Original Paper

Vibrational spectra and structure of ZrF_4–FeF_3–PbF_2–YF_3 fluoride glasses

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Results of the investigation of infrared and Raman spectra in heavy metal fluoride glasses based on the $ZrF_4-FeF_3-PbF_2-YF_3$ system are presented. Infrared and Raman bands in the spectra of these glasses are discussed. The coordination environments of both Zr^{4+} and Fe^{3+} ions have been extracted from the vibrational modes. A structural model for these glasses is proposed. It is composed of the basic network formers ZrF_7 polyhedra and FeF_6 octahedra, which are randomly linked by corners and/or edges to construct a disordered three-dimensional network, whereas the Pb^{2+} and Y^{3+} ions are assumed to play the role of network modifier and stabilizer, respectively.

Schwingungsspektren und Struktur von Fluoridgläsern des Systems ZrF_4–FeF_3–PbF_2–YF_3

Es werden Untersuchungsergebnisse der Infrarot- und Raman-Spektren von Schwermetallfluoridgläsern des Systems $ZrF_4-FeF_3-PbF_2-YF_3$ vorgestellt und die Infrarot- und Raman-Banden in den Spektren dieser Gläser diskutiert. Die koordinativen Umgebungen der Zr^{4+}- und Fe^{3+}-Ionen lassen sich aus den Schwingungszuständen erschließen. Ein Strukturmodell für diese Gläser wird vorgeschlagen. Es setzt sich zusammen aus netzwerkbildenden ZrF_7-Polyedern und FeF_6-Oktaedern, die durch willkürliche Verbindungen an Ecken und/oder Kanten zum Aufbau eines ungeordneten dreidimensionalen Netzwerkes beitragen; dagegen wird von den Pb^{2+}- und Y^{3+}-Ionen angenommen, daß sie als Netzwerkwandler bzw. als -stabilisator wirken.

1. Introduction

The occurrence of heavy metal fluoride glasses has attracted considerable interest in their potential uses as infrared optical components, ultra-low-loss optical fibres, and fluoride ion conductors [1 to 3]. Moreover, heavy metal fluoride glasses based on transition metal fluorides have also been explored and developed because of their peculiar characteristics of optical, electrical and magnetic behaviour [4 and 5].

Almeida and Mackenzie [6] reported the infrared and Raman spectra study of fluorozirconate glasses. They found that the basic structure of $2\,ZrF_4 \cdot BaF_2$ consists of zigzag chains of ZrF_6 octahedra, cross-linked by Ba–F ionic bands, and that the metafluorozirconate glass $ZrF_4 \cdot BaF_2$ contains 7-coordinated zirconium atoms. Employing the molecular dynamics computer simulation technique, Angell [7] came to the conclusion that zirconium is 7-coordinated by fluorine and the Zr–Zr distance is twice the Zr–F distance. The authors [8 and 9] suggested that chains of edge-shared as well as corner-shared ZrF_8 dodecahedra ionically linked by Ba^{2+} or Pb^{2+} cations be the basic structure of ZrF_4-based glasses. Structural investigations of transition metal fluoride glasses were made by vibrational spectroscopy [10], EXAFS, neutron and X-ray diffraction [11]. Results indicate that MF_6 (M = transition metal) octahedra are the basic structural unit of 3d transition metal fluoride glasses and that they are predominantly linked by corners but the possibility of edge sharing is not excluded.

The present paper reports the vibrational spectra study of $ZrF_4-FeF_3-PbF_2-YF_3$ glasses, a new kind of mixed fluorozirconate–transition metal fluoride glasses discovered recently [12].

Since Zr^{4+} and Fe^{3+} ions are able to act as glass network formers in ZrF_4-based glasses and transition metal fluoride glasses, it can be assumed that there might be two network formers existing simultaneously in the structure of these glasses. Hence, a new question referring to the structure of mixed fluorozirconate–transition metal fluoride glasses is raised.

2. Experimental procedures

The glass compositions used in this study are presented in table 1. The raw materials PbF_2, ZrO_2, Fe_2O_3 and Y_2O_3, obtained from a commercial source, were mixed completely with an excess of $NH_4F \cdot HF$ and melted in covered platinum crucibles under reactive atmospheres ($CCl_4 + N_2$) by a resistance-heated furnace. Melting was done for 4 to 6 h at maximum temperatures of 680 to 850 °C, depending on the given composition. The glass melts were then poured between two brass blocks and annealed near their transition temperature.

