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Oxide impurity absorptions in Ge–Se–Te glass fibres

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Oxide impurity absorptions in Ge–Se–Te glass fibres and the cause of the absorption loss around 943 cm^{-1}, the frequency of the CO_2 laser, have been investigated. The oxygen in the glass bounds preferentially to germanium and causes the absorptions due to Ge–O bond vibrations at 765 cm^{-1} (band I) and 1230 cm^{-1} (band II). The excess absorptions due to these bands were determined as 0.228 cm^{-1}/p.p.m. wt O_2 for band-I and 0.006 cm^{-1}/p.p.m. wt O_2 for band II. The loss of the fibre at 943 cm^{-1} increased with the oxygen content. It was, however, revealed from the deconvolution of the IR spectra into the independent absorption components that the absorption tails of band I and band II did not affect the loss at 943 cm^{-1}. The content of the impurities except oxygen analysed by a mass spectroscopy was too low to affect the loss at 943 cm^{-1}.

1. Introduction

Chalcogenide glasses are attractive materials for infrared transmitting fibres, which are useful for a wide range applications such as waveguides for CO_2 laser (10.6 μm) power delivery, IR imaging bundles and IR remote sensors. Recently we have reported the transmission losses of Ge–Se–Te and Ge–Se–Te–Tl glass fibres [1]. The lowest loss at 10.6 μm (943 cm^{-1}) of these fibres was less than 2 dB m^{-1}. However, the loss between 8 μm (1250 cm^{-1}) and 12 μm (833 cm^{-1}), the potential low loss region of the fibres, was still affected by some impurity absorptions. It was suggested that the extrinsic absorptions in this wavelength region was mainly caused by oxide impurities [2]. For example, the oxygen in Ge–Se or Ge–As–Se glasses bonds preferentially to germanium, causing the absorptions due to Ge–O bond vibrations around 1250 and 780 cm^{-1} [3, 4]. These absorption bands were also observed in Ge–Se–Te and Ge–Se–Te–Tl glass fibres at 1230 and 765 cm^{-1} and increased the transmission losses of the fibres. The intensity of these bands varied sensitively with the preparation processes of the fibres. Although many of the studies about the chalcogenide glass fibres have been reported [5–7], there has been no quantitative discussion of oxide impurity absorptions in fibres.

In this paper, we discuss the influence of the absorptions caused by oxide impurities on the transmission losses of Ge–Se–Te fibres. The absorption coefficients of Ge–O bands were determined from the intensities of their excess absorptions in Ge–Se–Te glasses doped with known amounts of GeO_2. In order to estimate the excess transmission loss of the fibre due to Ge–O bands at 943 cm^{-1}, the frequency of the CO_2 laser, the IR spectrum of the Ge–Se–Te glass was deconvoluted into the absorption bands due to Ge–O bond vibrations and the multiphonon processes of the base glass. Quantitative analysis of the oxygen and other impurities in the glass was carried out by an oxygen analyser and a mass spectrometer.

2. Experimental details

All of the glasses were prepared from elements of more than 6N purity. Germanium was treated with hydrogen gas at 900° C for 24 h. Selenium and tellurium were distilled in SiO_2 vessels under evacuation. The purified elements were weighed in a dried argon atmosphere, placed into a SiO_2 ampule, evacuated down to 5×10^{-7} Torr and then sealed. The ampules were heated in a rocking furnace at 850° C for 24 h and cooled to room temperature in air.

In the case of doping with GeO_2, a glass ingot of 150 g containing accurately weighed amount of 5N purity GeO_2 was remelted in a SiO_2 ampule at 850° C for 6 h in a rocking furnace and then quenched in air.

After annealing, the glasses were cut and polished into different thicknesses and measured the IR transmission spectra between 10 000 and 400 cm^{-1} (1 to 25 μm). The absorption coefficient α (cm^{-1}) was calculted from the following equation [3]

$$\alpha = \left(\frac{1}{d}\right) \cdot \ln(\{(1 - R)^2 + [(1 - R)^4 + 4R^2T^2]^{1/2}\}/2T) \qquad (1)$$

where T is the transmittance, R is the reflectivity and d is the sample thickness in cm.

