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The TeO_2-rich part of the TeO_2–Ga_2O_3 system: equilibrium and non-equilibrium phase diagram

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The TeO_2-rich part of the TeO_2–Ga_2O_3 system has been investigated, under equilibrium and non-equilibrium conditions, by temperature programmed X-ray diffraction and differential scanning calorimetry (DSC). Two invariant equilibria have been detected: one peritectic reaction and one eutectic reaction. The peritectic reaction corresponds to the incongruent melting at 620 °C ± 5 °C of the crystalline compound $Ga_2Te_4O_{11}$ (ΔH_P = 18.1 ± 2 kJ mol^{-1}) and to the equilibrium $Ga_2Te_4O_{11} \leftrightarrow L_P + Ga_2O_3$. The eutectic reaction (23 mol% $GaO_{1.5}$, T_E = 600 ± 5 °C, ΔH_E = 22.2 ± 2 kJ mol^{-1}) corresponds to the equilibrium $TeO_2 + Ga_2Te_4O_{11} \leftrightarrow L_E$. The glass forming domain ranges from 5 to 30 mol% $GaO_{1.5}$, and can be extended from 0 to 35 mol% by quenching the melt in a freezing mixture, consisting of ice, ethanol and NaCl (≈ -14 °C). The thermal behaviour of glasses has been studied. The glass transition and crystallization temperatures, and the phases which appear during the crystallization have been identified.

Introduction

To answer the increasing industrial demand for optoelectronics devices, many studies are presently devoted to tellurite glasses, which are very interesting materials because of their high linear and non-linear refractive indices and of their good visible and infrared light transmittance. Recent studies on TeO_2-based glasses have revealed that their non-linear refractive index could be up to 100 times as large as that of SiO_2[1–3] and our investigations within the TeO_2–Tl_2O system have shown that thallium–tellurite glasses exhibit the highest non-linear refractive indices measured for light wavelength 1.5 µm and reported for oxide glasses.[3] The origin of this non-linearity was attributed to the hyperpolarizability of the Te^{IV} atom lone pair, which is very often reinforced by addition of either a second lone pair holder (such as Tl^+, Bi^{3+}, Pb^{2+}) or of cations with empty d-orbitals (such as Ti^{4+} or Nb^{5+}); and presently many studies are underway to improve knowledge of the relationships between the structure and non-linear optical response of tellurite glasses.[3–31] In order to improve the mechanical strength of thallium–tellurite glasses, which are very promising for non-linear optical devices but are particularly brittle, we have investigated the possible addition of Ga_2O_3. From this point of view we are now working within the TeO_2–Tl_2O–Ga_2O_3 system. The TeO_2–Tl_2O equilibrium and non-equilibrium phase diagrams have been previously reinvestigated.[32] Up to now, studies related to gallium–tellurite glasses were essentially devoted to their structural determination.[33–36] An equilibrium phase diagram of the TeO_2–Ga_2O_3 system has been previously proposed for compositions ranging from 50 to 100 mol% of TeO_2 and has revealed the existence of a gallium–tellurite, $Ga_2Te_3O_9$, that melts congruently at 850 °C and forms two eutectics, respectively, with TeO_2 at 630 °C (for the 18.2 mol% $GaO_{1.5}$ composition) and with Ga_2O_3 at 610 °C (for the 50 mol% $GaO_{1.5}$ composition).[37] However, such results are particularly doubtful since all samples were fused in porcelain crucibles, which are not inert to tellurite compounds. We present in this paper, on one hand, an accurate determination of the phase diagram under equilibrium and non-equilibrium conditions for the TeO_2-rich part of the TeO_2–Ga_2O_3 system and, on the other hand, a study of the thermal behaviour of the glasses, including their structural change with temperature (especially the identification of the crystalline phases which appear during crystallization) and the determination of their glass transition (T_g), crystallization (T_c) and melting (T_l) temperatures.

