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Chalcogenide Glass Fibres for Contactless Temperature Sensing

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We have prepared different infrared transmitting chalcogenide fibres for noncontact temperature measuring systems. Arsenic sulfide glass fibres suitable for contactless thermal sensing show a background loss below 1 dBm^{-1} at a wavelength of 5 μm. Thermopile sensors (type TS-72fib), supplied with a fibre of 0.2 m length, show a maximum signal voltage of 250 μV at a black body temperature of 500 K. A fatigue test over 80 days shows no degradation of signal intensity.

1. Introduction

Infrared transparent fibres are suitable transmission media to transfer thermal radiation signals over distances up to 5 m for the sensing of small dimensioned or inaccessible objects. A further benefit is their insensitivity to strong electromagnetic fields. The sensing of object radiation of temperatures ≥ 200°C is typically performed in the middle infrared region (MIR).(1) Chalcogenide glasses are suitable low-loss transmission materials for near infrared (NIR) and particularly MIR spectral ranges due to their low phonon energy network interaction. The position and spectral width of the transparency window depends on the glass composition. For passive applications such as thermal radiation transfer, different chalcogenide glass materials are available. The transparency region can be shifted continuously from 0.8–8 μm in sulfur rich glasses to 2–14 μm in high tellurium containing glasses by the substitution of chalcogenides in the series sulfur - selenium -

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*Corresponding author, e-mail address: kobelke@adam.iphht-jena.de tellurium. In the transparency window attenuation values of 1 dBm^{-1} or lower can be obtained. The minimum value is reported to be approximately 0.02 dBm^{-1} at wavelengths of 2.2–2.7 μm.(2) The transmission of the fibre is closely related to the preparation process of the glass and is limited by absorption and scattering effects. The impurity of the raw materials and also thermally caused defect structures in the glass play an important role. Hydroxide impurities reduce the transmission at $\lambda \approx 2.7$–2.9 μm, SH groups at $\lambda \approx 4.03$ μm, SeH groups at $\lambda \approx 4.57$ μm. Carbon containing impurities lead both to absorptive transmission losses (CO_2, COS, CS_2), and scattering effects.(3,4) The concentration of hydroxide and hydrocarbon caused impurities can be decreased to a level below 1 ppm by suitable purification and preparation of the chalcogenide glass. Only this grade of material purity allows the full utilisation of the MIR transmission potential of the chalcogenide glass fibres.(5)

2. Materials and Methods

2.1 *Glass preparation*

We investigated the following glass compositions: As-S, As-S-Se, As-Se, As-S-Se-Te, As-Se-Te, As-Sb-S-Se, Ge-Sb-Se. The glasses were melted for 12 h in silica glass ampoules at temperatures of 900°C in rocking furnaces. The melts were cooled to room temperature by air quenching. The purities of the raw materials were As, Ge, Sb: 6N; Se, Te: 5N; sulfur was purified by dehydrocarbonation, dehydration and distillation. Figure 1 shows the transmission behaviour of different glass compositions (bulk thickness: 1 cm). The low-frequency shift of the infrared edge is obviously remarkable in the sequence sulfide - selenide - telluride glass. The partial substitution of arsenic by its heavier homologous antimony shifts the IR edge only negligibly. However, neither arsenic selenide nor arsenic selenide telluride glass are, despite their good infrared transparency,

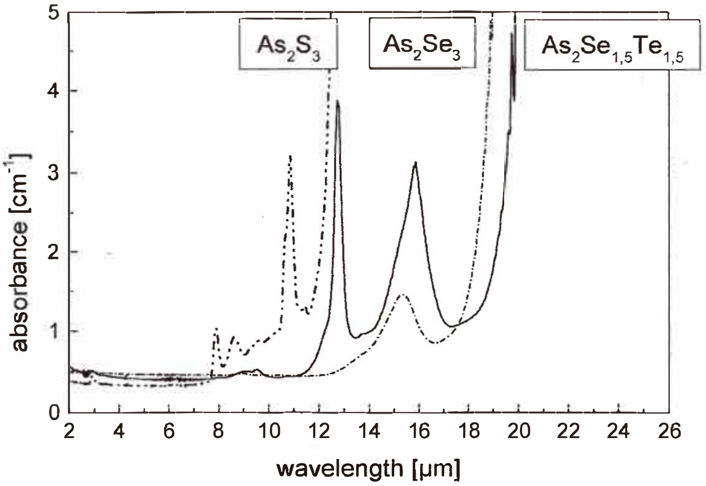

Fig. 1. Absorbance spectra of different arsenic containing chalcogenide glasses in the MIR region.

suitable for good quality fibre preparation because of their unfavourable thermochemical behaviour, particularly their crystallisation tendency during fibre drawing.

