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Local structure around Zr^{4+} in ZrF_4 – BaF_2 – $BaCl_2$ – EuF_3 glasses

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Abstract. The anion coordination environments around Zr^{4+} in ZrF_4 – BaF_2 – $BaCl_2$ – EuF_3 system glasses were examined by Zr K-EXAFS, Raman scattering, and IR absorption spectroscopies. Experiments were performed with $58ZrF_4 \cdot (39 - x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses in which the x values were changed from zero to 29 in batch composition. These spectroscopic analyses reveal that the anion coordination environments around Zr^{4+} are hardly changed by the successive substitution of Cl for F. These results agree with our previous study using molecular dynamics simulations.

1. Introduction

Heavy-metal fluoride glasses, which are represented by fluorozirconate glasses, have received much attention because of the potentiality of their practical application to various active optical materials [1, 2]. The potentiality originates from the peculiar properties of the glasses, e.g. optical transparency ranging from the middle infrared to the near ultraviolet, low light transmission losses, low phonon energies, and stable incorporation of rare earth ions available for generating active optical functions. Host materials for these optical devices are centred in the ZrF_4 glass system, because of its high glass forming ability.

As a host matrix of these optical devices, chlorofluorozirconate glasses have several unique characteristics. The introduction of chlorine into fluorozirconate glasses increases the refractive index, and fibre optics with a fluoride clad/chlorofluoride core exhibit an increased numerical aperture with extended infrared transmission [3]. There are several studies of the structures of chlorofluorozirconate glasses: Almeida *et al* have deduced the local structure of ZrF_4 – BaF_2 – $BaCl_2$ glass by measuring Raman and IR spectra [4]. Elyamani *et al* have reported some optical and physical properties of multicomponent chlorofluorozirconate glasses [3]. Recently, Inoue *et al* have examined the structure of fluoride glass containing chloride ions by means of computer simulation and x-ray diffraction [5]. These studies have suggested that $ZrClF$ polyhedra are present, and that Zr–Cl bonds bring some unique characteristics to the chlorofluorozirconate glasses. We have also reported the local structure of ZrF_4 – BaF_2 – $BaCl_2$ – EuF_3 system glasses produced by molecular dynamics simulation [6]. Our simulation results reveal that the local structure around Zr^{4+} is hardly influenced by anion substitution of Cl for F, but the network connectivity of ZrF polyhedra is slightly influenced by the introduction of Cl^- ions. The Zr–Cl bonds were hardly observed in our simulation glass of which the anion ratio, $[Cl]/([F] + [Cl])$, is below 0.1.

EXAFS spectroscopy is one of the most powerful methods to examine the local structure around glass constituent ions. For fluorozirconate glasses, several studies using EXAFS spectroscopy have reported for some fluoride glass constituent ions such as Zr^{4+} , Ba^{2+} and so on [7–10]. However no EXAFS analysis has been carried out for Zr^{4+} in a chlorofluoride glass system. This paper presents the local structure around Zr^{4+} in ZrF_4 – BaF_2 – $BaCl_2$ – EuF_3 glass systems by using Zr K-EXAFS, Raman scattering, and IR absorption spectroscopies.

2. Experimental procedure

2.1. Glass preparation

Glasses of $58ZrF_4 \cdot (39 - x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ compositions ($x = 0, 5, 10, 15, 19, 24,$ and 29) in mol% were prepared according to the following procedure. High-purity reagents ZrF_4 , BaF_2 , $BaCl_2$, and EuF_3 were used as raw materials. About 4 g batches of the raw materials were melted at $700^\circ C$ for about 20 min in Pt crucibles under an Ar atmosphere. Then the melts were poured into brass moulds kept at a temperature of about $100^\circ C$. The obtained glasses were annealed at the respective glass transition temperatures determined by DTA. The accurate Cl contents of the prepared glasses were determined by x-ray fluorescence analysis. The molar volumes of the glasses were obtained by density measurement with an Archimedean method. The refractive indexes were measured with an Abbe refractometer.

Hereafter the $x = 0, 5, 10, 15, 19, 24,$ and 29 glasses are abbreviated as glass 0Cl, 3Cl, 6Cl, 9Cl, 12Cl, 15Cl, and 18Cl, respectively, in terms of the anion ratio of Cl to (F + Cl) in batch composition, i.e. 0, 3, 6, 9, 12, 15, 18%.