Experimental

All the crystallized samples were obtained by heating at 500 °C for 12 h and then at 600 °C for 12 h in sealed gold tubes, intimate mixtures of commercial β-Ga_2O_3 (Aldrich, 99.9%) and TeO_2. TeO_2 were prepared in the laboratory by decomposition at 550 °C of commercial H_6TeO_6 (Aldrich, 99.9%). Glasses were obtained by first melting at 800 °C for 30 min, appropriate quantities of reagent grade Ga_2O_3 (Aldrich, 99.9%) and TeO_2 in a sealed gold tube, and then air-quenching the melts. In order to extend the glass forming range, the gold tube was quickly dipped in a freezing mixture, consisting of ice, ethanol and NaCl kept at about −14 °C. The glass formation domain and crystallized phase compositions were determined by using X-ray diffraction (Guinier-De Wolff camera, Cu Kα radiation). The structural evolution with the temperature of the glasses was followed under nitrogen by *in-situ* X-ray powder diffraction (XRPD) with a Siemens D5000 diffractometer (θ/θ mode, Cu Kα radiation) fitted with a high temperature furnace (Anton-Parr HTK10), a platinum heating sample holder and an Elphyse sensitive position detector (14° aperture). The heating rate was 5 °C min^{-1} and each XRPD pattern was recorded after an annealing time of 10 min at the chosen temperature (in the temperature range 20–700 °C), in the 2θ range 10–90° (step size: 0.029, time range: 18 min). Glass transition (T_g), crystallization (T_c) and melting (T_l) temperatures

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were measured by heat flux differential scanning calorimetry (DSC; Netzsch STA 409). The powdered samples (≈30 mg) were introduced into covered platinum crucibles and the DSC curves were recorded between 20 and 750 °C using a heating rate of 10 °C min^{-1} under nitrogen. The glass transition temperature was taken as the inflection point of the steep change of the calorimetric signal associated with this transition. The crystallization temperature was taken as the intersection of the slope of the exothermic peak with the extrapolated baseline. As for the liquidus temperature, T_l, it was considered to correspond to the bottom of the related endothermic peak. The energies of the different thermal events were obtained from the area under the corresponding peak after heat-flow rate calibration (calibration substance: sapphire (100% pure Al_2O_3)). The densities of both crystalline and glassy samples were measured on finely ground powders by helium pycnometry (Accupyc 1330 pycnometer).

Results and discussion

Equilibrium phase diagram

The DSC and temperature XRD results are consistent with the phase diagram shown in Fig. 1. Because of the possible TeO_2 evaporation for temperatures higher than 800 °C, the liquidus curve has not been determined for composition containing more than 35 mol% $GaO_{1.5}$. The existence of a stable $Ga_2Te_3O_9$ crystalline phase and of the two eutectic reactions (respectively at 50 mol% $GaO_{1.5}$ and 18.2 mol% $GaO_{1.5}$), previously evidenced by Pavlova *et al.*,[37] has not been confirmed. Many experiments were carried out in order to reproduce, from the raw oxide materials, the synthesis of the stable $Ga_2Te_3O_9$ compound and even under Pavlova's synthesis conditions we never confirmed the existence of such a crystalline phase.

Two invariant equilibria were detected (see Fig. 1): one peritectic reaction and one eutectic reaction. The peritectic reaction corresponds to the incongruent melting at 620 °C ± 5 °C of the crystalline compound $Ga_2Te_4O_{11}$ ($\Delta H_P = 18.1 \pm 2$ kJ mol^{-1}) according to the equilibrium $Ga_2Te_4O_{11} \leftrightarrow L_P + Ga_2O_3$. The eutectic reaction (23 mol% $GaO_{1.5}$, $T_E = 600 \pm 5$°C, $\Delta H_E = 22.2 \pm 2$ kJ mol^{-1}) corresponds to the equilibrium $TeO_2 + Ga_2Te_4O_{11} \leftrightarrow L_E$. The $Ga_2Te_4O_{11}$ crystal structure has been recently determined,[38] it crystallizes with triclinic symmetry (space group $P1$) and unit cell parameters: $a = 5.125(1)$ Å, $b = 6.559(1)$ Å, $c = 8.173(2)$ Å, $\alpha = 75.06(2)$, $\beta = 89.25(2)$, $\gamma = 69.62(2)$, $Z = 1$.