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Table 1. Glass compositions (in mol%)

glass	ZrF_4	FeF_3	PbF_2	YF_3
A	37.7	4.7	51.9	5.7
B	33.0	14.1	47.2	5.7
C	4.7	37.7	51.9	5.7
D	–	50	50	–

Infrared absorption spectra were measured by the KBr disc method with a Shimadzu IR-450 spectrophotometer (Shimadzu Scientific Instruments, Inc., Kyoto (Japan)) over a wave number range 4000 to 200 cm^{-1}. Polarized Raman spectra (40 to 700 cm^{-1}) were measured on a Spex 1403 spectrometer (Spex Industries, Inc., Edison, NJ (USA)) equipped with a coherent 90 argon ion laser, at 90° scattering geometry. The 514.5 nm laser line was used mostly for excitation. All spectra were recorded in the HH (//) configuration, and the spectral slit width was 5 cm^{-1}. Bulk samples of typically 1 to 1.5 mm in thickness were polished water-free on all sides, except for crystalline FeF_3, which was ground to powder and sealed in a fused silica tube for examination. All measurements were taken at room temperature.

3. Results and discussion

3.1. IR spectra

Figure 1 shows the IR absorption spectra for the glasses studied as well as a spectrum of a $2\,ZrF_4 \cdot PbF_2$ glass. Two main absorption bands appear for glasses A to D, a broad strong band at ≈450 to 490 cm^{-1} and a weak band at ≈255 to 275 cm^{-1}.

According to the results of Bendow et al. [13 and 14], the high-frequency band may be assigned to the stretching vibrations of glass formers, such as zirconium or hafnium complexes with fluorine, whereas the low-frequency band may be due to bending modes of zirconium or hafnium with fluorine and/or stretching vibrations of Ba–F or Pb–F. Therefore, for the glass $2\,ZrF_4 \cdot PbF_2$, whose structure consists mostly of short chains of ZrF_6 octahedra [15], the strong band at 485 cm^{-1} is assigned to the stretching vibrations of Zr–F and the weak band at 270 cm^{-1} to the bending modes of Zr–F as well as to the Pb–F stretching vibrations. For glass D, for which FeF_6 octahedra are the basic network formers [16], the strong band at 490 cm^{-1} is assigned to the stretching vibrations of Fe–F and the weak band at 255 cm^{-1} to the bending modes of Fe–F as well as to the Pb–F stretching vibrations. For the mixed fluorozirconate iron fluoride glasses A to C, it is therefore apparent that the strong bands at ≈450 to 475 cm^{-1} originate from the overlap of Zr–F and Fe–F stretching vibrations, and the weak bands at ≈270 to 275 cm^{-1} from the overlap of Zr–F and Fe–F bending modes

