IR Emission Spectra of Carbonate–Chloride Melts
2CsCl–NaCl–Cs₂CO₃ Containing Lithium and Beryllium Ions

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Abstract—The IR emission spectra of the molten systems NaCl–CsCl–Cs₂CO₃–MClₙ (M = Li, Be) have been obtained. Spectral data shows that, at a definite limiting molar ratio \( n_{\text{lim}} = [\text{CO}_3^2-]/[\text{M}^{n+}] \) characteristic for each \( \text{M}^{n+} \), carbonate–chloride melts based on the NaCl–CsCl eutectic contain carbonate complexes \([\text{Li(CO}_3^3]^{5-}\) and \([\text{Be(CO}_3^3]^{4-}\) and, if \( n < n_{\text{lim}} \), carbonato chloro complexes \([\text{M(CO}_3^m\text{Cl}_4-m]}\), where \( m = 1–2 \).

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Carbonate–chloride melts are promising electrolytes for high-temperature fuel elements and media for mineral processing [1]. Let us consider the problems that emerge during recording of IR spectra of carbonate melts. First, carbonate melts have high absorptances in the IR range. This property dictates the use of very thin melt layers in the experiment, \(~20 \mu\text{m}\) [2]. Second, to prevent the thermal decomposition of molten alkali metal carbonates, the experiment should be carried out in a carbon dioxide atmosphere. These difficulties can be eliminated if complex formation of carbonate ions with \( \text{M}^{n+} \) cations under consideration is studied in solutions of these carbonates in molten mixtures of alkali metal chlorides. Such carbonate–chloride mixtures have low absorptances, and the carbonate component of the mixture is stable in the course of experiment. It is worth noting that, in molten alkali metal chlorides, the \( \text{CO}_3^2- \) anion exhibits high substitution ability with respect to the chloride ions upon complexation with the cation of a medium. This makes it possible to select such a composition of the carbonate–chloride melt that only carbonate complexes of \( \text{M}^{n+} \) ions will form at a definite limiting ratio \( n_{\text{lim}} = [\text{CO}_3^2-]/[\text{M}^{n+}] \). Lithium and beryllium ions were taken as \( \text{M}^{n+} \) ions.

The IR spectra of dilute solutions of alkali metal carbonates in molten alkali metal chlorides [3] showed that \( \text{CO}_3^2- \) ions are triangular and have point group of symmetry \( D_{3h} \) [4]. At the same time, in the Raman spectra of analogous concentrated solutions [5, 6], the frequencies of doubly degenerate vibrations of the \( \text{CO}_3^2- \) ion are split, which is associated with lowering of the symmetry of the carbonate ion in these solutions.

EXPERIMENTAL

Experiments with carbonate–chloride melts containing lithium and beryllium ions were carried out in a platinum container as described in [7]. Alkali metal chlorides were purified from hydrolysis products and oxide impurities by zone melting [8]. Gaseous \( \text{CO}_2 \) was purified from molecular oxygen traces by passing it through copper chips heated to 830 K. Helium was purified by passing it through zirconium chips at 1130 K. The melt layer in the container was \(~1.5 \text{ mm} \) thick. Figure 1 shows a simple scheme of an experimental cell. It should be noted that all solutions used are transparent for IR radiation. In our experiment, the light flux from the chloride melt + substrate was recorded relative to the light flux of the radiation source of the reference channel of a double-beam spectrophotometer. The same measurement of the light flux was taken relative to the system carbonate–chloride melt + substrate. The relative spectral emissive power of a melt is calculated by the formula

\[
\varepsilon_{\text{rel}}(\nu, T) = \frac{E_i(\nu, T)}{E_0(\nu, T)}, \tag{1}
\]

where \( E_0 \) and \( E_i \) are the light fluxes arriving from the solution and solvent, respectively. As follows from (1),
ε_{ref}(v, T) is always larger than one. This is valid if measurements were taken in the region of spectral transparency of alkali metal chlorides. In the spectra of relative emissive power ε_{ref}(v, T), frequency characteristics can be distinguished. It is worth noting that, in our case, ε_{ref}(v, T) is not a thermophysical parameter since melts should be referenced to the black body. In the suggested variant of measurement of ε_{ref}(v, T), the system molten alkali metal chloride + platinum substrate was used as the reference. Figure 1 shows that if the atmosphere over the melt absorbs IR radiation, the IR emission spectra of the melt will be distorted by the absorption bands of the gas atmosphere.

