Structural Analysis of Species in NbCl₅-EMIC Room-Temperature Molten Salt with Raman Spectroscopic Measurement and Ab Initio Molecular Orbital Calculation

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Abstract. The structure of species formed in NbCl₅-1-ethyl-3-methylimidazolium chloride (EMIC) room-temperature molten salt (RTMS) was examined with the Raman spectroscopic measurement and ab initio molecular orbital calculation. The equilibrium structures of NbCl₅, NbCl₆, Nb₂Cl₉, Nb₂Cl₁₁, NbCl₅, EMIC• (in which NbCl₅ anion approaches EMIC• cation with strong interaction) and Nb₂Cl₁₁•-EMIC• were obtained with the HF/LANL2DZ level of calculation. The harmonic frequencies at each equilibrium structure were compared with Raman spectra. The harmonic frequencies of NbCl₆•-EMIC•, Nb₂Cl₁₁•-EMIC•, and NbCl₁₁ were in good agreement with the Raman spectra of RTMS melts. In the NbCl₅-EMIC RTMS, the main species were NbCl₅ and EMIC•. In the NbCl₅-EMIC RTMS added NbCl₅ over 50 mol%, small amount of Nb₂Cl₁₁ and NbCl₁₁ were also formed. The structures of anions and cation in the RTMS distorted from free ions with Coulomb force.

Key words: Room-temperature molten salt, Raman spectra, Ab initio molecular orbital calculation, EMIC

1. Introduction

Room-temperature molten salts (RTMS) have several unique properties, such as a wide electrochemical window, high inherent conductivity, negligible vapor pressure, and nonflammability. The commonly known application of RTMS is the electrodeposition of metal and alloy from the RTMS. The electrodeposition of alloys, such as amorphous Ni-Zn, Nb-Sn superconductor, and the control of crystal orientation of the deposit obtained from the RTMS has been reported. Moreover, many useful electrochemical depositions for industry, which does not occur in aqueous and organic solutions, have also been found in the RTMS. Although characteristics of electrochemical depositions in the RTMS originate mainly from the extension of potential windows, we consider that the molecular structure of species in the RTMS and the relative position of species to other species contribute to the characteristics of the deposit obtained from the RTMS.

In this study, the structure of species formed in NbCl₅-EMIC RTMS and the interaction between species are examined with ab initio molecular orbital calculation and the Raman spectra. The structure and the surrounding of the species in various compositions (various ratios of NbCl₅ and EMIC) of the RTMS are identified. The structure and relative position of species to other species are discussed in detail. The NbCl₅-EMIC RTMS is a constituent of NbCl₅-SnCl₂-EMIC RTMS, from which the Nb₃Sn superconductor is deposited electrochemically. In the elucidation of the structure of NbCl₅-SnCl₂-EMIC RTMS, the analysis of the structure of NbCl₅-EMIC RTMS is the first step.

2. Experimental

2.1. Preparation of the RTMS and Raman spectroscopic measurement

EMIC was synthesized based on the previous report. NbCl₅ (Wako Pure Chemical Industries, Ltd., Japan) is used without further purification. NbCl₅-EMIC RTMS was prepared by the addition of NbCl₅ to EMIC with stirring at 130°C. After the addition of NbCl₅, the melt was stirred at 130°C for 24 h under an atmosphere of argon. Five samples of NbCl₅ (33 mol%)-EMIC (67 mol%) RTMS (33/67 melt), 48/52, 52/48, 60/40, and 67/33 melts, sealed crystal tube and chilled by liquid nitrogen, were used for Raman spectroscopic measurement. Raman spectra were measured by a laser Raman spectrometer (NRS-2000, JASCO, Japan) equipped with an optical multichannel analyzer. The 514.5 nm line from an argon ion laser was used for excitation. The spectra were taken by 10 accumulations during 30 seconds exposures (2 cm⁻¹ resolution).