2.2. Zr K-EXAFS measurements

Zr K-EXAFS experiments were performed on the 0Cl–18Cl glasses at the EXAFS facilities at beam line 10B of the Photon Factory in the National Laboratory for High-Energy Physics. Details of the experimental procedure have already been described in previous papers [7, 8].

2.3. Vibrational spectra measurements

Raman scattering measurements were carried out at 5 cm^{-1} resolution with a Jeol JRS-400D spectrometer, using the 488.0 nm line of an Ar^+ gas laser. The measurements were made on the 0Cl, 6Cl, 12Cl, and 18Cl glasses. IR absorption measurements were made on the 0Cl, 6Cl, 12Cl, and 18Cl glasses at a resolution of 4 cm^{-1} with a Perkin–Elmer FT-IR 1760, using the polyethylene pellet technique.

3. Results

3.1. Physical and optical properties

The analysed Cl contents of the prepared $58ZrF_4 \cdot (39 - x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses ($x = 0, 5, 10, 15, 19, 24,$ and 29) are given as the Cl/(F + Cl) values in table 1, together with the refractive indexes, the glass transition temperatures, and the molar volumes. The analysed Cl contents were proportional to the Cl contents in batch composition. The glass transition temperatures decreased and the refractive indexes and molar volumes increased in proportion to the substituted Cl amounts. The respective tendencies were in agreement with the previous study [3].

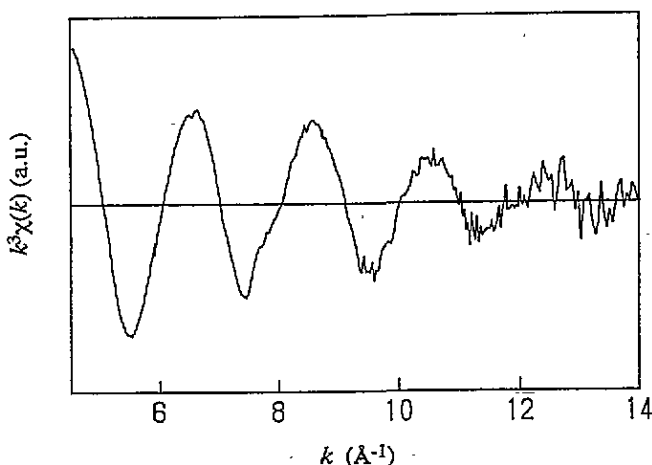
Table 1. Cl contents, Cl/(F + Cl), glass transition temperatures, T_g , refractive indexes, n , and molar volumes, V_m , of $58\text{ZrF}_4 \cdot (39 - x)\text{BaF}_2 \cdot x\text{BaCl}_2 \cdot 3\text{EuF}_3$ glasses.

Glass		Cl/(Cl + F)		n	T_g (°C)	V_m (cm ³ mol ⁻¹)
x	Notation	Batch	Analysed			
0	0Cl	0	0.00	1.5241	309	36.6
5	3Cl	3	1.71	1.5320	287	37.4
10	6Cl	6	3.20	1.5435	285	38.1
15	9Cl	9	5.09	1.5507	276	39.4
19	12Cl	12	6.23	1.5615	271	40.1
24	15Cl	15	7.50	1.5665	262	40.5
29	18Cl	18	8.95	1.5695	249	41.4

3.2. Zr K-EXAFS analysis

The Zr K-EXAFS oscillation, $k^3\chi(k)$, of 0Cl is shown in figure 1. The $k^3\chi(k)$ curves were analysed by using a XASANAL program [11]. Fourier transformation of $k^3\chi(k)$ was performed in the k range of 3.8 to 14.5 Å⁻¹ to obtain the Fourier transform magnitude, $|\phi(r)|$. The obtained $|\phi(r)|$ curves are shown in figure 2. Fourier backfiltering was conducted in the r range of 1.8 to 2.3 Å and then the curve fitting of $k^3\chi(k)$ was performed in the k region of 5.0 to 13.5 Å⁻¹ by employing a one-shell model where only F⁻ ions are scattering ions. The phase shift and backscattering amplitude values required in curve fitting were determined by simulation of the 0Cl glass using 2.10 Å and 7.08 for the Zr⁴⁺-F⁻ interionic distance and F coordination number of Zr, respectively; these were obtained by a previous x-ray diffraction study [12]. The features of curve fitting for the 0Cl glass are shown in figure 3.

