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Raman spectroscopic study of molten $ZnBr_2$–KBr mixtures

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Abstract

In this study, Raman spectra of molten $ZnBr_2$–KBr systems were measured at different compositions and temperatures to ensure the existence of tetrahedral $ZnBr_4^{2-}$ structural units. Each spectrum was deconvoluted in terms of the Gaussian function. Two polarized peaks were identified as the totally symmetric stretching vibration mode of tetrahedral $ZnBr_4^{2-}$ monomer and its dimer. The relative intensities of these peaks depended on both composition and temperature, probably reflecting the ratio of monomer to dimer in the melts. The relative intensities decreased until the $ZnBr_2$ composition decreased down to 25 mol.%, and were constant when the composition was less than 25 mol.%. In this work, we discuss the network structure on the basis of the relative intensities of these two peaks.

Keywords: Raman spectroscopy; Molten mixture; $ZnBr_2$; KBr; Complex

1. Introduction

The structure of glasses or melts of zinc halides and their mixtures with alkali halides have been investigated by X-ray diffraction [1], EXAFS [2], neutron diffraction [3,4], Raman spectroscopy [5–9] and molecular dynamics simulation [10]. These studies have revealed structural models for molten zinc halides, where anions form a close-packed structure and zinc ions are located at tetrahedral sites surrounded by four halide ions. The ZnX_4^{2-} (X = Cl, Br) tetrahedra form a network structure by vertex, edge and face sharing [1–9,11]. In this paper, Raman spectra of molten $ZnBr_2$–KBr were measured to study the change in network structure of $ZnBr_4^{2-}$ with composition or temperature from the view point of the existence of bridging and non-bridging anions.

2. Experimental

Since $ZnBr_2$ is very hygroscopic, guaranteed reagent grade $ZnBr_2$ was dehydrated at 613 K for 8 h under reduced pressure and then sublimated at 773 K. The chemical KBr was dehydrated in the usual manner and melted under dry N_2 atmosphere. The mixtures of $ZnBr_2$ and KBr with adequate compositions were prepared by accurately weighing the components, drying at 473 K for 2 h, melting, and rapidly quenching so as to obtain good homogeneity. The mixture was introduced into the transparent cylindrical fused silica cell of 4 mm inner diameter, 6 mm outer diameter, and 130 mm height [12] in a glovebox filled with dry N_2 gas and sealed under reduced pressure. Raman spectra were measured with a Raman spectrophotometer (Jasco NR-1800 equipped with triple monochromator) using an Ar^+ ion laser at wavelength 514.5 nm with an output of 200 mW as an excitation light source. The background of the Raman spectrum was assumed to be caused by the Rayleigh-wing and fitted by a summation of Gaussian and Lorentzian functions, $f_{G+L} = f_G + f_L = A \exp[-\{(v - v_0)/B\}^2] + C/[1 + \{(v - v_0)/D\}^2]$ where $v - v_0$ is the Raman shift, v_0 the wavenumber of the Rayleigh peak, A and C the peak heights, and B and D the half-widths. The parameters A, B, C and D were estimated by the non-linear least-squares method. After the background corrections, each Raman peak was approximated by the Gaussian function. Raman spectra were measured in the temperature range 653–

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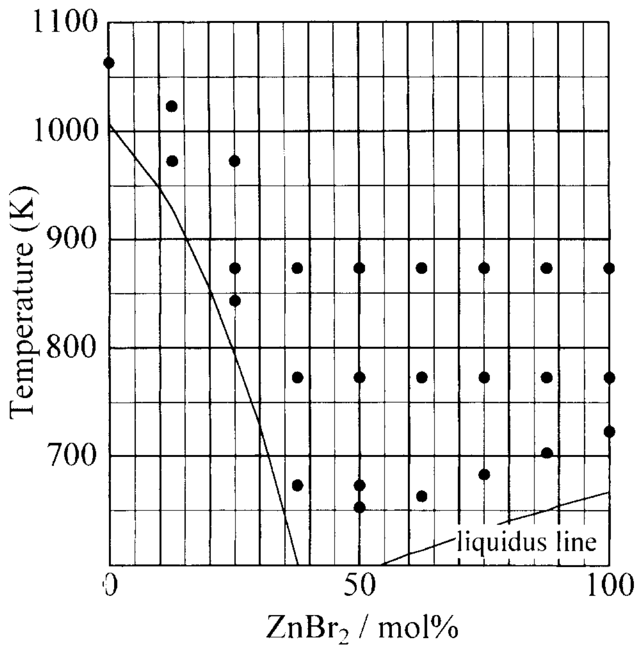

Fig. 1. Experimental points in Raman spectroscopic measurement.