2.2. Calculation method.

The calculations were carried out at the Hartree-Fock (HF) method with the LANL2DZ basis set by using the GAUSSIAN 98 program package on a Fujitsu VPP5000/3...
3. Results and Discussion

3.1. Raman spectra of NbCl₃-EMIC RTMS

Raman spectra for NbCl₃ (33 mol%) - EMIC (67 mol%) RTMS (33/67 melts), 48/52, 52/48, 60/40 and 67/33 melts have been obtained. These spectra are presented in Fig. 1. A strong band at 371 cm⁻¹ and two weak bands at 324 and 288 cm⁻¹ are found in the spectra of all RTMS melts. Two bands at 192 and 172 cm⁻¹ of 60/40 and 67/33 melts are recognized to be a broad band about 180 cm⁻¹ of 33/67, 48/52 and 52/48 melts because of low resolution. In the RTMS added NbCl₃ over 52 mol%, bands at 419 and 393 cm⁻¹ appear with an increase of the amount of NbCl₃ added in the NbCl₃-EMIC RTMS. The intensity of the bands at 393 cm⁻¹ of both 60/40 and 67/33 melts is very weak. These results indicate that the new species are produced in the NbCl₃-EMIC RTMS added NbCl₃ over 50 mol%, including the species of which bands appeared at 371, 324, 288 and about 180 cm⁻¹. It is well known that equilibria between the species are established in the RTMS composed of metal halides and alkylpyridinium halides or di-alkylimidazolium halides. Various species are also formed depending on the mixing ratio of the metal halides and alkylpyridinium halides or di-alkylimidazolium halides. For example, equilibria between the species in the AlCl₃-EMIC RTMS are commonly described as follows:

EMIC ↔ EMI⁺ + Cl⁻
2AlCl₃ ↔ Al₂Cl₆
1/2Al₂Cl₆ + Cl⁻ ↔ AlCl₄⁻
1/2Al₂Cl₆ + AlCl₄⁻ ↔ Al₂Cl₇⁻
1/2Al₂Cl₆ + Al₂Cl₇⁻ ↔ Al₃Cl₁₀⁻

The major species is AlCl₄⁻ for basic melts (<50 mol% AlCl₃), and Al₂Cl₇⁻ for acidic melts (>50 mol% AlCl₃). In CuCl₁₋₁-butylpyridinium chloride (BPC) and SnCl₂-BPC RTMS, similar equilibria have been also established. We also postulate similar equilibria (eqns. (1) and (6-9)) for the NbCl₃-EMIC RTMS as follows:

2 NbCl₃ ↔ Nb₂Cl₁₀
1/2 Nb₂Cl₁₀ + Cl⁻ ↔ NbCl₆⁻
1/2 Nb₂Cl₁₀ + NbCl₆⁻ ↔ Nb₂Cl₁₁⁻
1/2 Nb₂Cl₁₀ + Nb₂Cl₁₁⁻ ↔ Nb₃Cl₁₆⁻

Based on these equilibria, it is assumed that NbCl₃ and NbCl₆⁻ species exist in all the RTMS, and Nb₂Cl₁₀, Nb₂Cl₁₁⁻, and Nb₂Cl₁₆⁻ species are formed with an increase in the amount of added NbCl₃. The strong band at 371 cm⁻¹ and several weak bands observed in Fig. 1(a, b) originate from the NbCl₃ and/or NbCl₆⁻ species. Bands at 393 and 419 cm⁻¹ originated from the Nb₂Cl₁₀, Nb₂Cl₁₁⁻, and/or Nb₃Cl₁₆⁻ species.

3.2. Equilibrium structure

Figure 2 shows the equilibrium structures of NbCl₃ (a), NbCl₆⁻ (b), Nb₂Cl₁₀ (c), Nb₂Cl₁₁⁻ (d) and Nb₂Cl₁₆⁻ (e) with some bond lengths and angles. The stable structures of NbCl₃ and NbCl₆⁻ with HF/LANL2DZ level are in agreement with those of the CASSCF level of calculation by Rosenkilde, et al. The symmetries of NbCl₃ and NbCl₆⁻ are D₃h and O₆h, respectively. The axial and equatorial Nb-Cl bond lengths for NbCl₃ are different. On the other hand, the bond lengths of all Nb-Cl in NbCl₆⁻ show the same value (2.42Å). In the stable structure of Nb₂Cl₁₀ (C₅ᵥ symmetry), two Nb(V) ions, two Cl⁻ ions bridging Nb(V) ions and four Cl⁻ ions binding to Nb(V) ions lie in a plane. In the case of Nb₂Cl₁₁⁻ and Nb₂Cl₁₆⁻, Nb(V) ions are bridged through a Cl⁻. Two stable
The equilibrium structures of NbCl₅⁻-EMI⁺ with some bond lengths and angles are shown in Fig. 3. There is no difference of stabilization energy between NbCl₅⁻-EMI⁺ (I) and NbCl₆⁻-EMI⁺ (II) (NbCl₅⁻-EMI⁺ (I): 274 kJ/mol and NbCl₆⁻-EMI⁺ (II): 272 kJ/mol). From the values of the stabilization energies, it is found that NbCl₅⁻ and EMI⁺ are interacted by strong Coulomb force. No transition state between two local minima, (I) and (II), is found on the potential energy surface, because the same total energy is obtained with the single point calculations of several geometries between (I) and (II). By all of the geometry optimization of NbCl₅⁻-EMI⁺, the stable structure of (I) or (II) is obtained according to the initial geometry. The Nb-Cl bond lengths and Cl-Nb-Cl angles are slightly changed by the interaction between NbCl₅⁻ and EMI⁺.

