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Selenium modified $GeTe_4$ based glasses optical fibers for far-infrared sensing

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ABSTRACT

This study reports on the synthesis of telluride glasses that have transmission far beyond the second atmospheric window and are stable enough toward crystallisation to be drawn into optical fiber. These glasses are based on the $GeTe_4$ initial composition which has been stabilized by the introduction of few percents of Se and a modified the Te/Ge ratio. In that domain, $Ge_{21}Se_3Te_{76}$ constitute the optimum composition and some mono index optical fibers have been successfully drawn. It is shown that their optical transparencies extend from 5 to almost 16 μm in the mid-infrared, establishing a record for chalcogenide glass fibers. These fibers have been used to implement Fiber Evanescent Wave Spectroscopy experiments, permitting to detect infrared molecule signatures beyond 12 μm, infrared domain that was unreachable by now. These innovative fibers are also used to detect the broad absorption band of gaseous CO_2 lying from 13 to 16 μm and therefore hold promises in the framework of the Darwin mission of the European Space Agency. Both of these results suggest that these new optical fibers will become essential in the field of infrared remote sensing.

1. Introduction

Chalcogenide glasses have been studied for several decades in regards to different applications [1–9]. Sulphide glasses are mainly studied as hosts for rare earth doping and selenide glasses have excellent infrared transmission covering the two atmospheric windows at 3–5 and 8–14 μm. Telluride based compositions have been studied mostly as phase change materials for optical or electric storage of numerical data, as these compositions have a strong tendency to crystallize [10–12].

Nevertheless, telluride glasses can have transmission up to 25 μm far beyond the second atmospheric window [13–17] but this potential has attracted limited attention due to the lack of applications resulting from the strong atmospheric absorption in that range. More recently the research on these glasses have been intensified thanks to the European Space project Darwin whose objective is to discover extra solar earth-like planets and to analyse their atmosphere in the spectroscopic band of 6–20 μm. The system will be based in space and the operation band is set to cover the fundamental absorption of H_2O, O_3 and CO_2. These molecules are considered as markers for potential life on remote planets [18–21].

Carbon dioxide is also considered to be the most important green house gas responsible for global warming. The decrease of its production and its underground storage are important research subjects nowadays. The CO_2 molecule has a large absorption peak between 13 and 16 μm, much larger than the one in the 4.2 μm region. Tellurium based glass fibers are the only glass fibers having a large enough optical window to cover this large absorption peak, making the underground monitoring of CO_2 possible for example [22,23].

Stable tellurium glass compositions have previously been obtained by combining this element with halogens [24], giving glasses in the Te–Cl and Te–Br systems. These glasses are stable against crystallisation, but suffer from low glass transition temperature T_g and low environmental stability. Tentative has been made to increase the T_g by introducing other elements such as As and Ge [25,26] but significant selenium content is, in these cases, also necessary to get crystallisation resistant glass compositions.

More recently, tellurium based glasses have been studied starting from the $GeTe_4$ which is a bad glass former. Different third elements such as gallium, iodine or selenium have been introduced into this binary composition in order to improve its resistance towards crystallisation. More stable glasses have been obtained [13–15,17] and one of the most promising solutions appears to be the introduction of selenium in order to increase the difference between T_g and the crystallisation temperature to values greater than that of 79 °C for the $GeTe_4$. But while large selenium content can greatly improve the resistance towards crystallisation; it also induce unacceptable absorption beyond 16 μm [27–31]. Hence, in this study we investigated the Ge–Te–Se glassy system in order

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to optimize the glass stability while keeping the Te content at a maximum. The selenium content will be kept under 5% and the Te/Ge ratio will be modified in order to obtain sufficiently stable glasses for fiber drawing. The final aim is to show that the resulting fiber can be used for Fiber Evanescent Wave Spectroscopy (FEWS) to detect molecules with signals in the far infrared. The same fibers are also used in transmission mode in order to demonstrate their suitability for detection of CO_2 near 15 μm for the Darwin mission.

2. Experimental

Glasses in the Ge–Te–Se system have been synthesized with 5 N purity raw materials, Ge (Yunnan Dongrun imports and exports), Te (Zhuzhou Smelter Group), and Se (Umicore). Glasses in the Ge–Te–Se system have been synthesized with commercially available 5 N elements as starting materials. For determining the glass forming ability, as-received raw materials, stocked in controlled atmosphere, have been used without additional purification for synthesizing test samples. A batch of 10 g of the appropriate quantities of different elements were weighed in air and immediately put into a fused silica tube with a typical external diameter of 9 mm. The silica tube was sealed under a vacuum of a 10^{-4} mbar and was then put into a furnace. The mixture was heated up to 750 °C at a rate of 5 °C/min and kept at this temperature for several hours. The silica tube containing the melt was then quenched into water and the obtained glass samples were annealed at a temperature slightly below the glass transition temperature before being cooled down slowly to room temperature.

