Polarized Raman Spectra of Molten Carbonates Influenced by the Surface Acidity of the Coexisting Inorganic Powder

Minoru Mizuhata, Tatsuo Ohta, and Shigehito Deki

Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University (1-1 Rokkodai-cho, Nada, Kobe 657-8501, Japan)

Received April 21, 2009 ; Accepted June 26, 2009

Raman spectra and the polarization behaviors of molten alkali carbonates coexisting inorganic powder were measured. The deformation and the change of polarization properties by the coexisting with the solid phase are discussed. The symmetry of the band shape of the Raman spectra for CO$_2$$^+$ stretching band (ν) was deformed asymmetrically by coexisting with α-Al$_2$O$_3$ powder. The deconvolution of spectra of mixtures exhibited two band components. The observed bands are evidence of the existence of two different types of CO$_2$$^+$ ions in these systems. Raman depolarization ratio for molten carbonate systems increases from the base line with the decrease of the apparent average thickness. The degree of the anomalous behavior of the molten carbonate by the solid phase have been observed in the order of α-Al$_2$O$_3$ > γ-LiAlO$_2$ > ZrO$_2$ which is related to the surface acidity defined by the value of point of zero charge (pzc). Consequently, the carbonate ion is deformed asymmetrically by coexisting with inorganic oxide powder.

Key Words: Raman Spectroscopy, Molten Carbonates, Carbonate Eutectics, Surface Acidity of Metal Oxides, Polarized Raman Spectra

1 Introduction

Molten carbonate which is one of molten salts is one of suitable electrolytes for electrochemical devices such as molten carbonate fuel cells (MCFCs), CO$_2$ sensor, etc. For easier handling and stabilizing, the carbonate eutectic is supported by a porous ceramic body constituted with fine particles of about 0.1 μm, isolating, chemically inert and insoluble in the electrolyte, γ-LiAlO$_2$. This support, which is the most stable crystalline structure of lithium aluminate, is impregnated by the carbonate eutectic to form a paste structure. In such systems, the chemical and physical properties of carbonate are influenced by the interaction between the carbonate and the solid phase. Therefore, it becomes necessary to clarify the effect of the solid phase. However, there are few studies on the interaction between molten salts and porous solid materials.

We have reported about the ionic conduction, thermophysical properties of molten carbonate coexisting with inorganic oxide powder. In previous studies, the liquid phase at the interface of porous solid materials indicated the anomalous properties which were different from those of the bulk state. Therefore, it is important and necessary to clarify the properties for coexisting systems in detail.

In this paper, the authors performed Raman spectroscopy measurement to discuss the physicochemical properties of molten carbonate coexisting with inorganic powder. The authors particularly focuses on the intramolecular vibration of CO$_2$$^+$ ion to discuss the symmetry of CO$_2$$^+$ ion and performs polarized Raman spectroscopy measurements for (Li$_{0.52}$Na$_{0.48}$)$_2$CO$_3$ melt coexisting with α-Al$_2$O$_3$, γ-LiAlO$_2$, or ZrO$_2$ powder.

2 Experimental

Various kinds of oxide powder such as α-Al$_2$O$_3$ (0.27-328 m$^2$g$^{-1}$; Showa Denko K.K.), γ-LiAlO$_2$ (5.4-24.0 m$^2$g$^{-1}$; Wako Pure Chemical Industries, Ltd.), and ZrO$_2$ (8.7-27.8 m$^2$g$^{-1}$; Nippon Denko Co., Ltd.) were used for the solid phase. (Li$_{0.52}$Na$_{0.48}$)$_2$CO$_3$ was used for the liquid phase. A binary mixture of (Li$_{0.52}$Na$_{0.48}$)$_2$CO$_3$ were mixed Li$_2$CO$_3$ and Na$_2$CO$_3$, and were ground at room temperature after heating at above the bulk melting point in gold crucible under CO$_2$ atmosphere. Inorganic powder and molten alkali carbonate (M$_2$CO$_3$ (M = Li, Na). Nacalai Tesque, Inc., Guaranteed Reagent) were dried at 823 K, 473 K for 2 hours, 48 hours under an atmosphere of N$_2$.