By the geometry optimizations of Nb₂Cl₇⁻-EMI⁺, two stable structures, Nb₂Cl₇⁻-EMI⁺ (I) and Nb₂Cl₇⁻-EMI⁺ (II) are obtained as well as NbCl₅⁻-EMI⁺. Figure 4 shows two stable structures of Nb₂Cl₇⁻-EMI⁺ with some bond lengths and angles. The stabilization energies of 272 kJ/mol (I) and 265 kJ/mol (II) are the same essentially. There is no transition state between (I) and (II). The Nb₂Cl₇⁻ is slightly distorted by the Coulomb interaction with EMI⁺.

In the NbCl₅-EMI⁺ RTMS, there are two local structures of each NbCl₅⁻-EMI⁺ and Nb₂Cl₇⁻-EMI⁺ based on Coulomb interaction. Furthermore, in the equilibrium geometries both NbCl₅⁻-EMI⁺ and Nb₂Cl₇⁻-EMI⁺, common characteristics about the relation between anion and cation are found. The positive charge of the hydrogen attracted Cl atom is included from +0.19 (free EMI⁺) to +0.34 by forming NbCl₅⁻-EMI⁺ or Nb₂Cl₇⁻-EMI⁺. This value is the largest of all elements in EMI⁺ with NbCl₅⁻ or Nb₂Cl₇⁻. Mulliken charges of other hydrogen atoms in EMI⁺ show +0.20 - +0.26 region and slightly changed by the ion pair formation. One of carbon atom (2nd position) in imidazolium liging has also positive charge (+0.21) though other atoms of imidazolium ring have negative charges. On the other hand, in EMI⁺ - NbCl₅⁻ (I) and (II), the negative charges (-0.32) of three Cl atoms near EMI⁺ are larger than those (-0.18) of other Cl atoms. The negative charges of three Cl atoms are increased by the contact interactions.
with EMI⁺ (from -0.27 to -0.32). On the other hand, the negative charges of Cl atoms located outside the contact with EMI⁺ are decreased from -0.27 to -0.18 e⁻. In the case of EMI⁺ - Nb₂Cl₁₁⁺, (I) and (II), one Cl atom bridged two NbCl₅ units has large negative charge (-0.34). This negative charge is increased from -0.29 to -0.34 by the ion pair formation with EMI⁺. Mulliken charges of other Cl atoms show -0.17 - -0.26 region. Sum of Mulliken charges of NbCl₅ and Nb₂Cl₁₁⁺ is -0.95 and -0.78, respectively. Therefore, Cl atoms closed to EMI⁺ in NbCl₅ and Nb₂Cl₁₁⁺ mainly approaches to a hydrogen atom connected to carbon atom (2nd position) from the upper or lower side of imidazolium ring by Coulomb force, and small charge transfer from anion to cation is also found. The approach of NbCl₅ or Nb₂Cl₁₁⁺ to the hydrogen from the direction parallel to the imidazolium ring might be blocked by the steric hindrance between methyl or ethyl groups because NbCl₅ and Nb₂Cl₁₁⁺ have large molecular sizes.

3.3. Comparison of observed and calculated Raman spectra

Figure 5 shows the observed Raman spectra and calculated harmonic vibrational frequencies showing the Raman activation. Two observed Raman spectra, (a) and (b), are obtained in 33/67 and 67/33 melts, respectively. The harmonic vibrational frequencies of (c), (d), (e), (f) and (g) are calculated at the equilibrium structures of free NbCl₅, NbCl₆⁻, Nb₂Cl₁₀⁻, Nb₂Cl₁₁⁺ and Nb₂Cl₁₆⁺, respectively, without scaling. There is no strong band in the frequency analysis of EMI⁺. The experimental results of Raman spectra for NbCl₅-EMIC RTMS have been already discussed. In this section, the calculated vibrational frequencies are compared with the experimental.