Some glasses were drawn into fibres using a SiO_2 crucible with a nozzle at the bottom [1]. Transmission losses of fibres of 2.5 m in length were measured by the conventional cut back method. The diameter of the fibre was 400 μm.

The content of the oxygen and the other impurities in some of the glasses were measured by an oxygen

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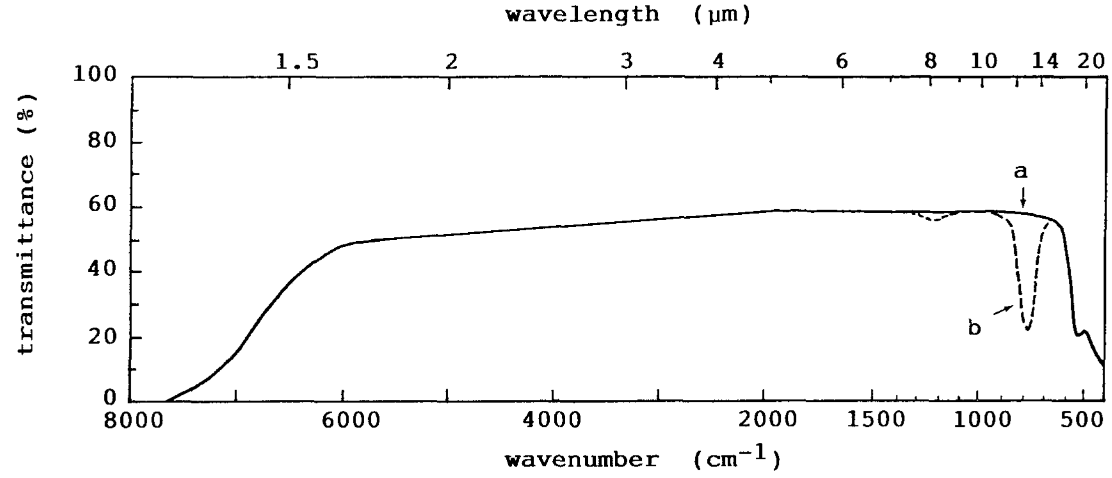

Figure 1 IR transmission spectra of $Ge_{25}Se_{15}Te_{60}$ glasses. Glass a was prepared from the purified raw elements. Glass b was doped with 70 p.p.m. GeO_2. The thickness of the glasses is 1.77 mm.

analyser (LECO TC-336) and a mass spectrometer (JEOL JMS-01BM3).

3. Results and discussion

Fig. 1a shows the IR spectrum of the purified $Ge_{25}Se_{15}Te_{60}$ glass, which is stable against crystallization in this ternary system [8]. The glass was transparent between 6000 and 800 cm^{-1}. As shown in curve b, two additional peaks were observed at 1230 cm^{-1} (8.13 μm) and 765 cm^{-1} (13.07 μm) for the glass doped with a small amount of GeO_2. These peaks have been also observed in Ge–Se [3], Ge–As–Se [4] and Ge–As–Te [9] glasses in similar positions. It is well known that the strong absorption band at 765 cm^{-1} (band I) is due to the stretching vibration of Ge–O bonds, which is precisely assigned in the hexagonal GeO_2 crystal and vitreous GeO_2 [10]. As suggested by Vlcek [3], the weak absorption at 1230 cm^{-1} (band II) might be attributed to a combination band of the stretching vibrations and the bending vibrations of the Ge–O–Ge bonds. Although there was no detailed description, band II was also observed in the IR spectrum of hexagonal GeO_2 at 1450 cm^{-1} [11]. The absorption caused by the bending vibration of the Ge–O–Ge bonds, which is located around 570 cm^{-1} for hexagonal GeO_2, could not be detected because of the overlap with intrinsic absorptions such as a two phonon process of the Ge–Se bond vibrations which are located in this region.

