Raman Spectra of ZnBr_2 -KBr- PbBr_2 Glasses

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ZnBr_2 -KBr- PbBr_2 ガラスのラマンスペクトル

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In Raman spectra of ZnBr_2 -KBr- PbBr_2 glasses, the dominant bands are observed at about 60 cm^{-1} and 155 cm^{-1} or 174 cm^{-1} . The 60 cm^{-1} band was assigned to the mode containing bending vibrations and the 155 cm^{-1} or 174 cm^{-1} band to the symmetric mode containing the stretching vibration between zinc and bridging or non-bridging bromine, respectively. The compositional dependence of the intensity of the 155 cm^{-1} and 174 cm^{-1} bands gives information about both the structural role of PbBr_2 and the network structure from the viewpoint of bridging and non-bridging bromines. The introduction of PbBr_2 increased the number of non-bridging bromine. This indicates that PbBr_2 has the same role of glass modifier as that of KBr. On the other hand, the 155 cm^{-1} band was observed even for a glass of the composition with 20 mol % PbBr_2 , in which the atomic ratio, Br/Zn , is 4. This suggests that there are free bromide ions and/or zinc ions coordinated with more than four bromide ions.

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1. Introduction

Zinc bromide is one of the glass formers of non-fluoride halide glasses and vitrifies in considerably large compositional regions of ternary ZnBr_2 -KBr-MBr₂ systems when the third component has a large cation such as Pb^{2+} , Ba^{2+} , Sr^{2+} and Ca^{2+} .¹⁾ In a previous paper,²⁾ we reported a Raman spectroscopic study on the network structure of ZnBr_2 -KBr and ZnBr_2 -KBr- CaBr_2 glasses. It was indicated that at the composition of the atomic ratio, Br/Zn , less than 3.3, CaBr_2 has the role of glass modifier as well as KBr in the sense of increasing the non-bridging bromines (*nbBr*'s) in the glass network. However, the bridging bromines (*bBr*'s) are observed for the system containing CaBr_2 even in the glasses of the composition of the Br/Zn ratio more than 4, though all bromide ions were expected to be non-bridging in this composition under the assumption of the four-fold coordinated zinc ions and the corner sharing tetrahedra.

The present paper reports a similar study on the ZnBr_2 -KBr- PbBr_2 glasses. In this system glasses are more easily obtained than the system containing alkaline earth bromide described above as the third component.¹⁾ The change in the network structure and the structural role of PbBr_2 are discussed from the view point of bridging and non-bridging bromines.

2. Experimental

Because of the high hygroscopicity of ZnBr_2 , glasses were prepared in a glove box filled up with N_2 . The impurity water and oxygen in the glove box were lower than 20 ppm and 10 ppm, respectively. The preparation method of glasses was described in detail elsewhere.¹⁾ For Raman scattering measurements, glass powder sealed in a silica tube (2.5 mm in diameter) under vacuum was remelted and quenched by immersing the tube in water. When it was difficult to obtain transparent glass by this method, small pieces of glass plate (2-3 mm in diameter) in a sealed silica tube were used. Raman spectra were measured by JEOL JRS-400 D spectrometer with 514.5 nm line of NEC GLS 3200 Ar^+ laser.

Figure 1 shows the glass forming region of the ZnBr_2 -KBr- PbBr_2 system and the compositions of glasses for Raman scattering measurements. Each symbol in this figure refers to a series of variation in composition; $\bigcirc$ to a variation keeping PbBr_2 content at 5 mol %, $\square$ to a variation keeping KBr content at 40 mol % and $\triangle$ to a variation at the constant atomic ratio of $\text{Br}/\text{Zn}=3$.

3. Results and discussion

3.1 Raman spectra of crystals

Raman spectra of ZnBr_2 , K_2ZnBr_4 and KPb_2Br_6 crystals are shown in Fig. 2. K_2ZnBr_4 likely has

Fig. 1. Glass forming region of ZnBr₂-KBr-PbBr₂ system and compositions of glasses for Raman scattering measurements. Atomic ratio, Br/Zn, is also indicated.

Fig. 2. Raman spectra of ZnBr₂, K₂ZnBr₄ and KPb₂Br₅ crystals.

the same structure as that of Rb₂ZnBr₄³⁾ or Cs₂ZnBr₄⁴⁾ containing tetrahedral ZnBr₄²⁻ ions. Four fundamental Raman active modes are expected for a tetrahedral XY₄ species, i.e., A₁(ν₁), E(ν₂), F₂(ν₃) and F₂(ν₄), and the vibrational frequency of each mode in Cs₂ZnBr₄ crystal is 178 cm⁻¹, 80 cm⁻¹, 212 cm⁻¹ and 89 cm⁻¹,