A mixture of (Li$_{0.52}$Na$_{0.48}$)$_2$CO$_3$ and inorganic powder were carefully mixed with agate mortar under N$_2$ atmosphere. The liquid content was ranging from 25 vol% to 45 vol%. The mixture was annealed to the temperature above melting point of contained carbonate in CO$_2$ gas flow for 3 hour, in order for liquid phase to impregnate well the surface of particles, and obtained by quenching. According to our previous studies, the carbonate melts spread on the surface of metal oxide powder and penetrate among the porous solid phase. The spreading liquid layer of carbonate which has an apparent average thickness on the solid surface was indicated as follows;

$$d = \frac{V}{wS_s} \quad (1)$$

where d, V, w, S, are the average thickness of liquid layer, Total volume of liquid phase (carbonate melts), weight of the solid phase, and specific surface area of the solid phase, respectively.

After this process, the mixture was loaded into a 5
mm diameter glass tube. The tube containing the sample was vertically set into the sample holder of the high temperature Raman cell (AABSPEC #2000-A). The temperature was controlled with a digital temperature control system (Chino DB1210), equipped with a K-type thermocouple. The cell was cooled with a water flow system.

In addition, lithium nitrate (LiNO₃, Nacalai Tesque, Inc., Guaranteed Reagent), carbon tetrachloride (CCl₄, Nacalai Tesque, Inc., Guaranteed Reagent), and 60% perchloric acid (HClO₄, 60%), Nacalai Tesque, Inc., Guaranteed Reagent) were used for the comparison of the liquid phase in polarized Raman spectroscopy measurement.

Raman spectra were recorded with a Horiba Ramanor T-64000 spectrometer. Figure 1 shows the optical alignment for polarized Raman spectroscopy using Horiba Ramanor T-64000 monochromator with AABSPEC #2000-A and detail schematic drawing of #2000-A. The excitation source was a 532 nm SHG of Nd:YVO₄ laser with a power of 20 mW at the sample point. The incident light was passed through a prism and perpendicularly focused onto the sample held within the high temperature cell. The scattered light was detected by Horiba CCD 2048 × 512–003 which has a resolution of 0.4 cm⁻¹. The wavenumber of monochromator was calibrated by silicon plate at 520 cm⁻¹. The back-scattered light was collected. For the polarization geometries Y(ZZ)Y (parallel position, Iₓ) and Y(ZX)Y (perpendicular position, Iᵧ), a polarizer was rotated by exactly 90° in front of the slit, where X, Y, and Z are the directions of laser beam and observation, respectively. The electric vector of the laser beam was maintained in the vertical Z direction for both geometries. A polarization scrambler was used between the slit and the polarizer. A depolarization ratio, ρ, is an indicator of symmetry of the vibration mode, and is expressed by ρ = Iₓ/Iᵧ, where Iₓ and Iᵧ are the intensities of the spectra observed with the polarizer oriented parallel and perpendicular to the incident laser beam, respectively. The data processing was carried out by WaveMetrics Igor Pro Ver. 3 software on Microsoft Windows Xp.

3 Results and discussion

3.1 Variation of n₁ mode of CO₂⁺ ion

Figure 2 shows Raman spectra for α-Al₂O₃ powder/(Li₅Na₃)₂CO₃ melt coexisting systems at 823 K. The authors focused on CO₂⁺ stretching band (ν₁) having D₃₃ symmetry, as the other Raman peak at the range of CO₂⁺-stretching band was weak enough to be detected. Symmetry of the band shape of the Raman spectra for CO₂⁺ stretching band (ν₁) was deformed asymmetrically by coexisting with α-Al₂O₃ powder. It was indicated that this result was a result of the interaction between ionic species and the other species such as counter ion and surface functional group of solid phase. In our previous study for the IR and Raman spectra for molten nitrates, the lower symmetric carbonate ionic species (C₃) was observed by coexisting with the inorganic powder. Since the Raman band of symmetric vibration of carbonate slightly deformed, it was suggested that the intensively interacted carbonate species appeared on the solid surface caused by the electrostatic interaction between ion and surface functional group on the oxide particles. Since there is no another bands assigned to

![Fig. 1](image1.png)

(a) Optical alignment and (b) detail schematic drawing of #2000-A.