The calculated frequencies at 188(E''), 290(A₁') and 382(A₁') cm⁻¹ of NbCl₅ are assigned to degenerate Cl-Nb-Cl bending, Cl-Nb stretching and Cl-Nb stretching modes.
respectively. As the band at 382 cm\(^{-1}\) is higher frequency than that of 33/67 (a) and 67/33 (b) melts (371 cm\(^{-1}\)), NbCl\(_6\) as a species in RTMS is not confirmed.

By the frequency analysis of free NbCl\(_6\), the harmonic vibrational frequencies of 174 (T\(_2\)), 258 (E\(_2\)) and 350 (A\(_{1g}\)) cm\(^{-1}\) are obtained (Fig. 5(d)). These frequencies are in good agreement with the Raman spectra of 33/67 melt when they are shifted to 20-30 cm\(^{-1}\) higher frequencies. We assume that these frequencies of free NbCl\(_6\) are shifted by the interaction with EMI\(^+\).

The harmonic frequencies at two equilibrium structures, (I) and (II), of NbCl\(_6\)-EMI\(^+\) are shown in Figure 6. The calculated frequencies of NbCl\(_6\)-EMI\(^+\) (I) are approximately similar to those of NbCl\(_6\)-EMI\(^+\) (II). The frequencies at 174 and 258 cm\(^{-1}\) assigned to degenerate CI-Nb-Cl bending and CI-Nb stretching modes, respectively, of free NbCl\(_6\) (Fig. 5(d)) shift to around 176 and 250 cm\(^{-1}\), respectively, and they are split in some peaks by forming the ion pair with EMI\(^+\). The band at 350 cm\(^{-1}\) of free NbCl\(_6\) shifts to 369 cm\(^{-1}\) of NbCl\(_6\)-EMI\(^+\). The band at 327 cm\(^{-1}\) assigned to CI-Nb stretching mode is appeared newly by forming ion pair of NbCl\(_6\) and EMI\(^+\). These calculated frequencies of NbCl\(_6\)-EMI\(^+\) except 250 cm\(^{-1}\) are in good agreement with the observed Raman spectra of 33/67 and 67/33 melts (180, 324 and 371 cm\(^{-1}\)). The calculated frequencies at around 250 cm\(^{-1}\) might be corresponded to the broad band at 288 cm\(^{-1}\) in Raman spectra of 33/67 and 67/33 melts.

The calculated vibrational frequencies of NbCl\(_{10}\) are shown in Fig. 5(e). Three large peaks of 349 (A\(_{1g}\)), 390 (B\(_2\)) and 412 cm\(^{-1}\) assigned to Cl-Nb-Cl bending, CI-Nb stretching and CI-Nb stretching, respectively, are compared with the experimental. The peak at 412 cm\(^{-1}\) is close to the band at 419 cm\(^{-1}\) of 67/33 melt. Bues, et al., have been reported that Raman spectrum of NbCl\(_{10}\) appears at 419 cm\(^{-1}\)\(^{19}\). As the NbCl\(_{10}\) is not ion pair with EMI\(^+\) but independent species, the band at 419 cm\(^{-1}\) in the Raman spectra is assigned to NbCl\(_{10}\).

In the theoretical Raman spectra of free Nb\(_2\)Cl\(_{11}\)\(^+\) (Fig. 5(f)), a strong peak appears at 372 cm\(^{-1}\). In RTMS melt, there is no free Nb\(_2\)Cl\(_{11}\)\(^+\), though this peak is close to the strong band at 371 cm\(^{-1}\) in 33/67 and 67/33 melts. The frequency analysis of Nb\(_2\)Cl\(_{11}\)-EMI\(^+\) system is required because this anion is able to interact with EMI\(^+\) strongly, as well as NbCl\(_6\)-EMI\(^+\) system. The calculated harmonic vibrational frequencies of Nb\(_2\)Cl\(_{11}\)-EMI\(^+\) (I) and (II) systems are shown in Fig. 6(e) and (f), respectively. The frequency of the strong peak at 392 cm\(^{-1}\) is in good agreement with the broad peak at 393 cm\(^{-1}\) in 67/33 melt. The band at 393 cm\(^{-1}\) is assigned to Nb\(_2\)Cl\(_{11}\)\(^+\) interacted with EMI\(^+\). In the Raman spectra of the melts, the intensity of 393 cm\(^{-1}\) is smaller than that of the strongest peak at 371 cm\(^{-1}\) assigned to NbCl\(_6\)\(^+\). This intensity means that amount of Nb\(_2\)Cl\(_{11}\)\(^+\) is less than that of NbCl\(_6\)\(^+\).

