Mat. Res. Bull., Vol. 23, pp. 59-64, 1988. Printed in the USA.
0025-5408/88 $3.00 + .00 

# THE TELLURIUM BROMIDE GLASSES : NEW I.R. TRANSMITTING MATERIALS

**Xiang Hua Zhang, Gilles Fonteneau et Jacques Lucas**
Laboratoire de Chimie Minérale D, Unité Associée au C.N.R.S. n° 254,
Université de Rennes-Beaulieu, Avenue du Général Leclerc - 35042 Rennes Cédex

(Received July 31, 1987; Communicated by A.W. Sleight)

**ABSTRACT :**

A new class of glasses has been discovered in the binary system Te-Br. The limits of the vitreous domain are $Te_2Br$ and TeBr. The composition $Te_3Br_2$ is the most stable toward crystallization and the addition of S or Se decreases strongly the devitrification rate. The glass temperatures are in the range 70-80° C and, in the case of Se doped glasses, there is no crystallization peak. The optical transmission range lies from 1.9 µm to 20 µm for $Te_3Br_2$ glass and makes it potential candidate for low loss fiber at 10.6 µm, a loss as low as $10^{-2}$ dB/km is estimated at this wavelength from the multiphonon contribution.

MATERIALS INDEX: tellurium, bromides

## INTRODUCTION

In a previous paper (1), we described the glass formation in tellurium chloride systems and emphasized the originality of this new family of glasses characterized by a good chemical durability in normal atmosphere and an interesting transmission in the I.R. with a multiphonon edge located in the 12-14 µm region.

Some metallic halides such as $ZnCl_2$, $ZnBr_2$, $ThCl_4$, $CdI_2$, ... are known to be glass formers but all are extremely hygroscopic and their optical properties are strongly affected by moisture corrosion (2).

This new class of vitreous material combines the strong covalent character of the bond between halide and chalcogenide and the disordering effect produced by the existence of lone pairs on tellurium atoms.

## GLASS FORMATION IN THE BINARY SYSTEM Te-Br

When calculated quantities of Te and $Br_2$ are heated at about 300° C in sealed glass tubes, the formation of a viscous melt is observed. By cooling the tubes in air, the melt solidifies as a complete vitreous material when the ratio Te/Br is approximately located between 1 and 2 ; $Te_2Br$ and TeBr are in these conditions of moderated quenching the limits of the vitreous area. The glass $Te_3Br_2$ located just in the middle of the diagram is considered as the prototype glass.

In order to prepare very pure glasses and due to the contamination of bromine by water, the experimental procedure is the following. The chips are first treated

by HBr and $Br_2$ containing solution for cleaning them from oxygen surface corrosion. As indicated on Fig. 1, the $Br_2$ solution always contaminated by water is treated with $P_2O_5$ in the first container and then transferred in the graduated tube where calculated amount is stored by condensation. Finally, this $Br_2$ is transferred again in the reaction tube containing the tellurium. After sealing under vacuum, the tube is heated two hours in a rocking furnace at 300° C and then cooled in air.

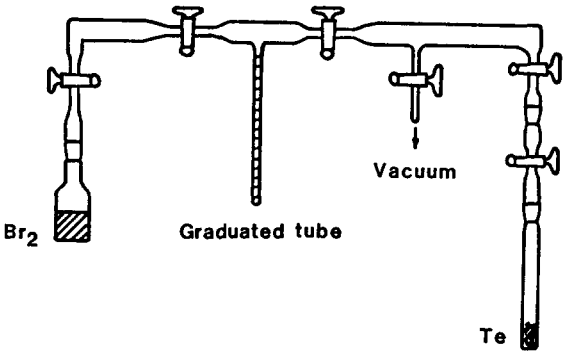


FIG. 1

Apparatus used for the preparation of the Te-Br glasses

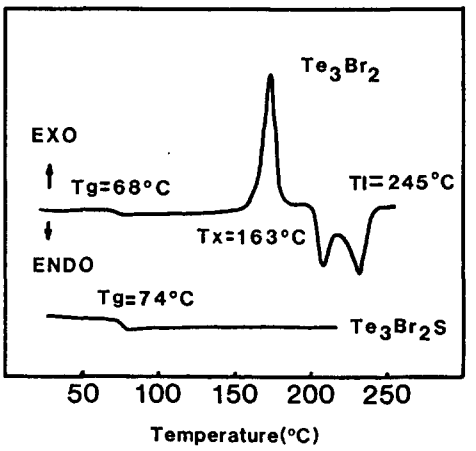


FIG. 2

D.S.C. analysis of the glasses $Te_3Br_2$ and $Te_3Br_2S$ In the latter glass, no crystallization peak is detected.