As listed in Table I, several glass samples doped with different amounts of GeO_2 were prepared. The oxygen contents measured by the LECO TC-336 are also listed in the table. Fig. 2 shows the dependence of the absorption coefficients of band-I (α_1) and band-II (α_2) in $Ge_{25}Se_{15}Te_{60}$ glasses on the oxygen content. The values of α_1 and α_2 increased linearly where the oxygen content was less than 50 p.p.m. When the oxygen content exceeded 100 p.p.m., there was a levelling off of these values and the segregation of the insoluble particles, possibly oxides of tellerium or germanium, was observed on the surface of the glasses. Within experimental error, the relationships between the values of α (cm^{-1}) and the oxygen content, $[O_2]$ (p.p.m. wt), for levels less than 50 p.p.m. are represented by the following equations

$$\alpha_1 = 0.228\,[O_2] \quad (2)$$

$$\alpha_2 = 0.006\,[O_2] \quad (3)$$

The values of the coefficient of correlation for these equations were more than 0.992. The content of oxygen bonding to germanium in the bulk glass and the fibre was estimated accurately from these equations. Fig. 3 shows the transmission loss spectra of unclad $Ge_{27}Se_{18}Te_{55}$ glass fibres. The fibre a was prepared from the commercially available raw elements of 6N grade, which were not purified. The absorption peak of band II was observed at 1230 cm^{-1} (8.13 μm).

TABLE I Absorption coefficients of band I and band II and the analysed oxygen content in $Ge_{25}Se_{15}Te_{60}$ glasses doped with various amounts of GeO_2

Number	Added amount of GeO_2 or O_2 (p.p.m. wt)		Absorption coefficient (cm^{-1})		Analysed oxygen content (p.p.m. wt)
	GeO_2	O_2	Band I (765 cm^{-1})	Band II (1230 cm^{-1})	
1	0	0	–	–	0.8
2	15.8	4.8	0.947	0.020	–
3	18.5	5.7	1.011	0.023	6.0
4	29.0	8.9	2.255	0.070	–
5	40.5	12.4	3.120	0.085	–
6	70.0	21.4	5.085	0.121	–
7	131.0	40.1	9.012	0.240	–
8	226.0	69.1	14.889	0.362	–
9	324.0	99.1	17.427	0.400	–
10	400.0	122.4	17.963	0.401	–

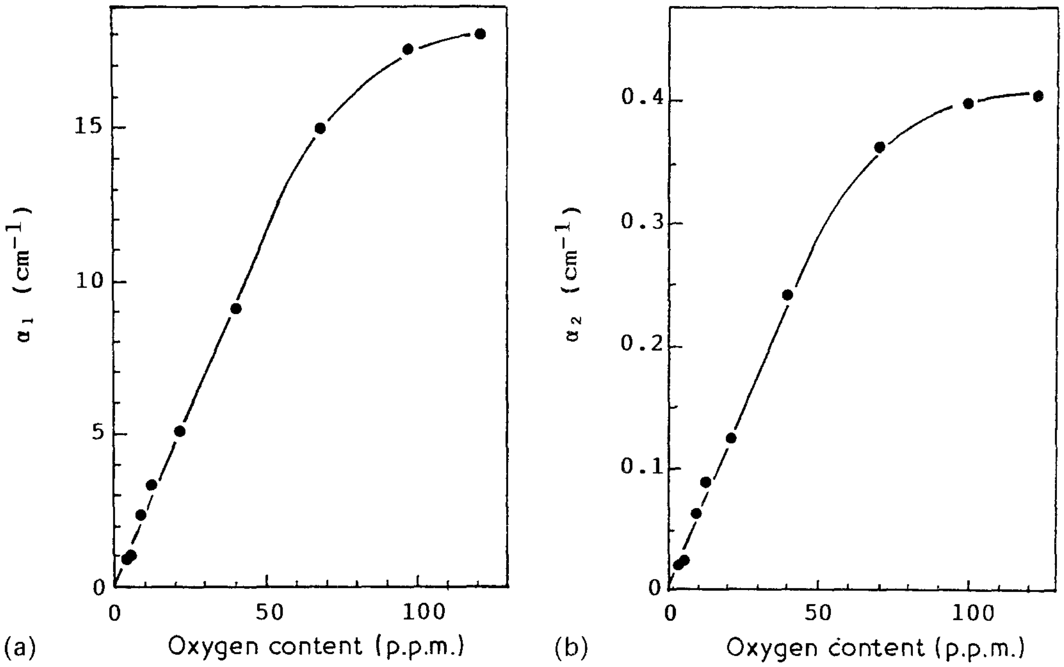

Figure 2 The dependence of the absorption coefficients of (a) band I (α_1) and (b) band II (α_2) in $Ge_{25}Se_{15}Te_{60}$ glasses on the oxygen content.

