Scattering loss characteristics of selenide-based chalcogenide glass optical fibers

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(Received 14 October 1991; accepted for publication 23 January 1992)

Scattering loss characteristics of Ge-Se binary chalcogenide glass optical fibers are investigated. It is found that there is a strong correlation between the wavelength-independent scattering loss and the absorption caused by H₂O impurities. Therefore, the amount of H₂O impurity mainly determines the wavelength-independent loss of these optical fibers. After removing the H₂O impurity and adjusting the fabrication conditions, the transmission loss is less than 1 dB/m over a wide infrared wavelength region of 2–8.5 μm, except for a small peak at 4.5 μm.

I. INTRODUCTION

Chalcogenide glass optical fibers are promising for operating in the mid-infrared range of 2–12 μm. There are potential applications in the fields of laser surgery and radiometric low-temperature measurement. To date, great progress has been made in reducing the transmission losses of such fibers.

In optical fibers, transmission losses can generally be classified into two categories: absorption losses and scattering losses. Absorption losses are mainly caused by impurities such as OH and other oxides. The mechanism of absorption losses caused by such impurities is now well understood and there are several methods of reducing absorption losses. For example, it has been reported that Al doping is effective for reducing absorption caused by oxides such as OH, H₂O, and Ge-O in Ge-Se chalcogenide glass optical fibers. Furthermore, the raw Se must be distilled in a reactive SeCl₂ gas atmosphere for reducing hydrogen impurities.

On the other hand, scattering losses are considered to be caused by extrinsic defects and crystallization of the chalcogenide glass itself. However, the mechanism of scattering loss is not yet fully understood because of its inherently complicated nature.

In this paper, we focus on Ge-Se binary chalcogenide glass optical fibers because Ge-Se glass has a simple composition with a stable vitreous state. We report here the relationships between the scattering losses and (1) absorption by impurities, (2) the amount of Al doping for reducing oxide absorption, (3) the SeCl₂ conditions for distilling the raw Se to reduce hydrogen impurities, and (4) the temperatures while melting the raw material in order to achieve a stable glass state. Experimental results show that H₂O impurity is the main cause of wavelength-independent scattering loss in Ge-Se chalcogenide glass optical fibers.

II. EXPERIMENTAL PROCEDURE

The raw materials for fabricating Ge-Se chalcogenide glass optical fibers were 5-N Se shots and 10-N Ge ingots. The Se shots were distilled in a reactive SeCl₂ gas atmosphere to eliminate hydrogen impurities. The distillation apparatus is shown in Fig. 1. As shown in the figure, SeCl₂ vapor was diluted in the Ar transport gas and flowed into a silica-glass tube. Then, part A was heated to a high temperature. The raw Se in part A reacts with the SeCl₂ gas. As a result, the following reactions occur:

\[ \text{H}_2 + \text{SeCl}_2 \rightarrow \text{Se} + 2\text{HCl} \]
\[ 2\text{H}_2\text{O} + 2\text{SeCl}_2 \rightarrow \text{Se} + \text{SeO}_2 + 4\text{HCl} \]

This removes the hydrogen impurities from the Se. The Ar flow rate is \(1.16 \times 10^{-5} \text{ m}^3/\text{s}\) and the SeCl₂ flow rate is \(3.0 \times 10^{-7} \text{ m}^3/\text{s}\). After the reaction, the Se powder deposited in part B was again heated at 200 °C, and was consolidated into bulk Se. The following section will discuss how the distillation temperature of the Se shots affects the scattering loss.

The Ge ingots and purified Se shots were weighed out and inserted into a water-free quartz ampoule, which was then evacuated and sealed under a vacuum of about \(10^{-6} \text{ Torr}\). A small amount of Al was added to minimize the impurity absorption caused by oxygen. The sealed ampoules were heated at 800 °C for 35 h in a rocking furnace to mix the constituents. Then, the glass blocks were drawn into fibers from the quartz nozzle at a temperature of 44%–500 °C and a pressure of 0.5–1.5 atm. The fiber diameter could be controlled between 100 and 400 μm by changing the drawing speed. The drawing apparatus and the temperature distribution in the furnace are schematically shown in Fig. 2.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Scattering loss caused by impurities

Scattering losses \(\alpha(\lambda)\) can be generally described by the following equation:

\[ \alpha(\lambda) = \alpha_0(\lambda) + \alpha_{\text{mod}}(\lambda) + \alpha_{\text{imp}}(\lambda) \]

where \(\alpha_0(\lambda)\) is the fundamental scattering loss, \(\alpha_{\text{mod}}(\lambda)\) is the scattering loss caused by impurities, and \(\alpha_{\text{imp}}(\lambda)\) is the scattering loss caused by intrinsic defects.