Formation of glasses

Under our experimental conditions (first melting at 800 °C and then air-quenching), the glass forming domain ranges from 5 to 30 mol% $GaO_{1.5}$, and can be extended from 0 to 35 mol% by quenching the melt in a freezing mixture, consisting of ice, ethanol and NaCl (≈ −14 °C). These results are in perfect agreement with those previously published.[33–37] All the glasses are transparent and bright yellow. The density of the glasses linearly decreases from 5.58 to 5.24 g cm^{-3} with increasing $GaO_{1.5}$ content. The DSC curves of some glassy samples and the evolution with composition of the glass transition (T_g) and first crystallization temperatures (T_c) are shown in Figs. 2 and 3. T_g and T_c increase linearly (respectively, from about 310 °C to 350 °C and from about 350 °C to 430 °C) with increasing $GaO_{1.5}$ content. The $T_g - T_c$ difference, and so the thermal stability of glasses, increases with $GaO_{1.5}$ content: from 35 °C for the 5 mol% $GaO_{1.5}$ composition up to 62 °C for the 30 mol% $GaO_{1.5}$ composition.

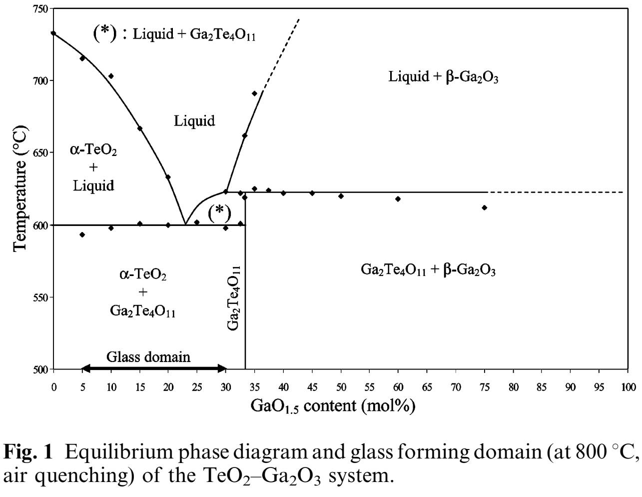

Fig. 1 Equilibrium phase diagram and glass forming domain (at 800 °C, air quenching) of the TeO_2–Ga_2O_3 system.

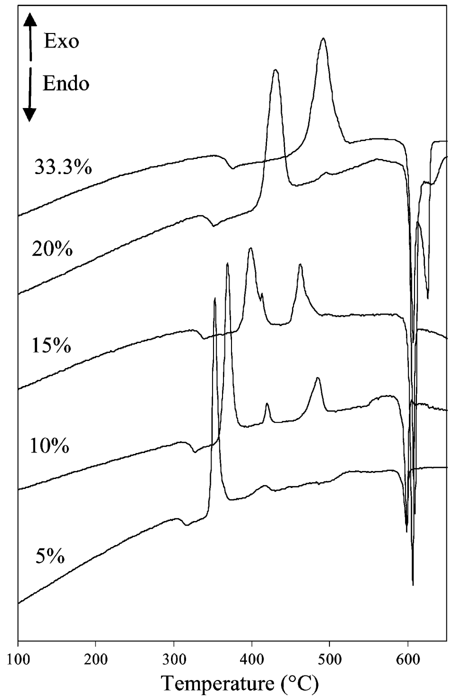

Fig. 2 DSC curves of some $(1 - x)TeO_2$–$xGaO_{1.5}$ glasses.

Thermal behaviour of glasses

The DSC peaks were unambiguously identified by the *in-situ* XRD studies. For pure TeO_2 glass, and as we have already reported,[39,40] the crystallization occurs with the simultaneous formation of α-TeO_2 and γ-TeO_2 polymorphs. For glassy samples in the range 4–10 mol% $GaO_{1.5}$ (as illustrated by the XRD patterns at various temperatures of the sample with 5 mol% $GaO_{1.5}$ shown in Fig. 4) three exothermic events are observed: first, the crystallization of γ-TeO_2; second, the crystallization of α-TeO_2; and third, the transformation of the γ-TeO_2 metastable polymorph into the stable α-TeO_2 one. The endothermic peak, observed in the range 580–600 °C, is

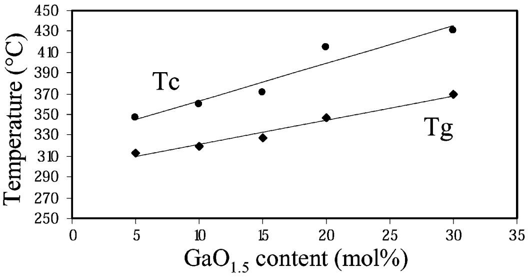

Fig. 3 Evolution with composition of the glass transition (T_g) and crystallization temperatures (T_c) of the TeO_2–Ga_2O_3 glasses.