The excess loss due to band II was 1.5 dB m^{-1} (3.5×10^{-3} cm^{-1}) and the oxygen content in the fibre calculated from Equation 3 was 0.6 p.p.m. As recognized from the loss curve of fibre b, the peak height of band II was decreased to 0.1 dB m^{-1} (2.3×10^{-4} cm^{-1}) by the purification of the raw elements, i.e., the hydrogen reduction for germanium and the distillation for selenium and tellurium. The estimated oxygen content was 0.04 p.p.m.

In order to estimate the contribution of band I and band II to the excess loss at 943 cm^{-1}, the IR spectra between 1400 and 500 cm^{-1} were deconvoluted into band I, band II and the other absorption bands due to the glass matrix by assuming Gaussian distribution functions for each band. Fig. 4 shows the IR spectrum synthesized from the deconvoluted Gaussian components of the $Ge_{25}Se_{15}Te_{60}$ glass doped with 70 p.p.m. GeO_2. Although the spectra around 650 to 500 cm^{-1} were ambiguous because of the overlap of the tails of band I and the several multiphonon absorptions of the

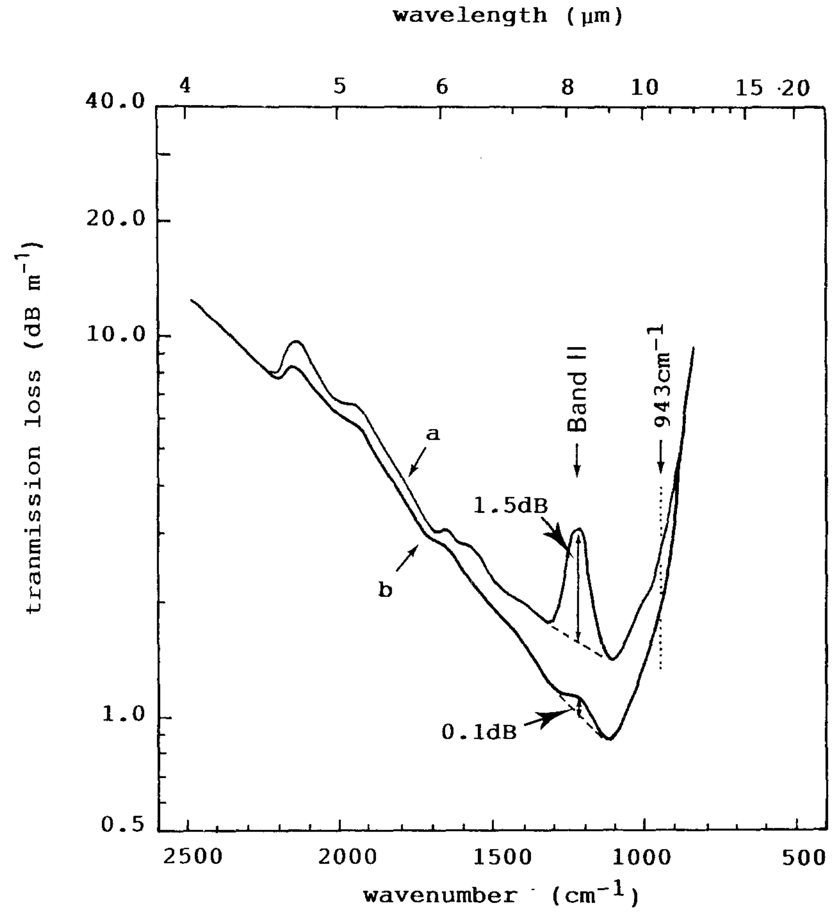

Figure 3 Transmission loss spectra of the unclad fibres of $Ge_{27}Se_{18}Te_{55}$ glasses. Fibre a was prepared from the raw elements of 6N grade, which was not purified before the glass preparation. The glass for fibre b was prepared from the purified raw elements.