FIG. 1. Apparatus for SeCl₂ distillation of raw Se.
\[ \alpha_\lambda(\lambda) = A\lambda^{-4} + B(\lambda) + C, \]  

where \( \lambda \) is the wavelength. In the equation, \( A\lambda^{-4} \) is the Rayleigh scattering loss, \( B(\lambda) \) includes the wavelength-dependent scattering losses such as the Mie scattering loss, and \( C \) includes the wavelength-independent scattering losses due to structural imperfections such as crystallization. In the Ge-Se optical fibers studied here, the scattering losses are independent of the wavelength. This is clear from Fig. 3, which shows a typical transmission loss spectrum for a Ge-Se optical fiber without any treatment to reduce scattering loss. The scattering loss shown by the broken line is almost constant for wavelengths from 2 to 9 \( \mu \)m. We examine this wavelength-independent scattering loss term \( C \) in more detail.

Figure 4 shows the relationship between the scattering loss and the absorption loss caused by Ge-O for various Ge-Se optical fibers. The glass composition was measured to be Ge:Se = 20:80 (mol%). The Ge-O absorption peaks appear at a wavelength of 7.8 \( \mu \)m.\(^5\) There is no correlation between the scattering loss and the Ge-O absorption. Therefore, the oxygen incorporated in the form of Ge-O does not affect the scattering loss. In contrast, Fig. 5 shows a strong correlation between the scattering loss and the absorption loss due to H\(_2\)O (wavelength: 6.3 \( \mu \)m).\(^5\) It is clear that the scattering loss depends largely on H\(_2\)O impurities. This implies that an H\(_2\)O impurity generates either structural imperfections resulting from H\(_2\)O segregation, or crystallites growing from H\(_2\)O nuclei.

It is interesting to compare this result with that obtained for fluoride glass optical fibers. In fluoride glass fibers, the scattering loss is caused by oxygen impurity, and not by H\(_2\)O.\(^6\)\(^7\) Therefore, the mechanism of forming imperfections or crystallites is slightly different between chalcogenide glasses and fluoride glasses.

**B. Scattering loss caused by Al doping**

We measured the relationship between the wavelength-independent scattering loss and the Al content for various Ge-Se (20:80 mol %) optical fibers. Al doping is carried out to reduce the absorption loss caused by oxygen, as discussed in Sec. II. Figure 6 shows that the scattering loss increases with increasing Al content. Furthermore, there is a clear critical point where the scattering loss increases.

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**FIG. 2.** Fiber-drawing apparatus.

**FIG. 3.** Typical transmission loss spectrum for Ge\(_{20}\)Se\(_{80}\), glass optical fiber without treatment to reduce scattering loss. The broken line shows the wavelength-independent scattering loss.

**FIG. 4.** Relationship between wavelength-independent scattering loss and Ge-O absorption loss at 7.8 \( \mu \)m for various Ge\(_{20}\)Se\(_{80}\) glass optical fibers.

**FIG. 5.** Relationship between wavelength-independent scattering loss and H\(_2\)O absorption loss at 6.3 \( \mu \)m for various Ge\(_{20}\)Se\(_{80}\) glass optical fibers.
abruptly, at an Al concentration of 100 ppm. Therefore, the Al content should be less than 100 ppm to suppress the scattering loss. This may be because excess Al in the glass produces nuclei for crystallization.

C. Scattering loss caused by SeCl₂ distillation

In oxide glasses, the scattering losses of optical fibers fabricated from Cl₂-treated glasses sometimes remained large. Since distillation of Se by SeCl₂ is used for reducing hydrogen impurities, similar behavior was anticipated for the chalcogenide glasses treated with SeCl₂. Therefore, we examined the influence of SeCl₂ distillation on the scattering loss. Figure 7 shows the transmission losses for two different Ge-Se (20:80 mol %) optical fibers. The difference between the fibers is the distillation temperature, 800 or 1000 °C. If the distillation temperature is above 1000 °C, the wavelength-independent scattering loss is reduced to as low as 0.1 dB/m. Since the increase in temperature corresponds to a reduction in the amount of residual Cl₂, the residual Cl₂ is thought to cause the scattering loss in Ge-Se optical fibers.