2.2 *Fibre preparation*

Unstructured fibres were drawn by using the crucible and preform drawing method.(6) Step index fibres with a core cladding diameter ratio of 1:1.25 were drawn by the double crucible method (Fig. 2). The core cladding diameter ratio of the fibres was adjusted by the cross section ratio of core and cladding glass run out nozzles of the crucibles. The numerical aperture can be tuned by adjusting the glass composition. Thus, the conditions of radiation coupling to the thermal detector can be optimised. For crucible drawing, glass bulks of 20 g weight were used.

Rods with 10 mm diameter were used for preform drawing. The mean viscosity in this drawing process can be increased by one order of magnitude (approx. 10^5 Pas) compared with crucible drawing. This means that the drawing process takes place at considerably lower temperatures. Moreover, the heating time can be minimised. Coincidentally, the dwell time of the glass in the initial crystallisation temperature region is minimised. This decreased "thermal load" during preform drawing permits the fibre drawing of crystallisation sensitive glasses such as arsenic selenide or arsenic selenide telluride, unlike the crucible method. The fibres were coated with UV curable acrylate (Desolite 3471 - DMSO Desotech) of 30–50 μm thickness to protect them from atmospheric corrosion and to increase their mechanical durability.

2.3 *Fibre characterisation*

The fibre transparency in the MIR spectral range was measured with a FTIR spectrometer and a special fibre coupling device (Bio-Rad FTS 3000). The loss measurement was achieved by the cut back method with fibre lengths of approximately 2 m. Arsenic sulfide

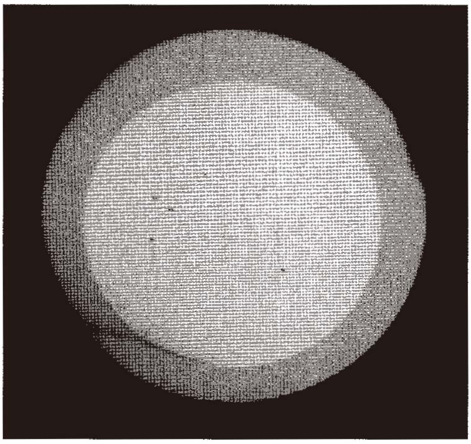

Fig. 2. Cross section of a core cladding fibre with arsenic sulfide core (diameter 160 μm) and arsenic selenide cladding (diameter 200 μm).

fibres allow a minimum attenuation below 1 dBm^{-1} up to wavelengths of 6 μm (Fig. 3). Arsenic selenide telluride fibres show approximately one order of magnitude higher background losses. The MIR transparency of these fibres is limited by additional absorption bands probably related to oxide impurities. This indicates that the level of hydroxide and oxide impurities in the starting materials selenium and tellurium is significantly higher than that in sulfur. The absorption bands of OH at 2.8 μm, SeH at 4.57 μm and the water bending oscillation at 6.32 μm have the highest intensivity. Because of the low vapour pressure of tellurium oxide, purification of tellurium is extremely difficult.

The tensile strength of the fibres was tested by the dynamic strength test method CEI-IEC 793-1-3 with a material testing device, ZWICK Z010. At least 15 pieces of the fibres with a diameter of 200 μm and a length of 500 mm were stretched with a constant velocity of 300 mm min^{-1} until fibre breakage. The tensile strengths of the fibres were measured depending on the material As_2S_3: 0.30 GPa, As_2Se_3: 0.09 GPa, $As_2Se_{2.14}Te_{0.86}$: 0.05 GPa.