The black pieces of glass are not hygroscopic and only those containing a large amount of Br such as $TeBr_2$ show a slow attack of the surface in normal atmosphere.

The Fig. 2 represents the D.S.C. analysis of the glass $Te_3Br_2$. The glass temperature $T_g$ = 68° C is located at about 100° C from the crystallization peak at $T_x$ = 163° C and the liquidus temperature is estimated around $T_l$ = 245° C. The $Te_3Br_2$ glass has a very broad optical transmission range lying from the bandgap absorption in the 1.9 μm region to the multiphonon edge in the 20-25 μm region.

The Fig. 3 represents the I.R. edge for the glass $Te_3Cl_2$, thickness = 8 mm and $Te_3Br_2$ thickness = 6 mm. It is clear that replacing Cl by Br shifts the I.R. edge approximately from the 12 to 20 μ region.

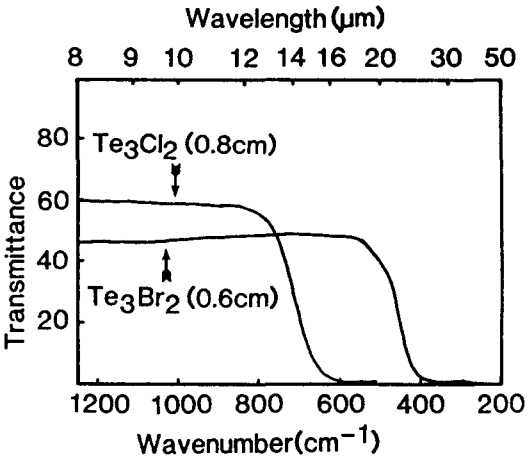


FIG. 3

I.R. multiphonon edge of the two glasses $Te_3Cl_2$ and $Te_3Br_2$

On the Fig. 4 is represented the extrapolation of the two intrinsic absorption mechanisms (bandgap and multiphonon) giving the V-shape curve. It is difficult to estimate the Rayleigh scattering contribution in the mid I.R. region, but in the case of a good optical glass, one can expected an ultratransparent behaviour in the strategic region of 10.6 μm : in : this hypothesis, attenuation losses in the 10 dB/km range are realistic.

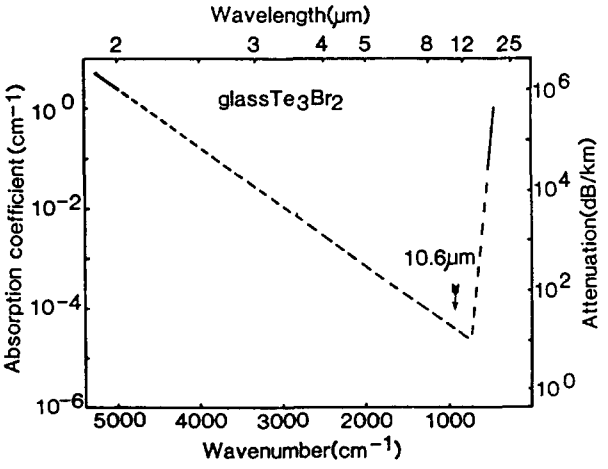


FIG. 4.

The V-shaped curve for the glass $Te_3Br$. The two intrinsic absorption factors considered are the bandgap and multiphonon mechanisms. The Rayleigh scattering is estimated negligible in the 8-12 μm region.

