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Te-As-Se glass destabilization using high energy milling

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ABSTRACT

The $Te_{20}As_{30}Se_{50}$ (TAS) glass has been studied under the extreme conditions of high energy milling. Starting from the raw materials, an amorphization process occurs progressively reaching an unstable intermediate state and the final stable state then. Despite its high resistance against crystallization when made using silica tubes, an intermediate state is reached when mechanically alloyed into powder. The evolution of the glass structure has been investigated using Raman spectroscopy and MAS NMR of ^{77}Se according to the milling time. Optimized parameters and conditions to compact milled powders by Spark Plasma Sintering show the possibility to design infrared windows transparent from 2 to 20 μm. A correlation to the thermo-mechanical properties of densified powder using hot pressing has been made.

1. Introduction

Night Vision is the first thing that comes to mind when speaking of chalcogenide glasses capable of transmitting light in the infrared [1–2]. But these glasses have other advantages; they are also very good candidate for chemical species sensors since most of the chemical or biochemical molecules present fundamental vibrations in the mid-infrared range, having a specific and recognizable signature. The optical fiber of chalcogenide glass can thus be used for the detection of chemical species in the liquid or gaseous state. Indeed, the use of this type of glass as a chemical sensor has already been demonstrated [3–4]. It is thus possible to produce biosensors from chalcogenide fibers such as $Te_{20}As_{30}Se_{50}$ (TAS) glass composition that enable faster and less invasive diagnostics for infectious diseases, chronic, and cancer [5]. Their efficiency can then be monitored by tapering the fiber diameter (about 100 μm). This step occurs after the fiber drawing on section of about 4 cm length that is heated again. This multistep process is very time consuming to obtain reproducible section diameters of sensors.

The objective of this work is therefore to develop a way to easily and rapidly shape the $Te_{20}As_{30}Se_{50}$ (TAS) glass into bulks or tapers. Thus, the possibility to obtain TAS amorphous powder by mechanical alloying, cheaper method than conventional melt-quenching method has been investigated. The possibility to mix and get amorphous alloys is commonly used to obtain metallic glasses [6–7]. This process has already been investigated in germanium based chalcogenide glasses [8–9]. Then, coupled to the mechanical synthesis, flash sintering using Spark Plasma Sintering (SPS) will be used to compact and mold the glass powder.

2. Experimental details

The synthesis of amorphous powders was carried out in a planetary mill (Retsch® PM 100), using a bowl (125 ml) and 6 balls (diameter 20 mm) in tungsten carbide from raw metals (Te, As and Se, 5N). Syntheses were performed under controlled atmosphere of argon in a glove box.

Furthermore, in order to avoid overheating of the system, a grinding cycle was imposed, alternating rotation for 3 min in a sense, a break of 3 min and a rotation for 3 min in the opposite direction. It may be noted in addition that the milling was regularly stopped in order to collect powder samples to monitor the structural evolution thereof.

In parallel, some TAS bulk glasses were synthesized using the process described by Zhang et al. [10]. Some samples were then grinded for 30 min in the planetary grinder, in order to compare the properties and structure reached in both methods.

Thus, samples have been defined as TAS-MM-Xh for mechanical milled powder, X being the time of milling and TAS-G for the base glass being grinded for 30 min. The reference will be the TAS glass made by melt quenching that will be called TAS base glass.

Thermo-mechanical analysis were performed using differential scanning calorimetry (DSC) (DSC Q20 TA Instruments) with a temperature ramp of 10 °C/min and Vickers hardness measurements using a Matsuzawa microindentor (100g, 5 s), average of 10 measures.

Structural analysis of amorphous powder has been investigated

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Table 1
Evolution of the characteristic temperatures of the TAS powder as a function of the milling time.

Milling time	T_g (°C) (± 2 °C)	T_x (°C) (± 2 °C)	ΔT ($T_x - T_g$)
1 h	47 (pure Se)	81	34
2 h	54	82	28
3 h	62	82	20
5 h	70	90	20
10 h	107	166	59
15 h	125	202	77
20 h	130	215	85
40 h	132	217	85
60 h	133	223	90
80 h	135	226	91
100 h	135	227	92
140 h	135	–	–
160 h	135	–	–

using XRD (Phillips PW3710 diffractometer), NMR of the ^{77}Se atom and Raman spectroscopy for different times of grinding.

Raman acquisitions are made with the HR800 - 785 nm optical density D2 with a laser at 785 nm. Studies were conducted on green pellets of powders taken after 100 h and 160 h of grinding and on a bulk sample compacted by SPS on powder of 160 h of milling.

All NMR spectra ^{77}Se (S = 1/2) were recorded at room temperature on the Avance 300 Bruker spectrometer operating at 57.28 MHz using a 4 mm rotor turned under magic angle of 54.74° (MAS, Magic Angle Spinning) at 14 kHz.

3. Results

The $Te_{20}As_{30}Se_{50}$ glass presents a high stability against crystallization having a Tg of 135 °C (± 2 °C) [11], showing no crystallization peak. This high stability allows its easy drawing into fibers of specific design with a high flexibility. The thermal properties of TAS powder obtained after different milling duration are listed in Table 1.