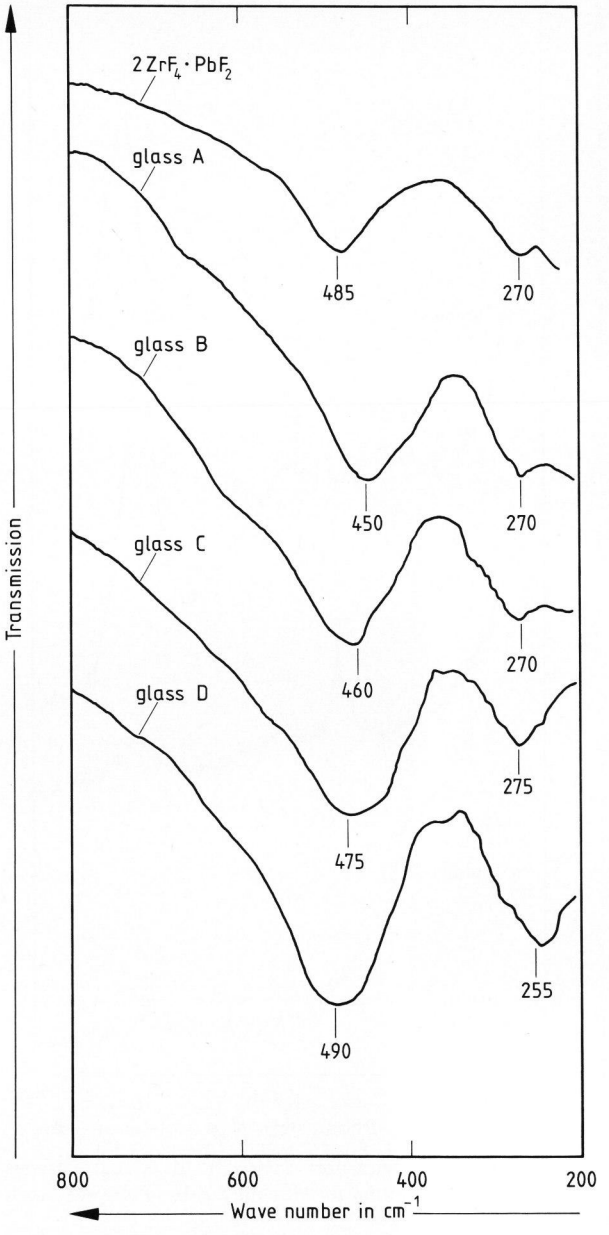

Figure 1. IR transmission versus wave number for glasses A to D and vitreous $2\,ZrF_4 \cdot PbF_2$.

and Pb–F stretching vibrations. On the other hand, the position of the high-frequency band might be connected with the coordination number (CN) of glass former complexes, as it is suggested that an increase in vibrational frequencies of fluorozirconate glasses indicate a decrease in the CN of zirconium and an increase in the degree of the network bridging [6]. If this is the case, the CN of zirconium for the investigated glasses will be higher than 6 in the $2\,ZrF_4 \cdot PbF_2$ glass, as the position of the strong band for the studied glasses (450 to 475 cm^{-1}) is lower than that for the glass $2\,ZrF_4 \cdot PbF_2$ (485 cm^{-1}). So it is tentatively assumed that the possible CN of zirconium for the present glasses is 7, which is also given further confirmation by Raman spectra (see section 3.2.). Moreover, there is a tendency for the position of the

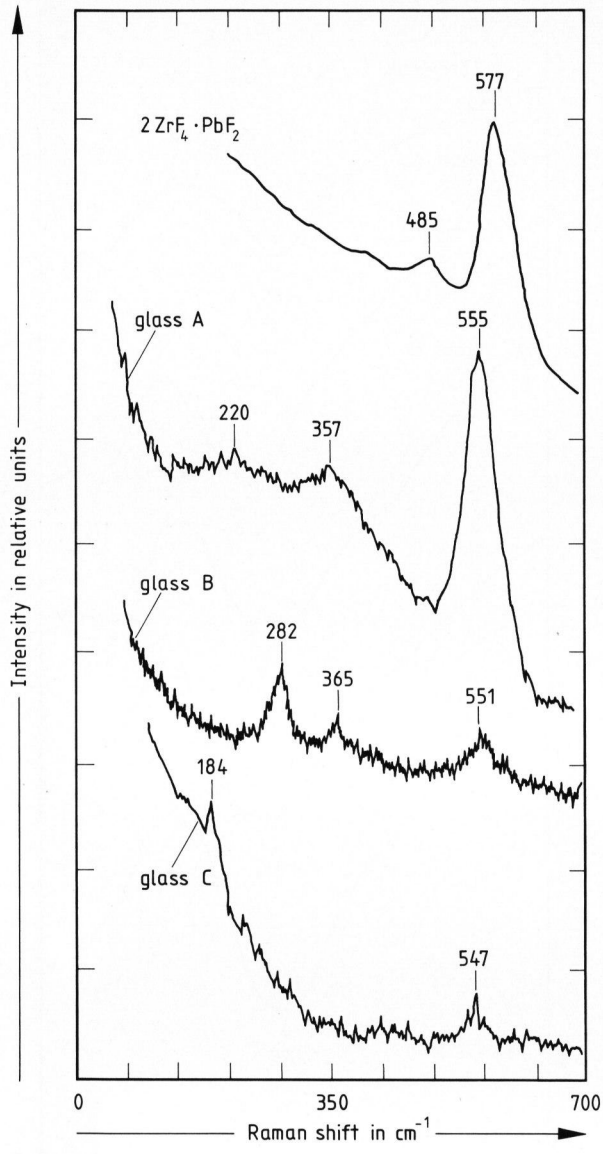

Figure 2. Raman spectra for glasses A to C and vitreous $2\ ZrF_4 \cdot PbF_2$ (the spectrum for vitreous $2\ ZrF_4 \cdot PbF_2$ was taken from [17]).