## STABILIZATION OF TELLURIUM BROMIDE GLASSES BY S OR Se

In order to obtain good I.R. transparent glasses having low scattering losses because of their high resistance to devitrification, sulfur or selenium has been added to the binary glasses. The vitreous domains are represented on the Fig. 5 for the system Te-Br-S and on the Fig. 6 for the TeBr-Se system. It can be seen that the latter system has a very broad glassy area due to the fact that Se itself exists in a glassy state. These two diagrams have been determined in using the same experimental procedure as dis-

cussed previously ; Se or S are, in these cases, introduced together with Te in the reacting tube.

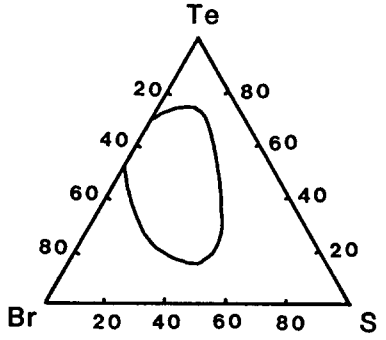


FIG. 5

Vitreous domain in the Te-Br-S diagram

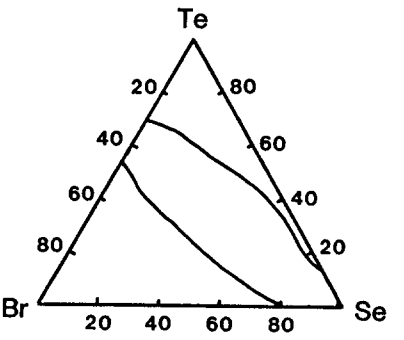


FIG. 6

Vitreous domain in the Te-Br-Se diagram.

All these glasses and specially those having the lowest content in Br are very stable in normal humidity conditions and are not hygroscopic.

## THERMAL AND OPTICAL PROPERTIES OF STABILIZED TELLURIUM BROMIDE GLASSES

As indicated on Fig. 2, addition of sulfur to the glass $Te_3Br_2$ has a strong effect on the devitrification rate. For instance, the glass $Te_3Br_2$ has a $T_g$ = 71° C, but it is impossible with a heating rate of 10° C/minute to detect any crystallization peak.

The addition of the light element S to tellurium bromide glasses has a strong effect on the I.R. edge and one observed that the multiphonon edge of the glass $Te_3Br_2S$ is the same as $Te_3Cl_2S$ which is represented in reference (2). The formation of Te-S bonds shifts the multiphonon edge in the 12 μm region like observed with the Te-Cl glasses.

In order to keep the good I.R. transparency until the 20 μm region and decrease the crystallization rate, the vitreous materials of the Te-Br-Se system have been examined. As indicated on the Fig. 6, the middle of the glassy domain is approximately extending along the $Te_3Br_2 \rightarrow$ Se line.

The examination of a glass having the composition $Te_3Br_2Se$ by D.S.C. analysis shows that the Tg of such glass is around 70° C and that no crystallization peak is detected for a heating rate of 10° C/minute.

On the Fig. 7 is represented the optical transmission spectra of the glass $Te_3Br_2Se$ which indicates that these Se containing glasses have the same optical window than the $Te_3Br_2$ glass lying from 2 μm to 20 μm.

The addition of Se to the binary glass has a very important effect on the stability of the glass towards crystallization and keeps in the same time the exceptional

transparency in the 20 μm region.

The glass belonging to the $Te_3Br_2Se$ system, and even those containing a small amount of Se, appear to be the best compromise in these tellurium halide glasses for having good optical properties and resistance to devitrification.

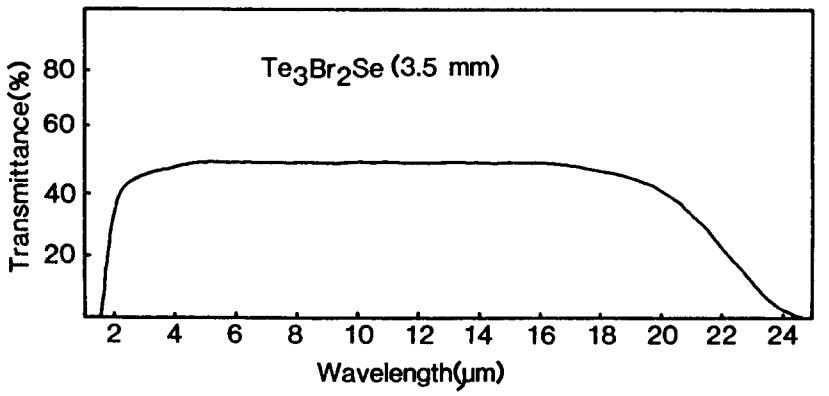


FIG. 7

Optical transmission spectra of the glass $Te_3Br_2Se$.