During the first 2 h of grinding, the thermal answer corresponds to pure amorphous Se. The gradual increase of Tg shows the progressive reaction of selenium, arsenic and tellurium to lead to the formation of the amorphous phase of the TAS after about 40 h.

While the theoretical Tg of the TAS glass can be rapidly reached, a residual crystallization peak can be observed at about 225 °C. With longer milling time, the Tg remains stable and the peak of crystallization shifts to higher temperatures until it disappears after 140 h.

Thereafter, the mechanical alloying could be stopped after 60 h of milling to compact and shape the glass as the Tg reached a plateau and the difference between Tx and Tg is high enough to ensure a compaction without crystallization by SPS. In fact, SPS is known as a fast and low temperature way to compact pellets into their final shape. Sintering is usually performed at a temperature close to Tg for several minutes.

The diffractograms showed no peak corresponding to crystalline selenium in the first hours of grinding demonstrating its rapid amorphization (Fig. 1). After 5 h of milling part of the tellurium and arsenic remains in their crystalline form. After 10 h of milling, tellurium is completely amorphous while crystalline arsenic disappears after 40 h of milling leading to a fully amorphous powder. It is important to note that no crystalline phase is generated during milling.

In order to understand the difficulty to stabilize the glassy matrix, crystallization experiments were performed on powder milled for 100 h, still presenting a crystallization peak in DSC curves.

Powders were heat treated at Tx (Tg + 90 °C) for 1 and 3 h in a ventilated furnace.

As shown in Fig. 2, As_2Se_3 crystals are quickly produced within the glassy matrix. This phase remains unchanged after 3 h of ceramization. This experiment clearly demonstrates the first interaction between Se and As which is favored compared to Te. One can assume that the high specific surface favors a fast and not homogeneous surfacic crystallization process.

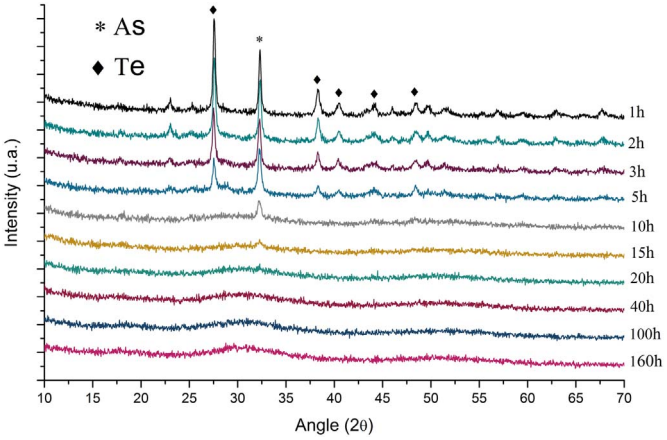

Fig. 1. Diffractograms of powders obtained after different grinding time by mechanical synthesis.

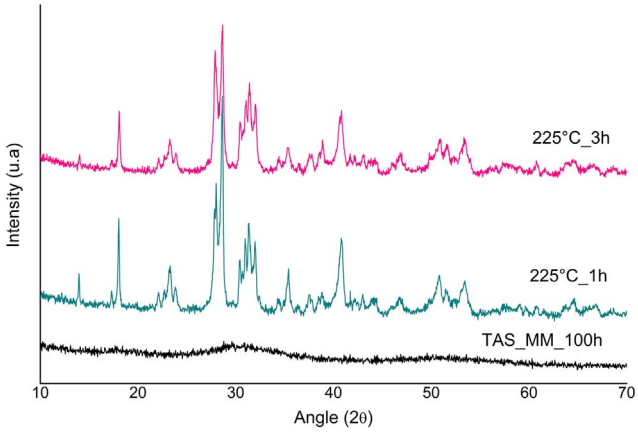

Fig. 2. XRD of 100 h milled powder heat treated for different duration at Tg + 90 °C meaning 225 °C.

4. Molding process

The first SPS sintering tests were conducted on molds made of graphite of 10 mm inner diameter using a sheet of Papyex® (flexible graphite sheet) to ensure the release of the solid as well as protect the diffusion of the graphite component from the mold. Green pellets (3 tons) were made to facilitate the shaping and avoid external pollution. Bertrand et al. showed the efficiency of this method to avoid graphite contamination depending on the grain size [12].

First experiments were carried on TAS-MM-160 h sintered in graphite molds at two temperatures close to Tg (± 5 °C), results of transmittance are presented in Fig. 3.

As observable in the Fig. 3, temperature appears as a major criterion to control the glass compaction. In fact, 5 °C below Tg pellets are not densified enough to transmit. However, samples sintered at 140 °C present a maximum of 35%, far from the theoretical TAS transmittance of 62%. The densification was calculated from the theoretical glass density (4,88). Even if a densification of 99% has been determined, the presence of carbon particles of hundreds of microns in the samples may explain the significant MIE scattering, phenomena already observed by Hubert et al. [8].

First, in order to optimize sintering parameters, a purified bulk TAS made by melt-quenching has been grinded for 30 min in the planetary grinder. This powder is called TAS-G30. Also, to obtain an effective barrier to carbon diffusion and thereby improve the transmission of the