RESULTS AND DISCUSSION

Figure 2 shows the IR spectrum of a cesium carbonate solution in molten cesium chloride (curve 1). The IR emission spectrum of this system was recorded in a CO₂ atmosphere (p = 1 atm). It is worth noting that the spectrum of the CsCl–Cs₂CO₃ melt displays, in addition to the emission bands of the CO₃²⁻ ion, the absorption band of the CO₂ gas in the range 700–600 cm⁻¹. At temperatures studied, thermal decomposition of alkali metal carbonates in the molten equimolar NaCl–KCl mixture and in the eutectic NaCl–CsCl is insignificant. This allows one to create an inert gas (helium) atmosphere over the melts. The IR emission spectra of dilute solutions of Cs₂CO₃ in the NaCl–CsCl melt and of NaKCO₃ in the NaCl–KCl melt are shown in Fig. 2 (curves 2 and 3, respectively), and their emission maxima are presented in the table. Let us consider common features of the spectra. The number of CO₃²⁻ vibrations and their activity are more consistent with symmetry group C₂ᵥ, rather than D₃h. Indeed, all six vibrations of the carbonate ion become IR-active. The IR emission spectra show the band of the totally symmetric vibration ν₁(A₁) at 1040–1070 cm⁻¹, which was previously determined by Raman spectroscopy [5, 6]. In addition, the degeneracy of all vibrations of the free carbonate ion is lifted; i.e., ν₃(E') is split into ν₃(A₁) and ν₃(B₂), and ν₄(E') is split into ν₄(A₁) and ν₄(B₂), where ν₄(E') and ν₄(E') are the vibration frequencies of the CO₃²⁻ ion with symmetry D₃h [4]. It is likely that specific features of the spectral characteristics of carbonate–chloride melts are due to anisotropy of the cationic field surrounding the CO₃²⁻ ion [5]. It is worth noting that the emission band ν₂(A₁) at 1350 cm⁻¹ has a doublet structure, which is associated with the Fermi resonance. Indeed, the first overtone frequency 2ν₃ is very close to the vibration frequency ν₁ (table). In addition, the overtone frequency 2ν₂ and the vibration frequency ν₃ are of the same type of symmetry, A₁. The Fermi resonance conditions are satisfied [9]. This leads to the removal of accidental degeneracy and the emergence of two strong emission bands.

The emission band of carbonate–chloride melts with several cations at 1450 cm⁻¹ has a complicated contour (band splitting). This is not observed for the melts with the common cation (CsCl–Cs₂CO₃) (Fig. 2, curve 1). The same is observed for the emission bands at 880 and 680 cm⁻¹. All these facts are evidence that complexes with different cations of a medium are formed in mixed-cation carbonate–chloride melts. Thus, the spectra of melts are superpositions of emission bands of carbonate chloro complexes of several cations of the melt. To assess the coordination mode of carbonate ions to the cations of a medium, it has been suggested to use the frequency of the out-of-plane bending vibration ν₆(B₁) [10, 11]. For the monodentate coordination mode, this frequency is close to the vibration of the free CO₃²⁻ ion (860 cm⁻¹); for the bidentate coordination mode, this frequency is close to 820 cm⁻¹. Another parameter characterizing the coordination mode of the carbonate ion to the cation is the splitting Δν₂₄ = (ν₂ – ν₃). Inasmuch as the ν₂(A₁) and ν₃(B₂) frequencies for carbonate–chloride mixtures have a doublet structure (table), their arithmetic mean was taken to estimate Δν₂₄. For the monodentate coordination mode, the splitting is about 100 cm⁻¹; for the bidentate coordination mode, this splitting is ~160 cm⁻¹ [10–12]. The parameter Δν₂₄ should be used with caution since its values are strongly scattered when the nature of the complex-forming cation is changed [12]. In our case, ν₆(B₁) is ~880 cm⁻¹ and Δν₂₄ = 70–120 cm⁻¹. Thus, the frequencies found for the CO₃²⁻ ion in the CsCl–Cs₂CO₃, NaCl–CsCl–Cs₂CO₃, and NaCl–KCl–NaKCO₃ melts are evidence of the monodentate coordination.