## POTENTIAL FOR ULTRATRANSPARENCY

As indicated on Fig. 4, in absence of informations on scattering absorption, the two important loss factors are : the bandgap absorption which originates from the possible delocalization of the electron belonging to the lone pair located on the Te atom, and the multiphonon absorption which is more easy to define and which is determined by the vibrational modes of the Te-Br, Te-Cl, TeS or TeSe bond strength.

The Fig. 8 represents the extrapolation of the absorption coefficients measured from the I.R. edge for the three glasses $Te_3Cl_2$, $Te_3Br_2Se$ et $Te_3Br_2$. The strategic region corresponding to the emission of the $CO_2$ laser at 10.6 μm is indicated for evaluating the multiphonon losses in this specific region. It is clear that the glasses containing Cl or S, such as $Te_3Cl_2$ or $Te_3Br_2S$ having their I.R. edge in the 13 μm region are not potentially very transparent at 10.6 μm where the attenuation is estimated to be around 1 dB/m.

On the other hand, the Br or Se containing glasses such as $Te_3Br_2$ or $Te_3Br_2Se$ have a potential multiphonon loss close to 0.1 dB/km, four order of magnitude more transparent than the Cl or S containing materials.

Despites the difficulty to estimate the bandgap absorption at 10.6 μm, one can conclude that this factor will be the more critical for the preparation of highly transparent waveguide at 10.6 μ in addition to the Rayleigh scattering.

These new glasses could be compared with the best chalcogenide glasses for the 10.6 μ transmission as discussed by Wehr and Le Sergent (3). According to these authors, the quaternary glass AsGeSeTe is the material having the best

transparency at 10.6 μm estimated around 2-3 dB/m. The comparison of the I.R. edge of this glass with the tellurium halide glass shows that they are very comparable to the Cl or S containing glasses.

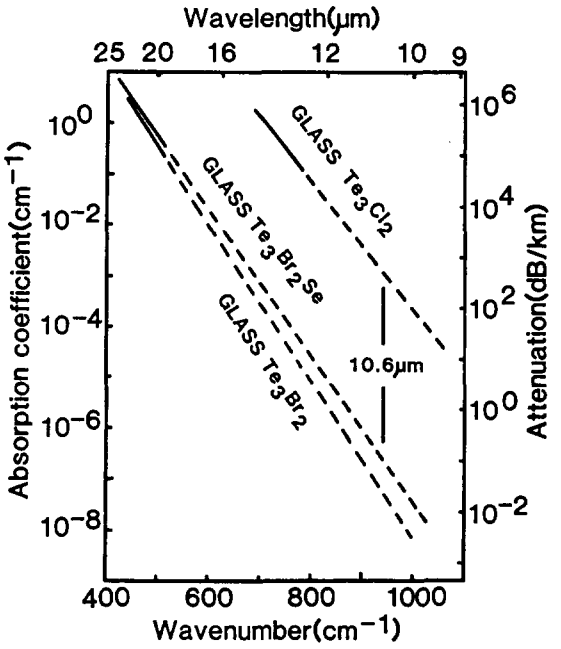


FIG. 8

Evolution of the absorption coefficient and optical loss versus λ for $Te_3Cl_2$ and $Te_3Br_2$ and $Te_3Br_2Se$.

In conclusion, the Br or Se containing tellurium glasses appear to be very promising candidates for the preparation of highly transparent I.R. optical fibers operating at 10.6 μm and in the 8-12 μm optical window.

## REFERENCES

1. J. Lucas, X.H. Zhang, Mat. Res. Bull., 21, 871 (1986)
2. J. Lucas, J. Non-Cryst. Solids, 80, 83 (1986)
3. M. Wehr, C. Le Sergent, SPIE, 618, Infrared Optical Materials and Fibers IV, 130 (1986)