The obtained Zr⁴⁺-F⁻ interionic distances, F⁻ coordination numbers of Zr⁴⁺, and Debye-Waller factors of glasses 0Cl-18Cl are summarized in table 2.

**Figure 1.** Zr K-EXAFS oscillation, $k^3\chi(k)$, of glass 0Cl.

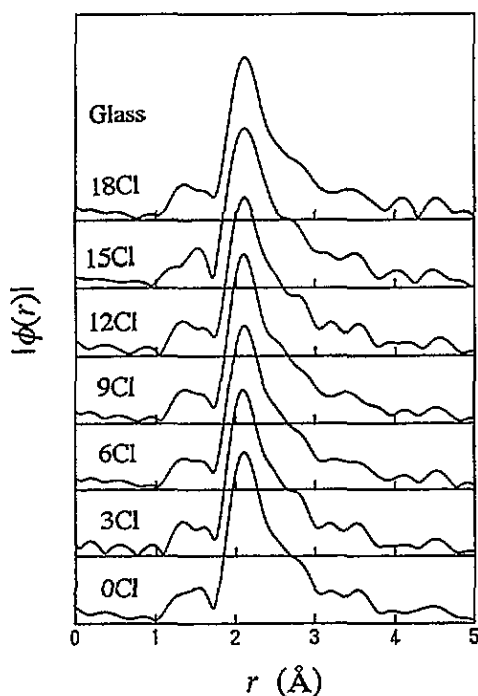


Figure 2. $|\phi(r)|$ curves of glasses.

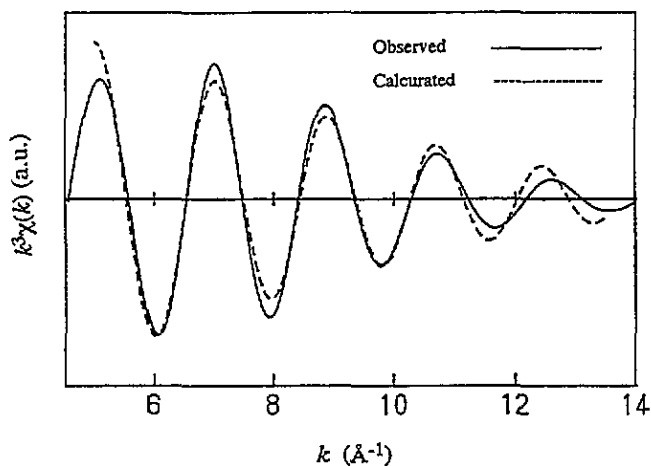


Figure 3. Feature of curve fitting for glass 0Cl.

3.3. Raman scattering spectra

The Raman scattering spectra of glasses 0Cl, 6Cl, 12Cl, and 18Cl are shown in figure 4. Each glass gave an intense scattering peak which is located at around 580 cm^{-1} . The accurate peak positions of the respective glasses are given in table 3.

Table 2. Interionic distances, $r_{\text{Zr-F}}$, anion coordinate numbers of Zr^{4+} , CN, and Debye–Waller factors, σ , in $58\text{ZrF}_4 \cdot (39-x)\text{BaF}_2 \cdot x\text{BaCl}_2 \cdot 3\text{EuF}_3$ glasses.

Glass	$r_{\text{Zr-F}}$ (Å)	CN	σ (Å ²)
0Cl	2.110 ^a	7.08 ^b	0.077
3Cl	2.108 ± 0.002	6.59 ± 1.3	0.077
6Cl	2.108 ± 0.002	6.87 ± 1.4	0.080
9Cl	2.107 ± 0.002	6.46 ± 1.3	0.076
12Cl	2.107 ± 0.002	6.46 ± 1.3	0.080
15Cl	2.105 ± 0.002	7.23 ± 1.4	0.083
18Cl	2.104 ± 0.002	6.46 ± 1.3	0.078

^{a,b} Obtained by x-ray diffraction [12].