![Fig. 2](image2.png)

Fig. 2 Raman spectra of CO₂⁺ stretching band (ν₁) in α-Al₂O₃ powder/(Li₅Na₃)₂CO₃ melt coexisting systems at 823 K. Specific surface area of powder: (a) 3.0 m²g⁻¹, (b) 32.8 m²g⁻¹.
lower symmetric bands, however, the effect of the solid phase indirectly appeared by the coexisting with $\alpha$-Al$_2$O$_3$ powder. According to Kloprogge’s study, an intensive interaction between solid surface of metal oxide and carbonate ion caused the formation of the M-O-C bond which corresponds a lower symmetric band. However, no other Raman band appeared in this system. It is suggested that the influence of the solid surface are indirectly and the ionic (electrostatic) interaction become more intensive.

Gaussian deconvolution of the $v_1$ mode of CO$_3^{2−}$ ions results two band components as shown in Fig. 3. The observed bands are evidence of the existence of two different types of CO$_3^{2−}$ ions in these systems. The position of the Band B was equal to that of pure molten salts, and was not changing with the kinds of inorganic powder. The position of the Band A shifted toward lower wavenumber with increasing the specific surface area of the $\alpha$-Al$_2$O$_3$ powder and with decreasing the melt content as shown in Fig. 4. Furthermore, the area ratio of the Band A increased with increasing the specific surface area of the $\alpha$-Al$_2$O$_3$ powder and with decreasing the melt content. It is suggested that the appearance of the Band A is attributed to the effect of the solid phase and presence of bound CO$_3^{2−}$ ion in the mixtures. Therefore, the interaction between carbonate ion and surface of the metal oxide was more intensive, and the wavenumber of $v_1$ decreased.

3.2 Polarized Raman spectra for inorganic powder/ (Li$_{132}$Na$_{40}$O$_{60}$)$_2$CO$_3$ melt system

Melten carbonate which was proved that CO$_3^{2−}$ ion has the interaction with solid phase from the results of the Raman measurement was used for the liquid phase. The planar carbonate ion (CO$_3^{2−}$) belongs to the point group $D_{3h}$ and has four fundamental vibration modes: (1) symmetric stretching vibration, $v_1(A_1)$ Raman active only (polarized), (2) out-of-plane bending, $v_2(A_2)$ infrared active only, (3) doubly degenerate asymmetric stretch, $v_3(E)$, and (4) another doubly degenerate bending mode, $v_4(E')$ Raman (depolarized) and infrared active. The exact frequencies depend on the crystal structure and the associated cation. In the case of (Li$_{132}$Na$_{40}$O$_{60}$)$_2$CO$_3$, as is shown in Fig. 5, the following frequencies $v_1$, 1065 cm$^{-1}$, $v_2$, 1409 cm$^{-1}$, and $v_4$, 698 cm$^{-1}$ were observed. In condensed states (solid and liquid), environmental effects are frequently sufficient to reduce the local symmetry from $D_{3h}$ to $C_3$ or $C_6$ as evidenced by splitting of the degenerate modes, $v_2$ and $v_4$, and in the case of substantial interaction, by appearance of $v_1$ in the infrared spectrum which is active for asymmetric intra–molecular vibrations, and $v_2$ in the Raman spectrum which is active for symmetric intra–molecular vibrations.