2.4 *Fibre sensor setup and test*

Examples of fibre coupled infrared sensors were prepared using unstructured acrylate-coated arsenic sulfide fibres.(7) The fibre diameters were 200 μm and 400 μm, respectively. The distance between the fibre end face and the sensor chip surface was 0.2 mm. As infrared sensors we have used the IPHT thermopile sensor types TS-72, TS-100 and TS-144 with detection areas of 0.2 mm^2, 1 mm^2 and 4 mm^2, respectively.(8) For example the model TS-72 is a miniaturized multijunction thermopile sensor made by thin-film technology. It consists of 72 radially arranged thermoelectric junction pairs formed from evaporated antimony and bismuth thin films. The centrally located active junctions comprising the active area of 0.2 mm^2 are blackened by metallic smoke or coated with an

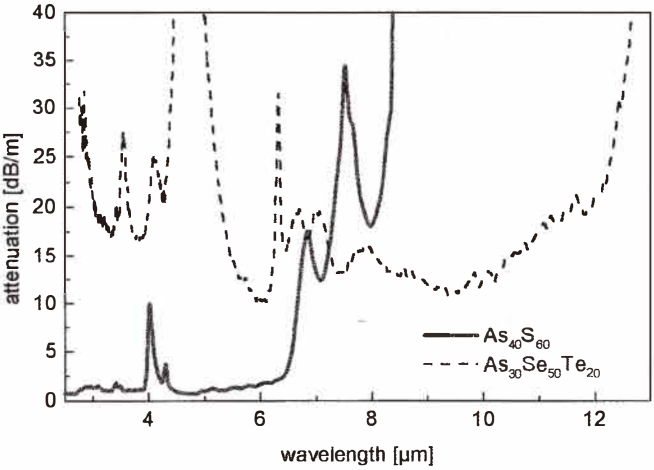

Fig. 3. Attenuation spectra of different arsenic chalcogenide glass fibres in the MIR range (unclad fibres, diameter 200 μm).

interference absorption multilayer system. The sensor chip is hermetically sealed and positioned in a small modified TO-5 package under an inert gas atmosphere. Typical performance parameters of the used (N_2-filled) TS-72 thermopile sensors are: responsivity = 140 V/W, time constant = 35 ms and specific detectivity $D \cdot (T = 500\ \mathrm{K, DC}) = 4 \times 10^8$ $\mathrm{cmHz^{1/2}/W}$.

By using sensor chips with differently sized detection areas, we have tested (Fig. 5) the sensitivity of various detecting systems consisting of the conventional IPHT thermopile sensor chips mounted on a TO-5 sensor socket. They were sealed hermetically with a TO-5 cap in which the arsenic sulfide fibre was tightly mounted before.

Additionally, we varied the gas atmosphere inside the package. We tested nitrogen and xenon because of their different thermal conductivities.

The signal voltage of the sensor U depends on the following parameters:

$U = \varepsilon \cdot \sigma \cdot A \cdot (T_0^4 - T_s^4) \cdot S \cdot NA^2/(1-NA^2)$

ε: emission coefficient
σ: Stefan-Boltzmann constant ($56.7 \cdot 10^{-9}\ \mathrm{WK^{-4}m^{-2}}$)
A: effective detection area
T_0: object temperature
T_s: sensor temperature
S: sensor sensitivity
NA: numerical aperture of the fibre

The test of the fibre supported sensors was undertaken using the measuring device shown in Figure 4. The standard test temperature of the black body radiator was 500 K. The accuracy of black body temperature adjustment was ± 1 K.

3. Results

The influence of the sensor type (detection area) on the signal voltage was tested with a standard grade arsenic sulfide fibre of 0.3 m length and a background loss of approxi-

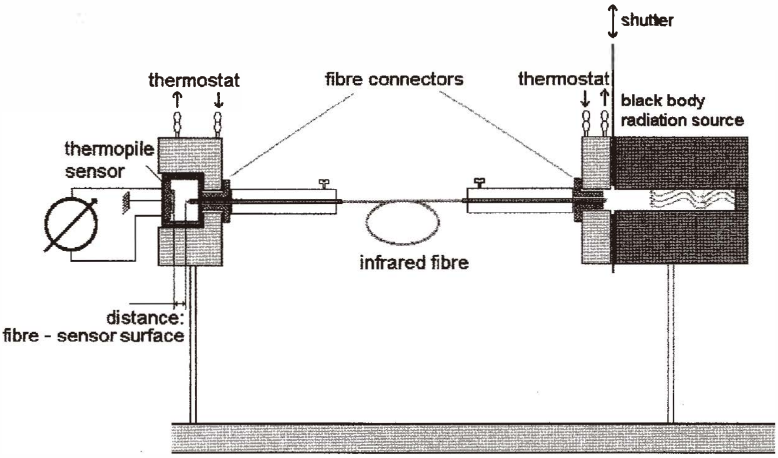

Fig. 4. Black body test device for fibre sensor characterisation.

