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Invited Paper

APPLICATIONS OF CHALCOGENIDE GLASS BULKS AND FIBRES

X. Zhang*, H. Ma, J. Lucas

UMR CNRS 6512 "Verres et Céramiques", Université de Rennes I, Bat. 10 A, Campus de Beaulieu, 35042 Rennes cedex, France

Chalcogenide glasses of different compositions have been studied for infrared applications. Compositions containing germanium are selected preferentially for producing lenses, as they have higher glass transition temperature and better thermal mechanic properties. These glasses have been successively moulded into lenses with high precision (the peak-to-valley defect is about 0.4 µm). The overall performance of the moulded optics is compared with that of germanium, which is almost the only material used for thermal imaging. It is shown that the optical performance is very similar for both materials, but the moulded optics are potentially much cheaper. Optical fibres have been drawn from the Te-As-Se-I glass and examples of applications for these fibres have been given by monitoring, in line and in real time the alcoholic fermentation process of grape juice. These fibres have also been used for remote temperature sensing.

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1. Introduction

There are very few materials which are transparent in the 8-12 µm region and which are environmentally stable enough for outdoor applications [1][2]. Thermal imaging at this wavelength region uses almost exclusively single crystalline germanium, which is rare and expensive element. Germanium has very interesting optical properties with very high refractive index and very low chromatic dispersion between 8-12 µm. Another mostly used material is the polycrystalline ZnSe that is produced with the long and expensive CVD (Chemical Vapour Deposition) technique. ZnSe has very low absorption at 10.6 µm and is mainly used for CO_2 laser transmission.

Because of their crystalline nature, no optical fibres can be produced with useful length from these two materials.

Chalcogenide glasses are transparent from visible or near infrared region up to 15 µm. The main advantage of these glasses, compared to germanium and ZnSe is the possibility of obtaining glass fibres and complex optical components by moulding thanks to their vitreous nature.

The first commercial and the today's most promising application for chalcogenide glasses concerns optical lenses for infrared transmission. They are mainly used for infrared radiometry. Recently, moulding technology has been developed, making possible the economical production of very complex and high efficient lenses, which are necessary for thermal imaging application[3][4]. Infrared cameras have been made with exclusively chalcogenide glass lenses. The optical performance of the system is the same as the ones using germanium optics which are much more expansive. The state-of-the-art of this application will be described in this paper.

Chalcogenide glass fibres have been intensively studied for chemical sensing, as these fibres are transparent in the region where many chemical and biological species have their fingerprints. It is, as an example, possible to monitor, in line and in real time, the alcoholic and lactic fermentation process. Other passive applications such as remote chemical analysis and temperature sensing will also be presented and discussed.

* Corresponding author: xzhang@univ-rennes1.fr

2. Experimental

The chalcogenide glass synthesis method is largely described in detail elsewhere[5-7]. Glasses for this study are from the Ge-As-Se, Ge-Sb-Se, Ga-Ge-Sb-Se and Te-As-Se-I glass forming systems. The glass synthesis can be summarized as follows: Highly pure (generally 99,999%) starting elements are used and put into silica ampoules, which are then sealed under vacuum (about 10^{-5} mbar). The mixture is homogenized in a rocking furnace at a temperature ranging from 600°C to 900°C depending on the glass composition. Glasses are obtained by cooling the silica ampoules in air. To obtain low optical absorption glass, distillation is generally used to eliminate impurities such as carbon or oxygen. Carbon usually leads to wavelength independent scattering losses and oxygen will react with the starting elements to form preferentially Ge-O, which leads to the strong absorption peak centred at 12.8μm. Several hundreds ppm (part per million) of oxygen getter, mostly metallic aluminium or magnesium, are generally added to the starting materials in order to form highly stable Al_2O_3 or MgO with oxygen impurity. These oxides will be eliminated by distillation.

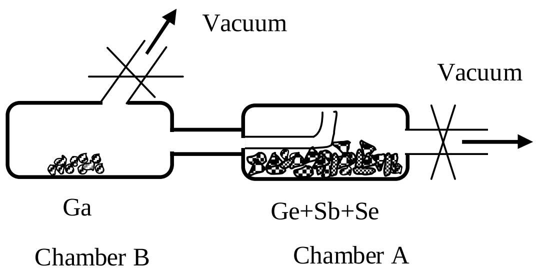

Fig. 1.Set-up in fused silica for the purification of chalcogenide glasses containing gallium.