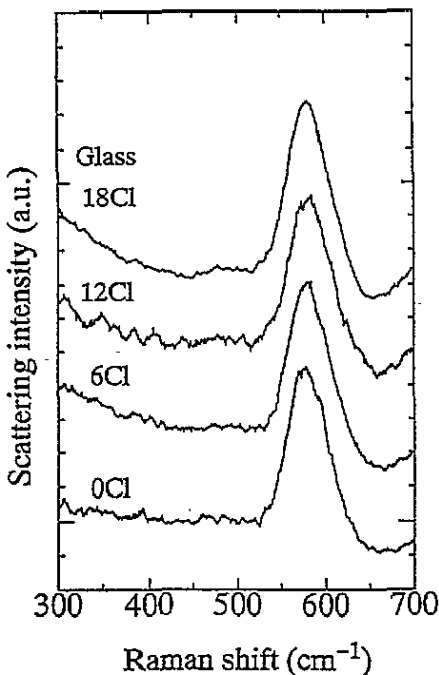


Figure 4. Raman scattering spectra of glasses 0Cl, 6Cl, 12Cl, and 18Cl.

3.4. IR absorption spectra

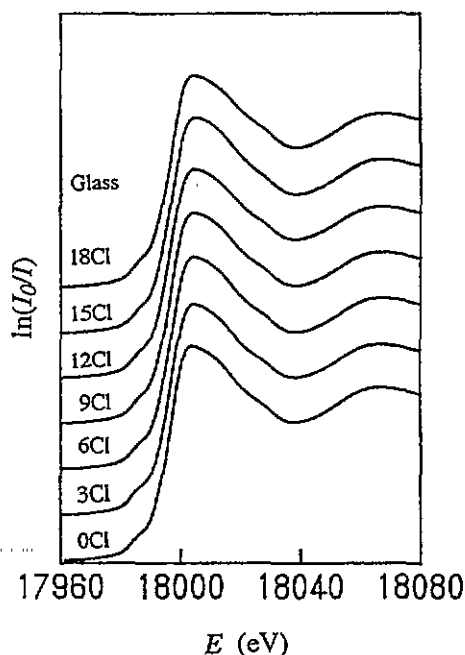
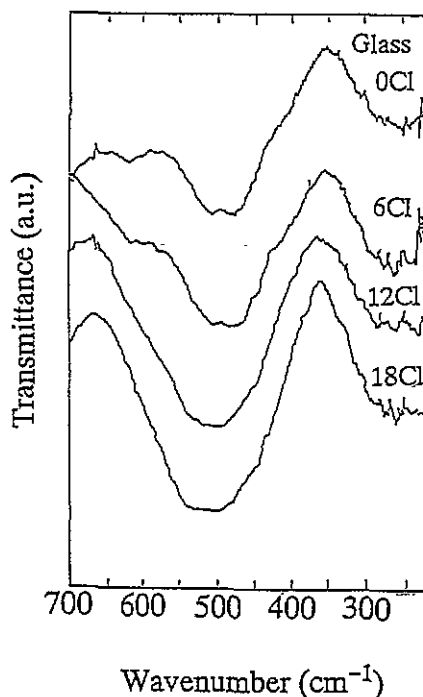
The IR absorption spectra of glasses 0Cl, 6Cl, 12Cl, and 18Cl are shown in figure 5. The strong absorption bands are observed at about 500 cm^{-1} in all the spectra. The accurate band positions of the 0Cl, 6Cl, 12Cl, and 18Cl glasses are given in table 3.

4. Discussion

Figure 6 shows the Zr K-XANES spectra of glasses. All spectra have similar profiles, and no major differences were detected between pure fluoride glass, 0Cl, and the other chlorofluoride glasses. This fact qualitatively suggests that the anion coordination structure

Table 3. Raman scattering and IR absorption bands of $58\text{ZrF}_4 \cdot (39-x)\text{BaF}_2 \cdot x\text{BaCl}_2 \cdot 3\text{EuF}_3$ glasses.

Glass	Raman (cm^{-1})	IR (cm^{-1})
0Cl	575 ± 5	493 ± 4
6Cl	578 ± 5	496 ± 4
12Cl	574 ± 5	505 ± 4
18Cl	579 ± 5	514 ± 4

**Figure 5.** IR absorption spectra of glasses 0Cl, 6Cl, 12Cl, and 18Cl.**Figure 6.** Zr K-XANES spectra of glasses.

around Zr in fluorozirconate glasses containing chloride ions is almost the same as that in pure fluoride glass, 0Cl.