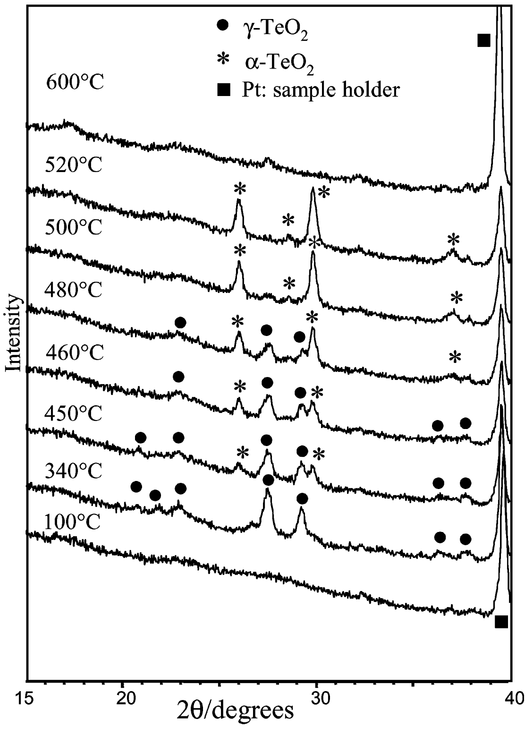

Fig. 4 XRD patterns at various temperatures of the $0.95TeO_2$–$0.05GaO_{1.5}$ glassy sample. ●, γ-TeO_2; *, α-TeO_2; ■, Pt (Pt diffraction peaks are those of the sample holder).

related to the melting of the mixtures. For samples containing more than 10 mol% and up to 18 mol% $GaO_{1.5}$ (Figs. 2 and 5) we first observed the crystallization of γ-TeO_2 and then, just a few °C above, the crystallization of α-TeO_2. The third large peak corresponds to two exothermic events: the transformation of γ-TeO_2 into α-TeO_2 and the crystallization of $Ga_2Te_4O_{11}$ compound. As previously observed within the TeO_2–WO_3[39] and the TeO_2–Nb_2O_5[40] systems, the crystallization of the two polymorphs, γ-TeO_2 and α-TeO_2, is observed more and more simultaneously with increasing content of doping cation. For samples containing more than 18 mol% $GaO_{1.5}$ (Fig. 2), two large peaks characteristics of nearly simultaneous thermal events are observed on the DSC curves. The γ-TeO_2 phase is no more observed and the first peak is associated with the crystallization of a new compound (called "X" in Fig. 6) and of α-TeO_2. The second peak of weak intensity corresponds to the transformation of this "X" phase into the $Ga_2Te_4O_{11}$ one.

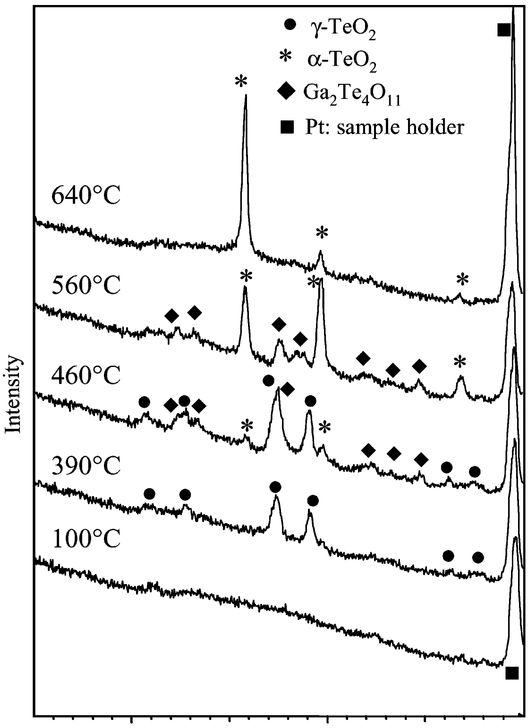

Fig. 5 XRD patterns at various temperatures of the $0.85TeO_2$–$0.15GaO_{1.5}$ glassy sample (●, γ-TeO_2; *, α-TeO_2; ◆, $Ga_2Te_4O_{11}$; ■, Pt (Pt diffraction peaks are those of the sample holder).