For preparing glasses containing gallium, which cannot be purified by distillation, the set-up illustrated in Fig. 1 is used. Gallium is introduced directly into the chamber B. Germanium, antimony and selenium, together with oxygen getter are distilled from chamber A to chamber B.

By using this technique, glass samples with a diameter ranging from 10 mm to 100 mm have been obtained and the thickness is generally between 50 – 100 mm.
The glass transition temperature is measured by using a differential scanning calorimeter (DSC) with a reproducibility of ±1°C. The viscosity of the glass is obtained by using the so-called “parallel plate” method, which consists of measuring the deformation of a disc under a given pressure.

Optical transmission of different materials has been measured with a Fourier Transform Infrared Spectrometer with a precision of about ±2%.

One of the main advantages of glasses, compared to crystals, is the possibility of obtaining complexes optical components by moulding. This is particularly useful, because asphero-diffractive surfaces are necessary when chalcogenide glass lenses are exclusively used for thermal imaging.

The set-up for moulding chalcogenide glasses is schematised in Fig. 2. It consists mainly of putting a chalcogenide glass disc inside a mould with appropriate surfaces (spherical, aspherical or asphero-diffractive). The temperature is increased progressively to the softening temperature of the glass and a pressure is then applied to the upper mould. The glass will duplicate the surfaces of the mould and a moulded optic is obtained after annealing around the glass transition temperature. An example of moulded asphero-diffractive lens is shown in Fig. 3.

The moulding precision is measured by using an interferometer at 630 nm for spherical surfaces. More complex surfaces are controlled by using a surface profilometer (Form Talysurf from Taylor Hobson Inc.). The moulded surfaces are compared with the designed surface. Moulded lenses have been used for thermal imaging.

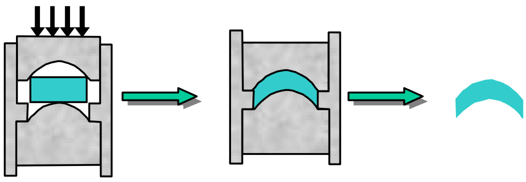

Fig. 2. Schematic representation for producing chalcogenide glass optic by molding.

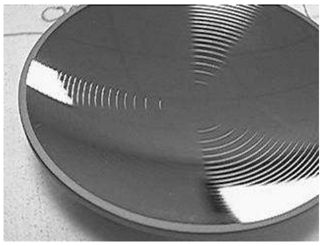

Fig. 3. Mold asphero-diffractive lens.

To evaluate the performance of chalcogenide glasses for thermal imaging, two imaging systems have been designed: one system uses the classical combination of Germanium – ZnSe and another one uses exclusively commercially available chalcogenide glasses. The expected optical performance of these two systems has been compared.

Chalcogenide glasses have also interesting applications as optical fibres because of their wide transmission window from 2-12 µm.

Single index fibres have been obtained by drawing high quality glass rods (typical dimension: diameter of 10 mm and length of 100 mm). The drawing temperature depends mainly on the glass transition temperature Tg. For example, the drawing temperature is respectively about 200°C for the $Te_{20}Se_{30}As_{40}I_{10}$ glass with a Tg of 118 °C and is about 400 °C for the $Ga_5Sb_{10}Ge_{25}Se_{60}$ glass with a Tg of 283°C. The fibre drawing speed is typically in the range of 1-2 meters/minute.

Double-index fibres have been obtained by using one of the following techniques:

- The preform technique: preforms are prepared by using the well-known rod-in-tube method, which consists of preparing separately a glass rod and a glass tube with a lower refractive index. The glass rod is polished to fit into the glass tube. The interface between the glass rod and the glass tube is evacuated under vacuum to avoid bubble formation during fibre drawing process.
- The double-crucible technique: two crucibles containing respectively the core glass and the cladding glass are used. The outlet of the crucible containing the core glass is put in the middle of the outlet of the crucible containing the cladding glass.