1063 K. These experimental points are plotted in Fig. 1.

3. Results and discussion

Owing to the structural information [1–9], tetrahedral units are expected to have four Raman active vibrational modes, and in fact these vibrational modes in Raman spectra, except the υ_3 mode, were assignable to those characteristic of tetrahedral configuration.

In the molten ZnBr$_2$, ZnBr$_4^{2-}$ tetrahedra were thought to form a network structure as observed in molten ZnBr$_2$–NaBr [11]. ZnBr$_2$–NaBr melts contained (ZnBr$_2$)$_n$ polymers or aggregates. These species consisted of corner-sharing ZnBr$_4^{2-}$ tetrahedra. After increasing the temperature or after the addition of NaBr, the (ZnBr$_2$)$_n$ polymers dissociated into smaller clusters. However Raman spectra of ZnBr$_2$–KBr glasses contain strong bands at 60, 155, and 174 cm^{-1}, and some weak bands between 200 and 300 cm^{-1}. The 155 and 174 cm^{-1} bands were assigned to symmetric stretching modes of tetrahedra consisting of four bridging and four non-bridging bromine atoms respectively [9]. Similar polymers and complex ions were considered to be in the molten ZnBr$_2$–KBr. Consulting with the data, we discuss the structure of molten ZnBr$_2$–KBr. According to MOPAC calculations (PM3), the frequency of the υ_1 mode for the ZnBr$_4^{2-}$ monomer is 169 cm^{-1} and that for the vertex-sharing dimer is 140 cm^{-1}. In contrast, those for the edge- and face-sharing dimer are 184 and 188 cm^{-1} respectively. In this paper, bridging and non-bridging states correspond to Zn$_2$Br$_7^{3-}$ (dimer of the ZnBr$_4^{2-}$ unit) and ZnBr$_4^{2-}$ (monomer) respectively. In the case of a trimer or more complex ions, spectroscopic features and phenomena were very complicated and too weak for deconvolution. Owing to the hypothetical existence of different bonding states, it was supposed that two kinds of peak (bridging or non-bridging) were observable in Raman spectra. Raman spectra of molten ZnBr$_2$–KBr are shown in Fig. 2, where (a), (b) and (c) are the results measured along the liquidus line at the liquidus temperatures +50, 773, and 873 K respectively.

In the Raman spectra of molten mixtures, two strong bands were present at about 145 and 170 cm^{-1}, and two weak bands were observed in the low wavenumber region. In comparison with vibrational modes of glasses [9] and the results of MOPAC calculations mentioned above, two strong polarized bands at about 145 and 170 cm^{-1} were assigned to the υ_1 mode of totally stretching vibration for bridging ZnBr$_4^{2-}$ tetrahedra (υ_1^{b}) and non-bridging ZnBr$_4^{2-}$ tetrahedra (υ_1^{nb}) respectively (Fig. 3). In a similar manner, two weak depolarized bands at about 55 and 85 cm^{-1} were assigned to the doubly degenerate bending vibration υ_2 and triply degenerate bending vibration υ_4 respectively by consulting with Raman spectra of glasses [9]. But these peaks were expected to be formed by overlapping of two or more contributions. The υ_3 mode assigned to triply degenerate stretching vibration was too weak to be observed in the spectra.

Weak peaks were numerically present at about 200 cm^{-1} according to the deconvolution of each spectrum, but quite difficult to discriminate. Since these peaks were too broad, they were due to the

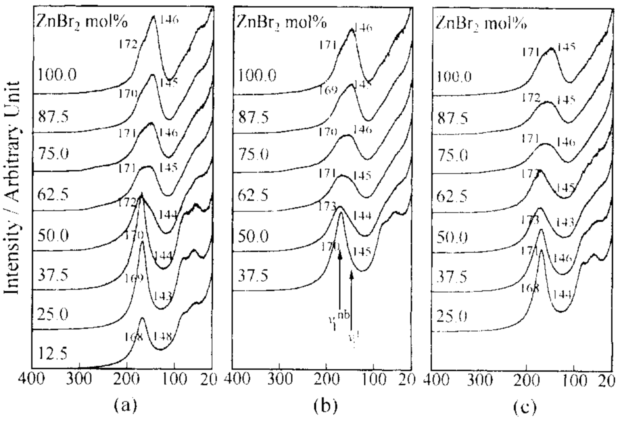

Fig. 2. Variation of Raman spectra with ZnBr$_2$ concentration in molten ZnBr$_2$–KBr: (a) liquidus temperature +50 K, (b) 773 K, (c) 873 K.