The authors focused on CO$_3^{2−}$ stretching band ($v_1$) having $D_{3h}$ symmetry, as the other Raman peak at the range of CO$_3^{2−}$ stretching band was weak enough to be detected.

Prior to the measurement for molten carbonate systems, we confirm the polarized Raman spectra for the system containing spherical molecular or ion such as CCl$_4$ and HClO$_4$ aq. coexisting with various inorganic powders have been measured. The baseline of the Raman depolarization ratio is increased by coexisting with various inorganic powders. It is indicated that the incident light reflects diffusely at the surface of solid phase and perpendicular component of the scattered light ($I_\perp$) increases. In other words, these results are not caused by the interaction with solid phase but are

**Fig. 3** Deconvolution of Raman band of CO$_3^{2−}$ stretching band ($v_1$) for $\alpha$-Al$_2$O$_3$ (32.8 m$^2$/g) powder/ (Li$_{132}$Na$_{40}$O$_{60}$)$_2$CO$_3$ melt coexisting systems. Melt content: 45 vol%.

**Fig. 4** Variations of Band A for $\alpha$-Al$_2$O$_3$/ (Li$_{132}$Na$_{40}$O$_{60}$)$_2$CO$_3$ melt coexisting systems. Melt content: 25vol%.

**Fig. 5** Polarized Raman spectra for CO$_3^{2−}$ stretching band ($v_1$) in (Li$_{132}$Na$_{40}$O$_{60}$)$_2$CO$_3$ melt at 823 K.
caused by the result of optical alignment.

The Raman depolarization ratio was calculated for (Li$_{0.52}$Na$_{0.48}$)$_2$CO$_3$ bulk and α-Al$_2$O$_3$, γ-LiAlO$_2$ or ZrO$_2$ powder/(Li$_{0.52}$Na$_{0.48}$)$_2$CO$_3$ melt coexisting systems. The Raman depolarization ratio at (Li$_{0.52}$Na$_{0.48}$)$_2$CO$_3$ bulk system was ca. 0.30. It is indicated that the symmetry of CO$_3^{2-}$ ion is slightly distorted by the influence of cation, but the distortion is little. Although the Raman depolarization ratio at (Li$_{0.52}$Na$_{0.48}$)$_2$CO$_3$ bulk system was ca. 0.30, all of that at coexisting systems obviously increased compared with bulk system. Figure 6 shows the apparent average thickness dependence of the Raman depolarization ratio for various inorganic powder/molten carbonate coexisting systems. The Raman depolarization ratio exponentially increased with a decrease of apparent average thickness of the liquid layer. The influence of the solid phase was intensive in the order of α-Al$_2$O$_3$ > γ-LiAlO$_2$ > ZrO$_2$, which was related to the surface acidity defined by the value of pzc. These results indicate that the symmetry of CO$_3^{2-}$ ion is distorted by the presence of the inorganic powder.

4 Conclusion
The Raman spectra for (Li$_{0.52}$Na$_{0.48}$)$_2$CO$_3$ coexisting with α-Al$_2$O$_3$ were measured, and the effect of the surface properties on the intra-molecular vibrational mode was discussed. The symmetry of the band shape of the Raman spectra for CO$_3^{2-}$ stretching band (ν$_1$) was deformed asymmetricly by coexisting with α-Al$_2$O$_3$ powder. The deconvolution of spectra of mixtures exhibited two band components. The observed bands are evidence of the existence of two different types of CO$_3^{2-}$ ions in these systems.

The Raman depolarization ratio for molten carbonate systems increases from the base line with the decrease of the apparent average thickness. Besides, the degree of the variation of apparent Raman depolarization ratio for ν$_1$(CO$_3^{2-}$) band was observed in the order of α-Al$_2$O$_3$ > γ-LiAlO$_2$ > ZrO$_2$ which is related to the surface acidity defined by the value of pzc. Consequently, the carbonate ion is deformed asymmetricly by coexisting with α-Al$_2$O$_3$, γ-LiAlO$_2$, or ZrO$_2$ powder.

References