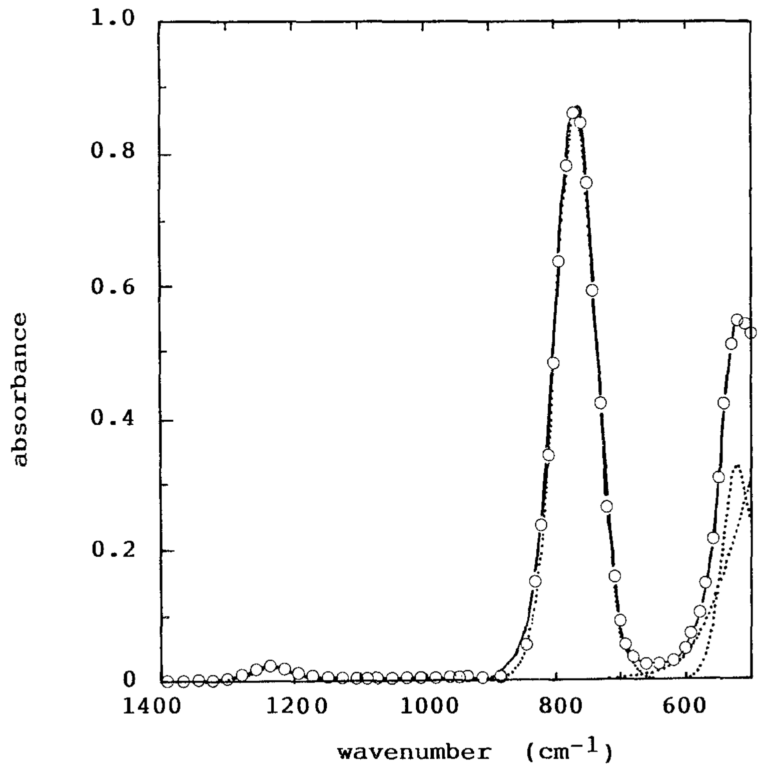

Figure 4 Deconvoluted IR spectrum of the $Ge_{25}Se_{15}Te_{60}$ glass doped with 70 p.p.m. GeO_2 (1.77 mm in thickness). The full curve is the measured spectrum. The spectrum synthesized from the deconvoluted components (broken curve) was shown by the open circles.

base glass, a good agreement between the measured spectra and the calculated spectra was obtained when two absorption bands due to the glass matrix were assumed at 520 and 330 cm^{-1}. The band at 520 cm^{-1} should be the two phonon process of the Ge–Se bond [3] and the band at 330 cm^{-1} was supposed to be caused by the other multiphonon absorptions. No apparent variation in the position and the halfwidth for each band was observed in the whole range of the spectra. The excess transmission losses due to band I and band II at 943 cm^{-1} estimated from the tails of the deconvoluted Gaussian components were 2.40×10^{-14} dB m^{-1} p.p.m. O_2 for band I and 4.12×10^{-12} dB m^{-1} p.p.m. O_2 for band II. Taking the experimental error into account, the content of oxygen forming the Ge–O bond in the purified Ge–Se–Te glass fibre was 0.04 ± 0.009 p.p.m. This value is negligibly low to affect the loss at 943 cm^{-1}.

Although, from our results represented above, the oxygen in Ge–Se–Te glasses bonds predominantly to germanium, it might be possible that a small fraction of the oxygen bonds to atoms other than germanium and causes absorption around 943 cm^{-1}.

Quantitative analysis of other residual impurities was carried out by the mass spectroscopy. Table II lists the contents of the impurities in the purified Ge–Se–Te glasses. The transmission losses at 943 cm^{-1} of the fibres drawn from these glasses are also shown in the table. Hilton *et al.* reported that the impurity affecting the transmission loss around 943 cm^{-1} was silicon [12], which forms the Si–O bond in the glass and causes the absorption around 1050 to 1000 cm^{-1}. Although the silicon content of these glasses varied from 0.02 to 0.9 p.p.m., there was no

TABLE II Impurities analysed by the mass spectroscopy in Ge–Se–Te glasses prepared from the purified raw elements