strong band to move from low frequencies to high frequencies with FeF_3 concentrations in the range from 5 to 40 mol%. It goes without saying that band shifting to high frequencies is due to an increase of FeF_6 octahedra (CN = 6) and a decrease of ZrF_7 polyhedra (CN = 7), probably accompanied by a decrease in the degree of network bridging. For glass D ($FeF_3 \cdot PbF_2$), where only the FeF_6 octahedron is the basic network former, the high-frequency band (490 cm^{-1}) is approximately the same as for the glass $2\ ZrF_4 \cdot PbF_2$ (485 cm^{-1}).

3.2. Raman spectra

Figure 2 presents the Raman spectra for glasses A to C and vitreous $2\ ZrF_4 \cdot PbF_2$ which was taken from [17]. The spectra observed for the present

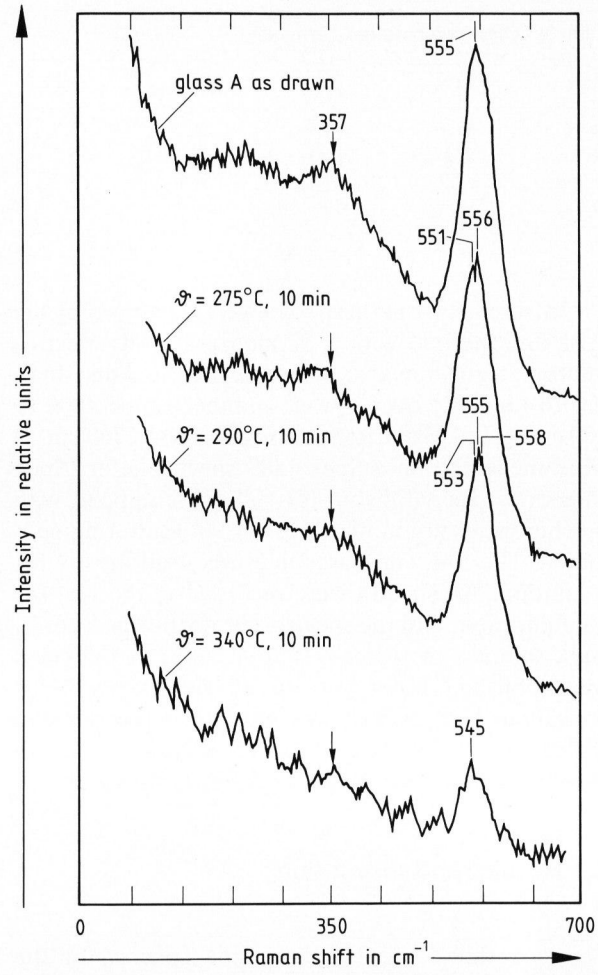

Figure 3. Different Raman spectra for glass A before and after various heat treatments.

$ZrF_4-FeF_3-PbF_2-YF_3$ glasses are characterized by a dominant band at ≈555 to 547 cm^{-1}, which, apart from the lower frequency, is quite similar to the band at ≈577 cm^{-1} for the glass $2\ ZrF_4 \cdot PbF_2$. The latter band was assigned to symmetric stretching modes (ν^s) of ZrF_6 octahedra [15]. As noted in section 3.1. for the infrared spectra, there is an inverse correlation between the symmetric stretching frequency and the CN of zirconium in the complex ions present in the structure of both crystalline compounds [18] and glasses [6]. Thus, the CN of zirconium for the present glasses may be higher than 6. Furthermore, in comparison with $\nu^s = 556\ cm^{-1}$ for 7-coordinated Na_3ZrF_7 [18], it is assumed that the possible CN of zirconium is 7. Therefore, such a dominant band for the studied glasses may be attributed to the symmetric stretching modes of 7-coordinated ZrF_7 polyhedra. A medium band at ≈357 to 365 cm^{-1} may be assigned to the symmetric stretching modes of the bridging fluorine atoms F_b with Zr^{4+} ions, while a similar band for fluorozirconate glasses is near 485 cm^{-1} [6]. This assignment is interpreted in the following manner. The Raman spectra of glass A were measured with a sequence of heat treatments