D. Scattering loss caused by raw material melting

The temperature during vacuum melting of raw materials in a rocking furnace affects the glass homogeneity, and equivalently affects the scattering loss of the fabricated optical fiber. Therefore, we measured the relationship between the melting temperature and wavelength-independent scattering loss. The melting temperatures used were 600, 800, and 1000 °C, and the melting time was fixed at 35 h. The glass composition was Ge₉₀Se₁₀ (mol %) with an Al content of 100 ppm. Figure 8 shows the obtained results. As shown in the figure, the wavelength-independent scattering loss drastically increases when the temperature falls below 800 °C. Furthermore, the increase in scattering loss was particularly large at wavelengths below 4 μm when the fiber was fabricated from the glass melted at
TABLE I. Fabrication conditions for Ge$_{20}$Se$_{80}$ glass optical fiber.

<table>
<thead>
<tr>
<th>Al doping</th>
<th>Temperature</th>
<th>SeCl$_2$ distillation</th>
<th>SeCl$_2$ gas</th>
<th>Glass melting in a rocking furnace</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ppm</td>
<td>1000 °C</td>
<td>1.16×10$^{-5}$ m$^3$/s</td>
<td>3.0×10$^{-5}$ m$^3$/s</td>
<td>800 °C</td>
</tr>
</tbody>
</table>

600 °C. This indicates that, at low temperatures, scattering centers with diameters less than about 4 μm are left even after melting the glass. The scattering centers originate from crystallites. Since the critical point in Fig. 8 is around 800 °C, one possible crystallite is GeSe$_2$, which is a stoichiometric compound with a melting point of 740 °C.8 Thus, it is important to melt the glass in a vacuum at a temperature above 800 °C.

E. Fabrication of low-loss optical fibers

Using the results described above, we fabricated Ge-Se chalcogenide glass optical fibers. The transmission loss spectrum for the Ge$_{20}$Se$_{80}$ optical fiber is shown in Fig. 9. The fabrication condition are shown in Table I. As shown in Fig. 9, the absorptions at 2.8 μm (OH), 6.3 μm (H$_2$O), and 7.8 μm (Ge-O) are nearly eliminated as a result of the gettering effect of Al. In addition, the absorption at 4.5 μm caused by Se-H is as low as around 5 dB/m. This reduction is caused by the distillation of the raw Se in SeCl$_2$.

The scattering loss is as small as 0.2 dB/m. This results from the following factors: (1) The Al content was reduced to 100 ppm, (2) the SeCl$_2$ distillation was done at a high temperature of 1000 °C, and (3) the melting temperature was maintained at 800 °C in order to avoid creating scattering centers.

The fabricated fiber has a wide spectral region with low loss. The transmission loss is less than 1 dB/m for wavelengths up to 8.5 μm, except for a small peak at 4.5 μm.

IV. SUMMARY

We have investigated the scattering loss characteristics of Ge-Se chalcogenide glass optical fibers and obtained the following results:

(1) There is a strong correlation between the wavelength-independent scattering loss and the absorption due to H$_2$O impurity. Therefore, the scattering loss is mainly influenced by H$_2$O impurity.

(2) The wavelength-independent scattering loss increases with increasing Al content. Al is doped to reduce oxygen impurities. Furthermore, there is a clear critical point where the scattering loss increases abruptly, at 100 ppm of Al.

(3) SeCl$_2$ distillation of raw Se is necessary for eliminating hydrogen impurities. However, the distillation temperature affects the wavelength-independent scattering loss. If the distillation temperature is above 1000 °C, the scattering loss is reduced to as low as 0.1 dB/m.

(4) The temperature during vacuum melting of the raw material in the rocking furnace also affects the wavelength-independent scattering loss. The scattering loss is drastically higher if the temperature is below 800 °C.

On the basis of the above results, we have fabricated low-loss Ge$_{20}$Se$_{80}$ chalcogenide glass optical fibers. The transmission loss of the fabricated fiber is less than 1 dB/m for wavelengths up to 8.5 μm, except for a small peak at 4.5 μm.