Composition	$Ge_{27}Se_{18}Te_{55}$	$Ge_{25}Se_{15}Te_{60}$		
Transmission loss (dB m^{-1}) at 943 cm^{-1}	2.0	2.1	2.3	2.0
Impurity (p.p.m. wt)				
C	0.2	0.02	0.05	0.05
Na	0.2	0.07	0.3	0.2
Mg	0.7	0.02	–	–
Al	0.03	0.02	0.02	0.1
Si	0.9	0.02	0.07	0.8
Cr	0.1	0.05	–	0.05
Fe	0.9	0.1	0.05	0.1
Zr	–	0.6	0.5	0.5
Ga	–	–	–	0.3
Mn	0.05	–	–	–
Tl	0.09	–	–	–
Total	3.17	0.90	0.99	2.10

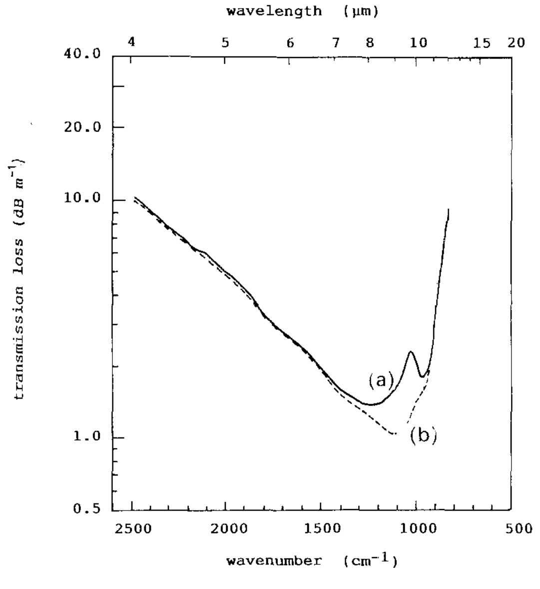

Figure 5 Transmission loss spectra of the $Ge_{27}Se_{18}Te_{55}$ glass fibre. Curve a is the loss of the fibre, which was kept in air for 7 days. The curve b is the loss of the same fibre measured immediately after the fibre preparation.

apparent correlation with the transmission losses of the fibres. The contents of the other impurities were considered to be too low to increase the loss of the fibre, even if these impurities form the oxides in the glass [9].

Another impurity absorption, which affects the loss around $1000\,cm^{-1}$, was observed in the loss spectrum of an unclad Ge–Se–Te glass fibre. The curve a in Fig. 5 is the transmission loss of the $Ge_{27}Se_{18}Te_{55}$ fibre, which was kept 7 days in air. An absorption peak is observed at $1030\,cm^{-1}$, which did not appear in the loss curve of the same fibre measured immediately after the fibre preparation (see curve b). This absorption could not be attributed to the absorption due to Ge–O bond vibration. Moynihan suggested that a small fraction of the oxygen in the As_2Se_3 glass bonds to selenium and causes the absorption due to Se–O bond vibration at $965\,cm^{-1}$ [13]. Although the origin of the absorption at $1030\,cm^{-1}$ remains unclear, this result indicates the possibility that a certain amount of the oxygen in Ge–Se–Te glasses bonds to selenium and tellerium. In order to minimize the increase of loss due to oxide impurities at $1030\,cm^{-1}$, the further purification of raw elements and the careful atmosphere control during the preparation of bulk glasses and fibres are required.

4. Conclusions

The oxygen in Ge–Se–Te glasses are bonded preferentially to germanium, causing the absorptions due to Ge–O bond vibrations at $765\,cm^{-1}$ (band I) and $1230\,cm^{-1}$ (band II). The excess absorptions due to these bands were determined at $0.228\,cm^{-1}$/p.p.m. O_2 for band I and $0.006\,cm^{-1}$/p.p.m. O_2 for band II. The oxygen content in the purified Ge–Se–Te glass fibre estimated from the transmission loss curve was 0.04 ± 0.009 p.p.m. It was revealed from the deconvoluted IR spectra that the absorption tails of band I and band II did not affect the loss at $943\,cm^{-1}$, even if all of the oxygen in the fibre bonds to germanium. The content of other residual impurities analysed by the mass spectroscopy were negligibly low. Another absorption peak, which could not be attributed to Ge–O bond vibration, was observed at $1030\,cm^{-1}$ in the loss curve of the fibre kept in air for 7 days.

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