respectively.⁵⁾ Thus it is reasonable to assign the 179 cm⁻¹, 65 cm⁻¹ and 85 cm⁻¹ bands in the spectrum of K₂ZnBr₄ to A₁(ν₁), E(ν₂) and F₂(ν₄) modes of the tetrahedral ZnBr₄²⁻ ion. The considerably broad and weak band about 215 cm⁻¹ is assigned to the F₂(ν₃) mode. The 179 cm⁻¹ band assigned to A₁(ν₁) mode is the totally symmetric stretching vibration of the Zn-*nb*Br tetrahedron. On the other hand, ZnBr₂ has a structure of close-packed bromide ions and tetrahedrally coordinated zinc ions. Since all bromide ions are bridging in the structure, the 160 cm⁻¹ band in the spectrum of ZnBr₂ is assigned to the mode of the stretching of the Zn-*b*Br tetrahedron. This assignment is supported by the lower frequency of the stretching mode of Zn-*b*Br than that of Zn-*nb*Br. Low frequency bands in the range from 40 cm⁻¹ to 120 cm⁻¹ are attributed to modes containing bending vibrations.

Bands of the spectrum of KPb₂Br₅ have not been assigned probably because of the complex crystal structure of KPb₂Br₅. However, the highest frequency band at 133 cm⁻¹ is likely assigned to a mode containing the stretching vibration of Pb-Br. Low frequency bands will again include contributions from bending vibrations.

3.2 Raman spectra of glasses

In Fig. 3 and Fig. 4 are shown Raman spectra of the three series of compositional variation and polarized Raman spectra, respectively. Figure 3 (a) shows the variation of spectra with the replacement of ZnBr₂ by KBr at 5 mol % PbBr₂. All spectra consist of strong bands at about 60 cm⁻¹ and 155 cm⁻¹, a shoulder at 174 cm⁻¹, a subsidiary band at 130 cm⁻¹ and some weak bands above 200 cm⁻¹. Among them, the 60 cm⁻¹ band, which is found to be depolarized from Fig. 4, is due to the mode containing bending vibrations. Since KBr is a network modifier in this glass system as well as KCl in ZnCl₂ glasses or alkaline oxide in silicate glasses, the replacement of ZnBr₂ by KBr increases the number of *nb*Br in the glass network. On the other hand, the relative intensity of the 174 cm⁻¹ band to that of the 155 cm⁻¹ band increases with the KBr content in Fig. 3 (a). Both of this compositional dependence of the spectra and the assignment of the 160 cm⁻¹ and 179 cm⁻¹ bands in the spectra of ZnBr₂ and K₂ZnBr₄ crystals indicate that the 155 cm⁻¹ and 174 cm⁻¹ bands are assigned to the modes containing the stretching vibrations of Zn-*b*Br and Zn-*nb*Br in the glass network, respectively. The polarized Raman spectra in Fig. 4 show that the 155 cm⁻¹ and 174 cm⁻¹ bands are highly polarized and are therefore due to symmetric stretching modes. The present assignment on

Fig. 3. (a) Raman spectra of $(70-x)\text{ZnBr}_2 \cdot (25+x)\text{KBr} \cdot 5\text{PbBr}_2$ glasses ($x=0, 10, 25$).

(b) Raman spectra of $(60-x)\text{ZnBr}_2 \cdot 40\text{KBr} \cdot x\text{PbBr}_2$ glasses ($x=5, 10, 15, 20$).

(c) Raman spectra of $(50+x/2)\text{ZnBr}_2 \cdot (50-3x/2)\text{KBr} \cdot x\text{PbBr}_2$ glasses ($x=5, 10, 15$).

Fig. 4. Polarized Raman spectra of $\text{ZnBr}_2\text{-KBr-PbBr}_2$ glasses.

these bands is not contrary to the results of Raman spectroscopy of $\text{ZnBr}_2\text{-KBr}$ molten mixture.⁶⁾

The subsidiary band at 130 cm^{-1} which is also highly polarized as shown in Fig. 4 may be due to a symmetric mode containing Pb-Br stretching in comparison with the 133 cm^{-1} band in the spectrum of KPb_2Br_5 crystal. The intensity of the band is invariant with the change in composition at constant PbBr_2 .

Figures 3(b) and 3(c) show the variation of Raman spectra with the replacement of ZnBr_2 by PbBr_2 at 40 mol % KBr and with the replacement of KBr by PbBr_2 at the constant Br/Zn ratio ($=3$), respectively. As shown in the spectra in both variations, the 130 cm^{-1} band increases in the intensity compared to the 155 cm^{-1} or 174 cm^{-1} band with the increase of PbBr_2 . This supports the above assignment of the 130 cm^{-1} band. The pronounced increase of the band in the region lower than 110 cm^{-1} is due to strong intensity of the modes containing bending vibrations of bromide ion coordinating to lead, which are also observed as strong bands at frequency lower than 100 cm^{-1} in the spectrum of KPb_2Br_5 crystal in Fig. 2.