The preform technique is relatively easy to be implemented. The core-cladding diameter ratio of the obtained fibre is highly stable and is not influenced by the fluctuation of the drawing conditions (variation of drawing temperature, speed). However, the interface quality is not as good as with double-crucible technique.

The double-crucible method uses higher drawing temperature, leading generally to a better core-cladding interface. By changing the pressure in the two crucibles and their outlet diameter, it is possible to modifier greatly the diameter ratio of the core/the cladding. For example, fibres with the ratios of 420 µm/450 µm and 40 µm/270 µm have been prepared.

The fibre losses have been measured by using the classic “cut-back” method, by using a FTIR Spectrometer over a length of 1-2 meters in the wavelength region of 3 – 12 µm.

The set-up illustrated in Fig. 4 is used for remote chemical analysis. The infrared light is injected into a single index fibre, which is partially immersed in the liquid or gas to be analysed. The light propagating inside the fibre by total reflection is partially absorbed when the fibre is in contact with the substances in the reactor. By analysing the absorption spectrum, it is then possible to monitor the reaction in real time.

An example of applications is given by monitoring grape juice fermentation in the wine production process.

These infrared transmitting fibres are also used for remote temperature sensing.

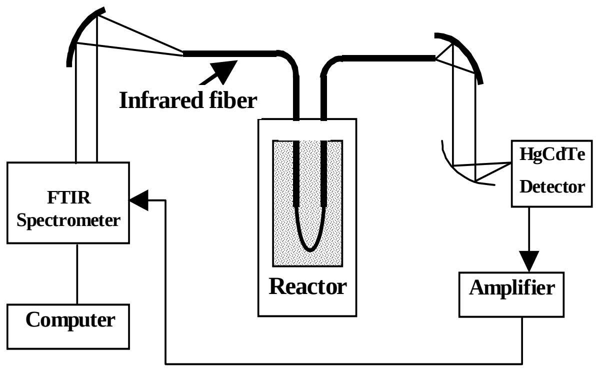

Fig. 4. Set-up for remote spectroscopy using infrared glass fiber.

3. Results

3.1. Moulded optics in chalcogenide glasses

Fig. 4 shows the infrared transmission of a commercially available chalcogenide glass, $Ge_{22}As_{20}Se_{58}$, at different temperatures ranging from room temperature up to 120 °C. It is clear that no significant transmission change is observed. As comparison, the transmission of germanium is deeply affected when the temperature is higher than 100 °C, as shown in Fig. 5.

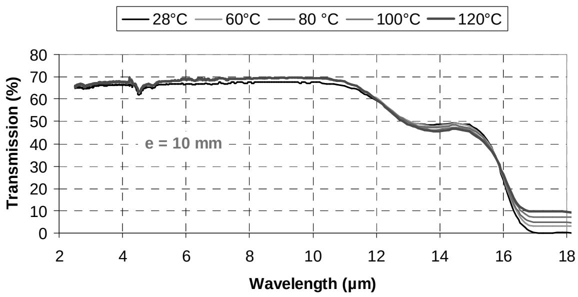

Fig. 4. Transmission of the $Ge_{22}As_{20}Se_{58}$ glass at different temperatures.

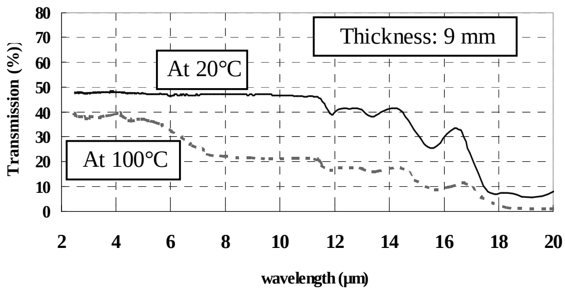

Fig. 5. Transmission of Germanium at 20 °C and 100 °C.

Fig. 6 compares the transmission of a moulded and a mechanically polished discs of $Ga_5Sb_{10}Ge_{25}Se_{60}$ glass. Only a very slight difference in transmission can be observed around 12 µm. It can be concluded that the moulding process will not deteriorate the excellent transmission of chalcogenide glass.