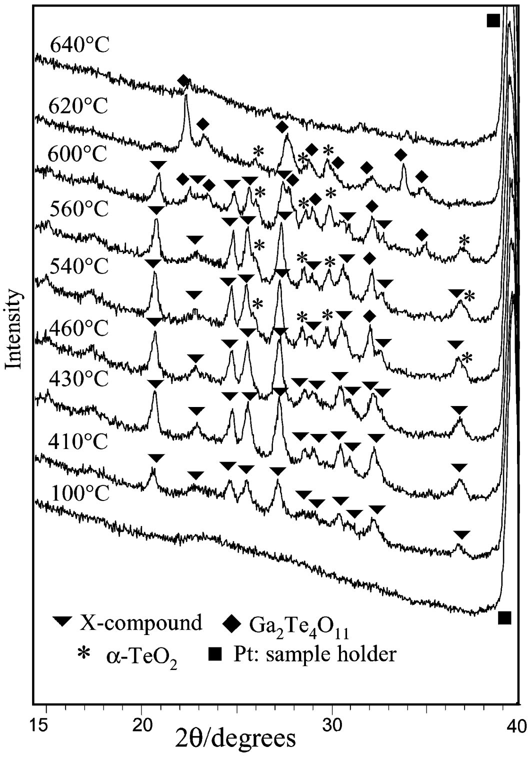

Fig. 6 XRD patterns at various temperatures of the $0.70TeO_2$–$0.30GaO_{1.5}$ glassy sample (*, α-TeO_2; ◆, $Ga_2Te_4O_{11}$; ▼, "X" compound; ■, Pt (Pt diffraction peaks are those of the sample holder).

It is interesting to notice that this new metastable "X" phase has only been observed during the crystallization of glassy samples in the range 18–33.3 mol% $GaO_{1.5}$. Various experiments performed in order to prepare this phase from α-TeO_2 and β-Ga_2O_3 materials were unsuccessful. It has been synthesized, as a relatively well crystallized compound, after annealing for 12 h at 540 °C a glass with a 33.3 mol% $GaO_{1.5}$ composition. The corresponding X-ray powder diffraction pattern is identical to that previously proposed by Pavlova for the announced $Ga_2Te_3O_9$ phase.[37] According to an automatic determination procedure[41,42] and refinement calculations,[43] it crystallizes with monoclinic symmetry and unit cell parameters: a = 19.325(6) Å, b = 5.753(2) Å, c = 15.270(6) Å and β = 105.92(3). The XRD patterns at various temperatures of the 66.7 mol% TeO_2 – 33.3 mol% $GaO_{1.5}$ glassy sample have clearly shown the crystallization at about 400–420 °C of this "X" phase, which transforms progressively to $Ga_2Te_4O_{11}$ above 500 °C. According to such results it could be reasonable to think that this "X" phase could be a metastable polymorph of the $Ga_2Te_4O_{11}$ compound. A structural study of this compound is now in progress and should allow confirmation of such a hypothesis.

Conclusion

Our investigations within the TeO_2-rich part of the TeO_2–Ga_2O_3 system have allowed both to determine the equilibrium phase diagram (two invariant equilibria have been detected) and to observe a large glass-forming domain (in the range 5–30 mol% $GaO_{1.5}$). The complex thermal behaviour of those glasses has been clarified, in relation with the corresponding equilibrium compounds, using both differential scanning calorimetry and temperature-programmed XRD. Such results are of prime importance for the understanding of the relationships between the structure and the non-linear optical properties of tellurite glasses. Especially the knowledge of the first phase that crystallizes from glass and should be very helpful for further structural studies of such tellurite glasses.

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