melt made from NaCl, KCl, CaCl₂ and MgCl₂·2H₂O (35-35-15-15 mole %). The fiberoptic probe can be also used to measure Raman spectra of
powder samples. Figure 5 gives the Raman spectrum of MgCl₂ powder measured with the same probe.

CONCLUSIONS

A calibration curve of Raman intensities vs. concentration of MgCl₂ in molten chloride salts has been obtained. An all-quartz fiberoptic probe was successfully applied to measure Raman spectra of these melts which are similar to melts used in the production of Mg metal.

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FIGURE 1 Raman spectra of molten NaCl-KCl-CaCl₂ (41-41:18 mole%) containing varying mole% of MgCl₂ at 720°C, a) 19%; (b) 14.2%; (d) 10.2%; (e) 5.8%; (f) 4.8%.

FIGURE 2 The calibration curve of MgCl₂ concentration using Rayleigh line as an internal standard.

FIGURE 3 Raman spectra of MgCl₂ in molten NaCl-KCl-CaCl₂-MgCl₂ 35-35-15-15 mole%, at 720°C (a) recorded by the use of the fiberoptic probe (b) recorded by conventional method. The frequency of the exciting laser was 514.5 nm, argon-ion laser.
FIGURE 4 Baseline corrected Raman spectrum shown in Figure 3a.

FIGURE 5 Raman spectrum of MgCl$_2$ powder recorded by an all silica fiberoptic probe. The frequency of the exciting laser was 514.5 nm, argon-ion laser, at 800 mW power.