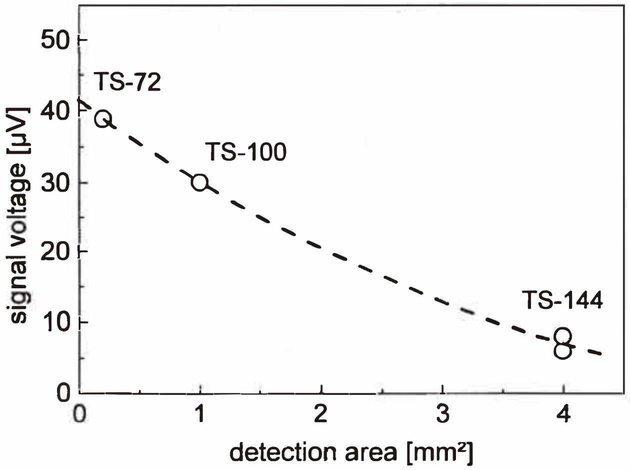

Fig. 5. Influence of the sensor type (detection area) on the signal voltage.

mately 2 dBm^{-1} at a wavelength of 5 μm. The gas atmosphere in the sensor package was nitrogen. The radiation temperature for the tests was 500 K. The accuracy of the signal voltage measurement was ±2%.

Figure 5 shows that sensors with large detection area (TS-144) result in lower signal voltages than sensors with small area (TS-72). The high numerical aperture of the fibres (approx. 0.6–0.7) effects a sufficient illumination of the detection areas of all the sensor types. The signal voltage is influenced by the sensor sensitivity. Small area sensors (TS-72) show a higher detection element density related to TS-100 and TS-144. The higher detection element density of the small area sensor is mostly responsible for the higher signal voltage.

The application of arsenic sulfide fibres with improved purity and background losses < 1 dBm^{-1} at 5 μm increased the signal intensity. Using a TS-72 sensor with nitrogen filling, an arsenic sulfide fibre of a diameter of 400 μm and a length of 0.3 m, we obtained a signal voltage of 110 μV, whereas in a xenon atmosphere it showed a signal of 250 μV at a temperature of 500 K.

Fatigue tests over 80 days showed that the sensor sensitivity does not decrease. This demonstrated that no leakage of the sensor filling gas and no degradation of the fibre end face occurred.

4. Discussion

Fibre supported sensors based on Sb/Bi thermopile chips of type TS-72 yield, with xenon as filling gas and a fibre length of about 0.3 m in the radiation temperature range of 200°C, signal voltage amounts of more than 250 μV (Fig. 6). The prepared chalcogenide glass fibres based on arsenic sulfide show background loss values in the MIR spectral

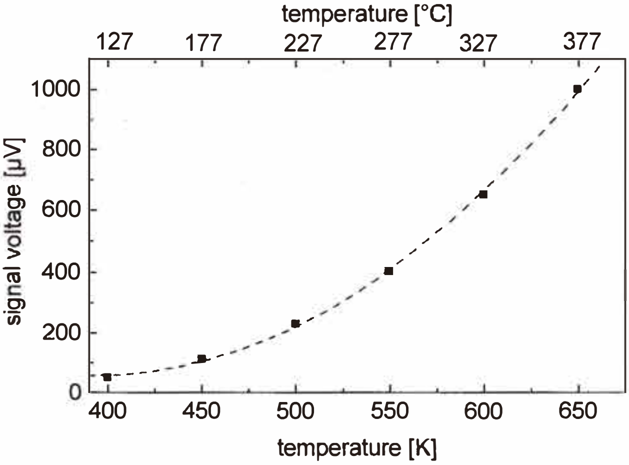

Fig. 6. Influence of radiation temperature on signal voltage of a xenon-filled TS-72 fibre sensor (400 μm arsenic sulfide fibre, length 0.3 m).

region below 1 dBm^{-1}. They are highly suitable for application in temperature sensing in the temperature region above 200°C. Selenide or telluride based glasses present, despite their low phonon energy, higher transmission losses of the fibres in the MIR region. The losses are caused by oxide impurities and scattering effects which appear to be related to the beginning of crystallisation.

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