For fiber drawing, the obtained glass were mixed with an oxygen getter such as metallic aluminium, and then distilled in order to eliminate oxygen impurity and insoluble scattering particles, which are mostly carbon. The obtained glass rods were then drawn into fibers with a specially designed drawing tower for glasses with relatively low softening temperature.

Visual examination of broken surfaces of the obtained samples is generally enough to determine if the sample is vitreous. In case of doubt, further examination with infrared camera and infrared transmission measurement as well as X-ray diffraction were used.

The characteristic temperatures, the glass transition temperature T_g and the crystallisation temperature T_x, were determined with Differential Scanning Calorimeter (DSC) model 2010 from TA instrument with a heating rate of 10 °C/min. Infrared transmission was measured with a Bruker Vector 22 Fourier Transform infrared spectrometer equipped for bulk and fiber measurement. The transmission on bulk samples was performed on disks of thickness 2 mm and the fiber attenuation measurement was performed by using the cut-back method with a different lengths ranging from 40 to 50 cm.

3. Results and discussion

All the glass compositions studied are shown on the Ge–Te–Se ternary phase diagram in Fig. 1. Glass compositions from the $Ge_{20}Te_xSe_{80-x}$ (x = 0–80) tie line were previously reported and show an almost continuous glass forming range from $GeTe_4$ to $GeSe_4$ except a small de-mixing zone in the middle of two well defined compositions [17]. However for this study, in order to keep the far infrared transmission wide as possible, it was concluded that the selenium content should be as low as possible below 5 at.%.

It is believed that, in pure tellurium glass the structural network is built up from $GeTe_4$ tetrahedra [32]. The optical window is consequently limited by a multiphonon cut-off of very low energy due to vibrational modes associated with Ge–Te covalent bonds. Similarly, for selenium content below 5%, it was shown that the phonon edge remains mainly associated with Ge–Te vibrations and it was observed that the substitution of Te by low at.% of Se does not significantly affect the IR cut-off of the bulk glass. However, in this case, no glass was stable enough against the crystallisation to withstand fiber drawing process.

In this study different compositions particularly with 3 or 4 at.% Se have been investigated by modifying the Ge/Te ratio. The characteristic temperatures of all these investigated glass compositions are listed in Table 1. Three glass compositions, $Ge_{21.5}Se_{3.5}Te_{75}$, $Ge_{21}Se_3Te_{76}$, $Ge_{20.5}Se_4Te_{75.5}$ have a difference between T_x and T_g of at least 120 °C. The $Ge_{21}Se_3Te_{76}$ has been selected for further

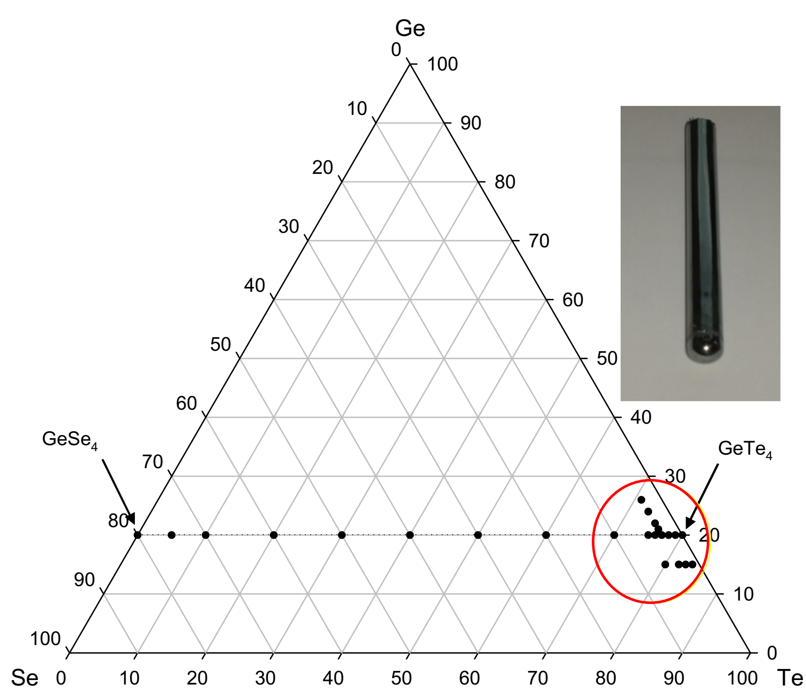

Fig. 1. Investigated glass composition in the Ge–Te–Se system. The strategy consists in introducing few percent of Se and to slightly modify the Ge/Te ratio to stabilize the $GeTe_4$ initial glass composition.