In the frequency analysis of free Nb\(_2\)Cl\(_{16}\), two strong peaks at 356 and 385 cm\(^{-1}\) are obtained (Fig. 5(g)). It is considered that the amount of Nb\(_2\)Cl\(_{16}\) is less than that of Nb\(_2\)Cl\(_{11}\) when the RTMS melt contains Nb\(_2\)Cl\(_{16}\) based on eqs. (8) and (9). Furthermore, the frequency analysis of Nb\(_2\)Cl\(_{16}\)-EMI\(^+\) system is required for the confirmation of Nb\(_2\)Cl\(_{16}\) as the component species of melts. However, we are not able to obtain the optimized geometry and harmonic vibrational frequencies of Nb\(_2\)Cl\(_{16}\)-EMI\(^+\) system because of the computational limit.

From the comparison between calculated harmonic frequencies of all examined species and Raman spectra of 33/67 melts, it is found that only NbCl\(_6\)\(^+\) ion interacted with EMI\(^+\) is containing in the NbCl\(_6\)-EMIC RTMS added below 50 mol\% NbCl\(_6\). In Fig. 6(b), the band at 419 cm\(^{-1}\) is assigned to NbCl\(_{10}\) from both experimental and theoretical results. Broad band at 393 cm\(^{-1}\) is assigned to Nb\(_2\)Cl\(_{11}\) with EMI\(^+\). The strongest peak at 371 cm\(^{-1}\) is assigned to NbCl\(_6\) with EMI\(^+\). Therefore, in the NbCl\(_6\)-EMIC RTMS added over 50 mol\% NbCl\(_6\), it is found that NbCl\(_6\)\(^+\), Nb\(_2\)Cl\(_{10}\) and Nb\(_2\)Cl\(_{11}\)\(^+\) are containing, by the comparison between calculated harmonic frequencies and Raman spectra of 67/33 melts. From both Raman spectra and theoretical approach, we cannot confirm that there is Nb\(_2\)Cl\(_{16}\) in 67/33 melts. Both Nb\(_2\)Cl\(_{16}\) and Nb\(_2\)Cl\(_{11}\)\(^+\) ions interact with EMI\(^+\) in RTMS. Certainly, two species, Nb\(_2\)Cl\(_{10}\) and Nb\(_2\)Cl\(_{11}\), are formed according to the reactions of eqs. (6) and (8), respectively. The Raman intensities of 67/33 melt suggest that the amounts of Nb\(_2\)Cl\(_{10}\) and Nb\(_2\)Cl\(_{11}\) are small in 67/33 melt.
4. Conclusion

The stable structures of NbCl₆⁻, NbCl₆⁻, Nb₂Cl₁₀, Nb₂Cl₁₁⁻, Nb₂Cl₁₆⁻, NbCl₆⁻-EMI⁺ and Nb₂Cl₁₁⁻-EMI⁺ as the chemical species in NbCl₆-EMIC RTMS were obtained with ab initio molecular orbital calculation. The stabilization energies of NbCl₆⁻-EMI⁺ and Nb₂Cl₁₁⁻-EMI⁺ suggested that the anions interacted with EMI⁺ by strong Coulomb force. The harmonic frequencies at the equilibrium geometries of all examined species were compared with Raman spectra of 33/67 and 67/33 melts. Raman spectra of 33/67 melt were in good agreement with the calculated harmonic frequencies of NbCl₆⁻-EMI⁺ system. The peaks of other species was not containing in Raman spectra of 33/67 melt. From the comparison between Raman spectra of 67/33 melt and calculated harmonic frequencies of all examined species, it was found that three species, NbCl₆⁻, Nb₂Cl₁₀, Nb₂Cl₁₁⁻, are containing in 67/33 melt. Both NbCl₆⁻ and Nb₂Cl₁₁⁻ are interacted with EMI⁺ in 67/33 melt.

References