As shown in Fig. 3 (b), the replacement of ZnBr_2 by PbBr_2 increases the intensity of the 174 cm^{-1} band comparing with that of the 155 cm^{-1} band indicating that the number of $n\text{bBr}$ increases. This is partly because the amount of KBr relative to that of ZnBr_2 increases. Another possible reason is that $n\text{bBr}$'s are also formed by the introduction of PbBr_2 itself. This is inferred from

Fig. 5. Reduced Raman spectra and curve fittings by Gaussian lines of $(60-x)\text{ZnBr}_2 \cdot 40\text{KBr} \cdot x\text{PbBr}_2$ glasses; (a) $x=5$, (b) $x=10$, (c) $x=15$, (d) $x=20$. The residuals are also shown in the upper side of the each figure.

the fact in Fig. 3 (c) that the relative intensity of the 174 cm^{-1} band to that of the 155 cm^{-1} band seems to be invariant with composition. The replacement of KBr by PbBr_2 decreases the amount of KBr to that of ZnBr_2 , and the intensity of the 174 cm^{-1} band should decrease if $n\text{bBr}$'s were formed only by the introduction of KBr. Therefore, PbBr_2 substituted for KBr in this compositional range qualitatively has the same effect on the network structure as that of KBr. For the more detailed discussion on the structural role of PbBr_2 , the correction of the spectra for frequency and temperature dependence and deconvolution of the reduced Raman spectra were carried out. This will be described in the next section.

3.3 Curve fitting of spectra

The compositional dependence of the intensity of $\text{Zn}-b\text{Br}$ and $\text{Zn}-nb\text{Br}$ stretching bands were elucidated in more detail by the correction of Raman spectra for temperature and frequency dependence and the deconvolution into Gaussian lines. Figure 5 shows some reduced Raman spec-

tra and the Gaussian curves derived from the deconvolution as dotted lines for the series of the constant KBr content (40 mol %) shown in Fig. 3 (b). The superimposed spectra of the Gaussian lines are depicted by solid lines. The reduced Raman spectra of the glasses containing 5 mol % and 10 mol % PbBr_2 were fitted by six Gaussian lines, peaks of which are located at around 80 cm^{-1} , 132 cm^{-1} , 155 cm^{-1} , 174 cm^{-1} , 205 cm^{-1} and 245 cm^{-1} . For the spectra of the glasses containing 15 mol % and 20 mol % PbBr_2 , curve fittings by five Gaussian lines having peaks at around 80 cm^{-1} , 132 cm^{-1} , 155 cm^{-1} , 174 cm^{-1} and 200 cm^{-1} were better than the fittings with six lines. The residuals shown in Fig. 5 indicate that the curve fittings were satisfactory. The intensity of a band was calculated from the area of each Gaussian line. The relative intensity of the 155 cm^{-1} band to the 174 cm^{-1} band ($I_{155}/(I_{155} + I_{174})$) were plotted against the Br/Zn ratio in Fig. 6 for the ZnBr_2 -KBr- PbBr_2 system and for the ZnBr_2 -KBr system.¹⁾ The number of $n\text{bBr}$ per Zn is calculated by the equation; $n\text{bBr}/\text{Zn} = 2^*$

Fig. 6. Relative intensity of the band at 155 cm^{-1} of the ZnBr_2 -KBr-PbBr₂ and the ZnBr_2 -KBr glasses as a function of Br/Zn ratio.

(Br/Zn-2), assuming that zinc ion is four-fold coordinated and that bromide ion is bound to one or two zinc ions which corresponds to $nb\text{Br}$ or $b\text{Br}$, respectively.

As mentioned in Section 3.2 the relative intensity is invariable within error of the curve fitting for the replacement of KBr by PbBr₂ (referred by Δ in Fig. 6). This indicates that PbBr₂ has the same role as that of KBr in the sense of increasing $nb\text{Br}$ in the network structure. Moreover, it is interesting that the relative intensity of the 155 cm^{-1} band is not zero even at the composition of Br/Zn=4 in the ZnBr_2 -KBr-PbBr₂ system, though extrapolated value of $I_{155}/(I_{155} + I_{174})$ to Br/Zn=4 depicted by dotted line is zero for the ZnBr_2 -KBr system. The existence of $b\text{Br}$ at this composition suggests that there are free bromide ions and/or zinc ions coordinated by more than four bromines. Since it has been suggested that there are free oxide ions in oxide

glasses,⁷⁾ the existence of free bromide ion is not so surprising in consideration of the more ionic property of halide melts. However further examination will be necessary for a discussion on the possibility of zinc ion existing in the state coordinated by more than four bromines.

4. Conclusion

The 155 cm^{-1} and 174 cm^{-1} bands observed in the Raman spectra of ZnBr_2 -KBr-PbBr₂ glasses were assigned to the modes containing Zn- $b\text{Br}$ and Zn- $nb\text{Br}$ stretching, respectively, in comparison with the Raman spectra of ZnBr_2 and K_2ZnBr_4 crystals and also taking account of the compositional dependence of the intensity of these bands. PbBr₂ was found to have the same role on the network structure as that of KBr in the sense of increasing $nb\text{Br}$. Moreover, the existence of free bromide ions and/or zinc ions coordinated by more than four bromines was suggested in the glasses containing 20 mol % PbBr₂.

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