Fig. 7 shows the typical form defect of a moulded spherical lens in chalcogenide glass. This form defect is the difference between the moulded surface profile and the designed surface profile. This defect is about 0.4 µm, which is an excellent result for lenses operating at 8-12 µm region.

3.2. Thermal imaging with moulded optics

The possibility of obtaining complex lenses in chalcogenide glasses by moulding, gives a great flexibility to design high performance and low cost optics for thermal imaging. The use of aspheric surfaces allows for example to significantly decrease the number of lenses.

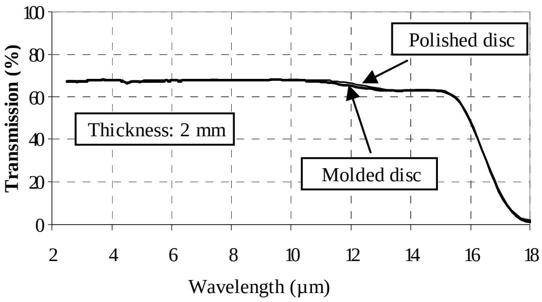

Fig. 6. Infrared transmission of a molded disc and a mechanically polished disc.

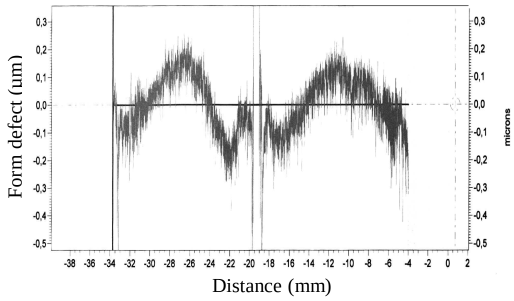

Fig. 7. Form defect of a molded chalcogenide glass lens (peak-to-valley: about 0.4 µm).

To demonstrate the possibility of using exclusively the chalcogenide glasses for thermal imaging, two optics have been designed: the first one is a classic germanium – ZnSe combination and the second one uses only the commercially available $Ge_{22}As_{20}Se_{58}$ glass. As germanium has very low chromatic dispersion between 8-12 µm, only aspheric surfaces are used in the Ge-ZnSe optic. In the glass-glass combination, one asphero-diffractive and one aspheric surface are used. The function transfer modulus FTM, which describes the spatial resolution of the optic is given, in Table 1, for these two optics at different fields of view. The selected resolution of 12 cycles/mm corresponds roughly to the resolution of the uncooled focal plan micro-bolometer detector. A higher FTM value is of course better. It is clear that the expected optical performance of these two optics is very similar. The aspheric Ge-ZnSe should be produced by the costly single-point diamond turning, while the asphero-diffractive glass-glass combination is produced directly by moulding.

An example of thermal images obtained with a moulded chalcogenide glass optic is given in Fig. 8. Images of the same quality were obtained by using the Ge-ZnSe optic.

Table 1. FTM values at 12 cycles/mm for 2 set of optics.

Field of view (°)	0	5,71	7,46	7,94	9,25
Ge-ZnSe	0,70	0,64	0,49	0,44	0,43
Glass-glass	0,78	0,61	0,53	0,50	0,26

Fig. 8. Example of thermal images obtained with molded chalcogenide glass optic.

3.2.1. Chalcogenide glass fibres for different applications

Typical attenuation of the obtained chalcogenide glass fibre is presented in Fig. 9. The absorption peaks centred at 4.7 µm and 6.2 µm are respectively due to the chemical bond H-Se and molecule water. The minimum absorption of about 0.2-0.3 dB/m is located in the wavelength region of 6 – 9 µm.

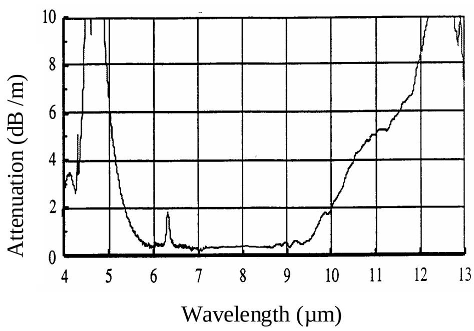

Fig. 9. Typical attenuation curve of chalcogenide glass fibres, represented by the $Te_{20}Se_{30}As_{40}I_{10}$ glass.