The $|\phi(r)|$ curves obtained by Fourier transformation of $k^3\chi(k)$ give the radial distribution of the nearest-neighbouring anions around Zr^{4+} . As can be seen from figure 2, prominent peaks due to the Zr^{4+} -anion pairs locate at around 2.1 \AA regardless of the Cl content and, in addition, all the $|\phi(r)|$ curve profiles are almost the same. Here the following fact should be noted: curve fitting of $k^3\chi(k)$ should be attempted by employing a two-shell model where both F^- ions and Cl^- ions are scattering ions, but the calculations were impossible for all glasses because of divergence. These facts indirectly indicate that most of the Cl^- ions in $58\text{ZrF}_4 \cdot (39-x)\text{BaF}_2 \cdot x\text{BaCl}_2 \cdot 3\text{EuF}_3$ glasses take no part in

the anion coordination to Zr^{4+} ions, and most of the Zr^{4+} ions are coordinated by F^- ions alone. Therefore, the Zr^{4+} -anion interionic distance and the anion coordination number of Zr^{4+} , which are given in table 2, mean the Zr^{4+} - F^- interionic distance, r_{Zr-F} , and the F^- coordination number of Zr^{4+} , CN, respectively.

Figure 7 shows the r_{Zr-F} values plotted against the $Cl/(F + Cl)$ values. As seen from the figure, r_{Zr-F} tends to slightly decrease with increasing $Cl/(F + Cl)$ values, although such a slight decrease should be considered to be within experimental error.

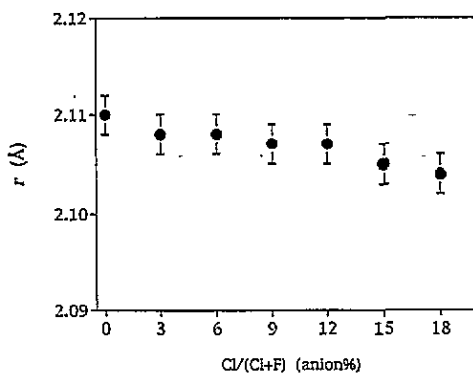


Figure 7. Interatomic distances, r_{Zr-F} , as a function of $Cl/(F + Cl)$ values.

The Raman bands around 580 cm^{-1} and the IR bands around 500 cm^{-1} have been assigned to the totally symmetric stretching vibration, ν^s , and antisymmetric stretching vibration, ν^{as} , of ZrF polyhedra [13, 14]. As given in table 3, the ν^s frequencies remain almost unchanged in spite of the successive Cl substitution, while the ν^{as} frequencies shift from 493 cm^{-1} for the 0Cl glass to 514 cm^{-1} for the 18Cl glass. From a quantum mechanical point of view, vibrations in which the dipole moment of molecules is changed are IR active and those in which the polarizability of molecules is changed are Raman active. The Raman scattering and IR absorption spectra observed for the $58ZrF_4 \cdot (39 - x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses suggest that the r_{Zr-F} and CN values are almost unchanged with the Cl substitution, but the F^- coordination configurations around Zr^{4+} are slightly changed, causing an IR active vibration mode to shift to higher frequencies.

Finally it is concluded that, when the F^- ions in $58ZrF_4 \cdot 39BaF_2 \cdot 3EuF_3$ glasses were partly substituted by Cl^- ions, the F^- ions placed in the ZrF polyhedra are hardly replaced by the Cl^- ions, though slight amounts of replacement are not ruled out. In other words, it is presumed that the F^- ions participating in the $Eu-F-Ba$ and $Ba-F-Ba$ linkages are preferentially replaced by the Cl^- ions. These results are in good agreement with our previous simulation study [6].

5. Conclusion

The anion coordination environments around Zr^{4+} in chlorofluorozirconate glasses were investigated by choosing $58ZrF_4 \cdot (39 - x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ compositions. The Zr K-EXAFS, Raman scattering, and IR absorption spectroscopic experiments on the glasses revealed that the successive substitution of Cl for F hardly changes the anion coordination environments around Zr^{4+} .

Acknowledgment

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