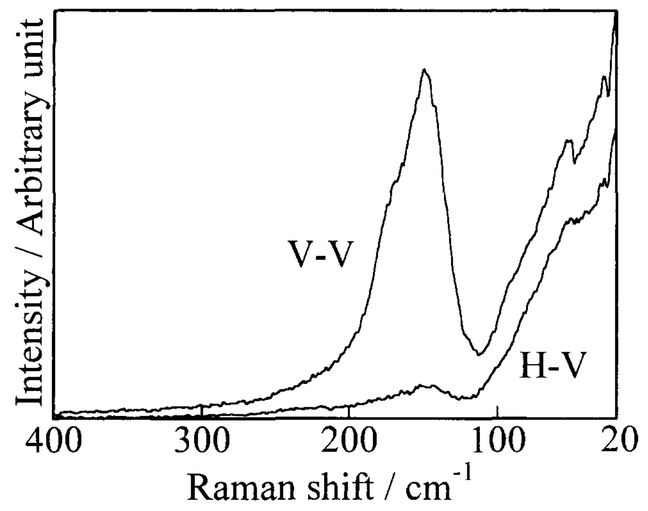

Fig. 3. Polarized and depolarized bands for molten $ZnBr_2$ at 723 K.

overlapping of bridging and non-bridging spectra of $ZnBr_4^{2-}$ or more polymerized units.

Raman shifts of v_1^b (145 cm^{-1}) and v_1^{nb} (170 cm^{-1}) in molten $ZnBr_2$–KBr depended little on composition or temperature. The relative intensities v_1^b/v_1^{nb} plotted against $ZnBr_2$ concentration are shown in Fig. 4. The relative intensities decreased until the $ZnBr_2$ concentration decreased down to 25 mol.%, and were constant when the composition was less than 25 mol.%. The bridging $ZnBr_4^{2-}$ was supposed to be broken with an increase of KBr composition or a rise of temperature, and the whole bridging $ZnBr_4^{2-}$ might be changed to non-bridging $ZnBr_4^{2-}$ at this concentration. This linear variation in relative intensity of molten $ZnBr_2$–KBr in the high concentration range of $ZnBr_2$ was different from that observed in $ZnBr_2$–KBr glasses [9]. Since v_2 and v_4 bands were broad and shifted little, it is difficult to discuss any further.

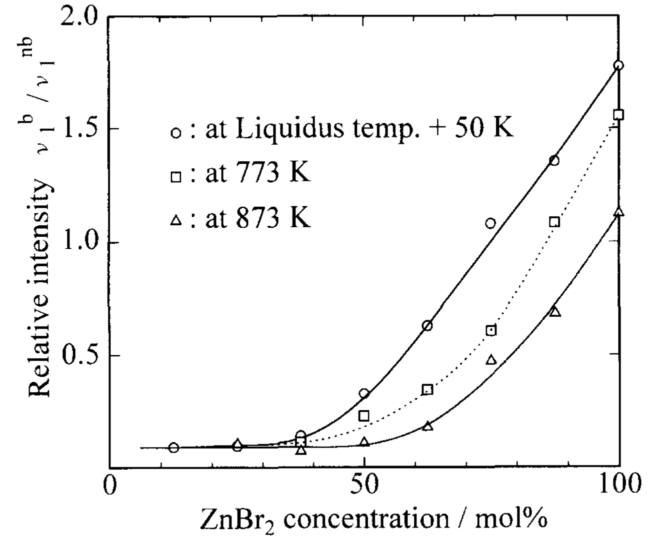

Fig. 4. Variation of relative intensity with $ZnBr_2$ concentration in molten $ZnBr_2$–KBr.

Acknowledgements

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