(for glass A, $T_g = 249\,°C$, $T_x = 340\,°C$, T_x is the crystallization temperature of fluoride glasses) as shown in figure 3. After different heat treatments, the band near $357\,cm^{-1}$ gradually vanishes with the increase of the degree of crystallization. Since it is reasonable to assume that the crystallization process of the investigated glass may break the bridging fluorine (in order to fulfil the structural rearrangement) and result in a decrease of F_b simultaneously, it could be anticipated that the decrease of F_b would be responsible for the disappearance of the band near $357\,cm^{-1}$. Thus, this band may arise from the symmetric stretching modes of Zr–F_b. In addition, the obvious modified line shape in the 551 to $556\,cm^{-1}$ region for the heat-treated glass A could also be expected from the phase separation and crystallization of the glass, as discussed in detail [19]. The third band at 220 to $280\,cm^{-1}$ is tentatively assigned to the vibrational modes of Fe–F, whose intensity increases with the increase of FeF_3 content (compare also with the Raman spectrum of FeF_3 (figure 4)).

The replacement of ZrF_4 by FeF_3 results in a systematic decrease of the intensity of the high-frequency band near $555\,cm^{-1}$, and an increase of the intensity of the band at $220\,cm^{-1}$. Both bands are consistent with the decrease of ZrF_7 polyhedra and the increase of FeF_6 octahedra, respectively. When the concentration of FeF_3 significantly increases, there only remain many featureless and weak peaks or shoulders in the Raman spectra (glass C in figure 2), which are assumed to be due to the interference by the fluorescence originating from the high concentration of the Fe^{3+} ion.

Finally, similar to the IR spectra, the dominant band at high frequency shifting to low frequency with increasing FeF_3 content may be attributed partly to a decrease in the degree of network bridging.

4. Structure

The information on the structure given by the vibrational spectra of ZrF_4–FeF_3–PbF_2–YF_3 glasses provides the evidence that each zirconium atom is coordinated by seven F^- ions and the CN of iron is 6. Therefore, a structural model for the glasses studied is proposed in which the ZrF_7 polyhedra and FeF_6 octahedra, as the basic network formers, are randomly linked by corners and/or edges to construct a disordered three-dimensional network, whereas the Pb^{2+} and Y^{3+} ions are assumed to play the role of network modifier and stabilizer, respectively. Considering the flexibility of the coordination number of zirconium in heavy metal fluoride glasses, ZrF_6 and ZrF_8 polyhedra could also be expected in the glass structure. In addition, it appears that an increase in Fe^{3+} concentration may bring about a decrease in the degree of network bridging in the glass structure.

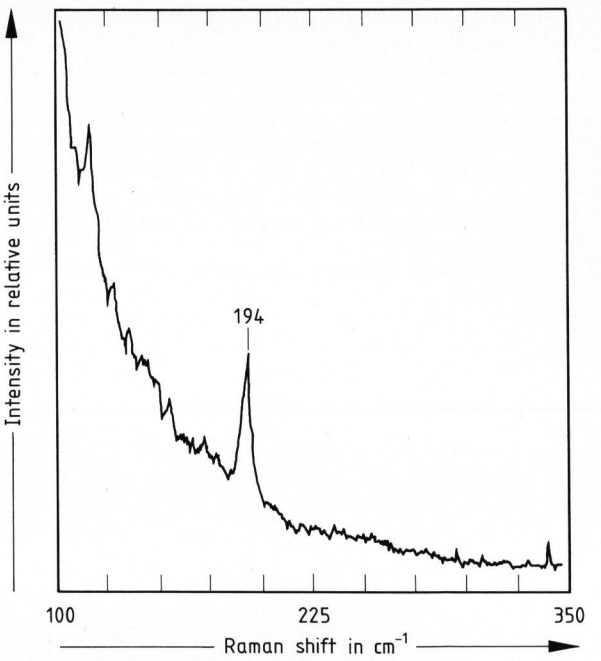

Figure 4. Raman spectrum for crystalline FeF_3.

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