One of the potential applications of chalcogenide glass fibres is today for remote chemical analysis. The example here is given by monitoring an alcoholic fermentation from grape juice. The results are represented in Fig. 10, which indicates the absorption spectrum of the solution at different stages of the alcoholic fermentation. The most important absorption peak for glucose and alcohol is centred respectively at 9.4 µm and 9.55 µm. It is clear that the glucose content decrease progressively during the fermentation process, while the alcohol content increase at the same time.

The infrared fibres are also used for remote temperature sensing. The set-up is mainly composed of an infrared fibre-coupled HgCdTe detector, which is cooled by liquid nitrogen. The fibre has a length of about 2 meters. The target temperature is measured by using a thermo-resistance and this temperature is served as reference. The analysis of the output signal of the detector as a function of the target temperatures, leads to Fig. 11, which indicates the thermal resolution of this set-up. The precision of measurement is about 1°C at room temperature and is 0.5 °C at 100 °C.

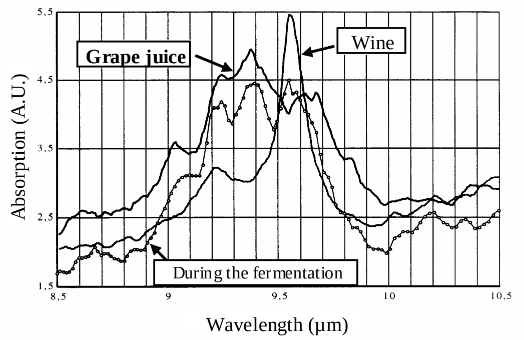

Fig. 10. Monitoring of the alcoholic fermentation process by using remote spectroscopy using a infrared fibre.

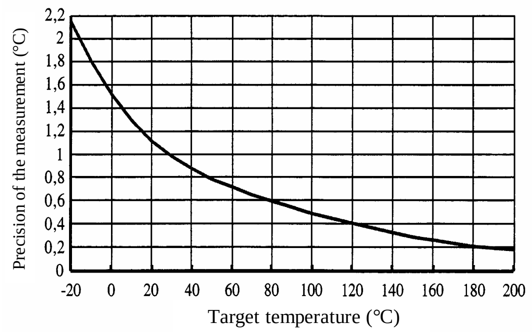

Fig. 11. Thermal resolution of a remote temperature sensing set-up, by using an infrared fibre.

4. Discussion

The currently used material for thermal imaging is single crystalline germanium, which has outstanding optical properties, especially high refractive index, and very low chromatic dispersion between 8-12 µm. ZnSe has excellent transmission, but is highly dispersive. Consequently, if it is used alone for imaging, expensive asphero-diffractive surfaces will be needed to achieve acceptable performance. Germanium has unquestionable advantages over ZnSe for thermal imaging.

Chalcogenide glasses have been studied over several decades. But only recently they are considered for replacing germanium as thermal imaging optics. There are mainly two reasons for this fact

- The development of uncooled infrared detector array has led to very important cost decrease of thermal cameras[8][9]. The part of the cost devoted to optics has significantly increased.
- The moulding technology for producing complex chalcogenide glass lenses have been recently developed, making possible high performance and low-cost glass lenses for thermal imaging.

Compared to germanium, the main shortcoming of chalcogenide glasses is associated with the relatively poor thermal mechanical properties (thermal expansion coefficient, hardness…). If this point can be addressed accordingly, that will boost chalcogenide glasses as the first choice for thermal imaging.

As optical fibres, chalcogenide glasses have many potential applications which however could alternative solutions. A lot of work is still ahead in order to improve the performance/cost ratio of systems using chalcogenide glass fibres.

5. Conclusion

Moulded chalcogenide glass lenses have been successfully used for thermal imaging and they perform as good as germanium optics which are much more expensive. It has been demonstrated clearly that chalcogenide glass is an inexpensive alternative to currently used germanium.

Chalcogenide glass fibres have many potential applications such as remote chemical and temperature sensing, laser power delivery. However, much effort is still needed to have these fibres for commercial uses.

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