TeO_2-based heavy metal oxide glasses for nonlinear optical applications.

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Glass formation domains in the Tl_2O-TeO_2-Bi_2O_3, Tl_2O-TeO_2-PbO and Tl_2O-TeO_2-Ga_2O_3 systems have been evidenced at 800°C and are presented for the first time. Densities, glass transition (Tg) and crystallization (Tc) temperatures have been determined. Nonlinear refractive indices of some glasses have been measured at 0.8 µm and 1.5 µm.

Introduction

Tellurium dioxide-based glasses are promising materials for nonlinear optical applications since they exhibit high linear and non linear refractive indices and good visible and infrared transmittance. Our studies within the TeO_2-Tl_2O system have shown that non-linear index of thallium tellurite glasses could be from 50 up to 100 times as large as that of SiO_2 [1]. The origin of this nonlinearity was attributed to the hyperpolarizability of the Te^{IV} atoms lone pairs, which is as a rule reinforced by addition of either a second lone pair holder (such as Tl^+, Bi^{3+}, Pb^{2+}) or of cations with empty d-orbitals, e.g. Ti^{4+} or Nb^{5+}. As thallium tellurites glasses have shown the largest non-linear indices it is interesting to investigate now the effect of addition to such glasses of either an oxide containing a third lone pair holder (PbO or Bi_2O_3), or either an oxide improving their mechanical strength (Ga_2O_3). The aim of this study was to evidence the glass formation domains within the Tl_2O-TeO_2-Bi_2O_3, Tl_2O-TeO_2-PbO and Tl_2O-TeO_2-Ga_2O_3 systems and to determine the densities, the glass transition (Tg) and crystallization (Tc) temperatures of glassy samples. The third order nonlinearity of some glasses are also under study.

Experimental

Glasses were obtained by, first melting at 800°C during 1 hour, appropriate quantities of reagent grade with respect to the different systems studied: PbO (Aldrich, 99.5%), Bi_2O_3 (Aldrich, 99.9%), Ga_2O_3 (Aldrich, 99.9%), TeO_2 and Tl_2TeO_3 in sealed gold tube, and then air-quenching of the melts. TeO_2 was prepared by decomposition at 550°C of commercial H_6TeO_6 (Aldrich, 99.9%). Tl_2TeO_3 was synthesised by heating at 350°C for 18 hours an intimate mixture of TeO_2 and Tl_2CO_3. Glassy pellets were prepared by melting the same mixtures in platinum crucibles, for half an hour at 800°C. The melts were then quickly quenched by flattening between two brass blocks separated by a brass ring to obtain cylindrical samples 10 mm wide and 1.5 mm thick (cooling rate about 10^4°C/s). Glass formation domains and crystallised phase compositions were determined by using X-ray diffraction (Guinier-De Wolff camera, Cu Kα radiation). Glass transition (Tg) and crystallisation (Tc) temperatures were measured by heat flux differential scanning calorimetry (DSC, Netzsch STA 409 apparatus). The densities of glassy samples were measured by helium pycnometry (Accupyc 1330 pycnometer). Vickers hardness measurements have been

performed on polished pellets (indentation during 15 seconds using a 500 g weight mass). Third order nonlinear indexes were measured at 0.8 μm and 1.5 μm using a Mach-Zehnder interferometer [2].

Results

Under our experimental conditions, large glassy domains were observed within the Tl_2O-TeO_2-Bi_2O_3, Tl_2O-TeO_2-PbO and Tl_2O-TeO_2-Ga_2O_3 systems (figure 1). All glasses were transparent and yellowish and have refractive indices in range 2.2-2.4. In order to extend the glass forming range up to the TeO_2 composition, pure TeO_2 glass was obtained after fast quenching the melt in a mixture of ice, ethanol and NaCl (temperature about ≈-10°C).

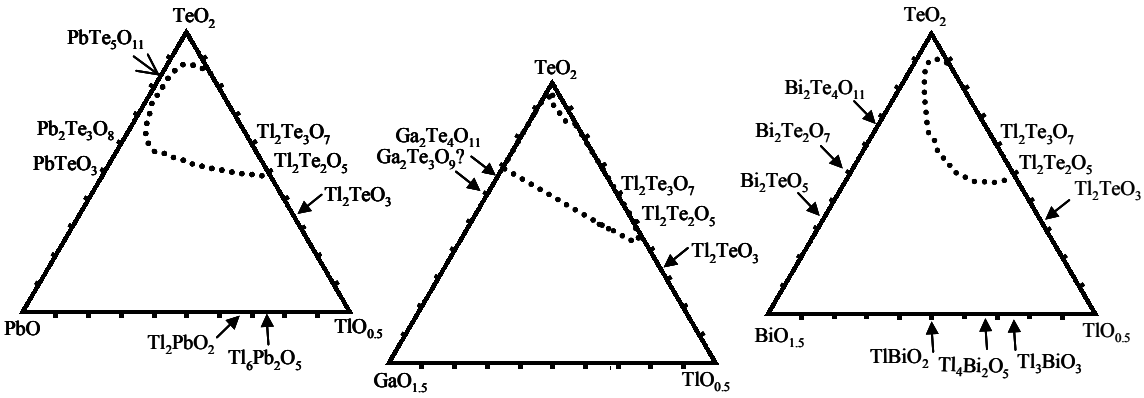

Figure 1: Crystalline phases and glass formation domains, at 800°C, within the Tl_2O-TeO_2-PbO, Tl_2O-TeO_2-Ga_2O_3 and Tl_2O-TeO_2-Bi_2O_3 systems

Influence of Bi_2O_3, PbO or Ga_2O_3 addition on some physical properties of TeO_2-Tl_2O glasses

The density, the glass transition and crystallisation temperatures, the thermal stability (difference Tc-Tg) of the different glassy samples have been reported elsewhere [3,4,5,6]. We shall concentrate on the effects resulting from the addition of Bi_2O_3, PbO or Ga_2O_3 to the 60mol% TeO_2-40mol%$TlO_{0.5}$ compositional glass which has shown large value of third order nonlinearity. The evolution with composition of the density, the glass transition and crystallisation temperatures, with respect to the modifying oxide content, are depicted in figure 2. The densities increase logically with the increasing atomic weight of the adding cation: it increases with addition of Bi and Pb atoms and decreases with addition of Ga atoms. It is worth noting that addition of Bi leads to a decrease of the thermal stability of glassy samples, addition of Pb remains it constant whereas addition of Ga allows to increase it significantly. Addition of Bi_2O_3, PbO or Ga_2O_3 to the 60mol%TeO_2 - 40mol%$TlO_{0.5}$ glass improves the Vickers hardness of samples: 60mol%TeO_2 - 40mol%$TlO_{0.5}$: Hv=206g/μm^2; 90mol% (60mol%TeO_2 - 40mol%$TlO_{0.5}$) - 10mol%$GaO_{1.5}$: Hv=275g/μm^2; 90mol% (60mol%TeO_2 - 40mol%$TlO_{0.5}$) - 10mol%$BiO_{1.5}$: Hv=250g/μm^2; 90mol% (60mol%TeO_2 - 40mol%$TlO_{0.5}$) - 10mol%PbO: Hv=254g/μm^2. The largest value of hardness is obtained with Ga_2O_3 addition.

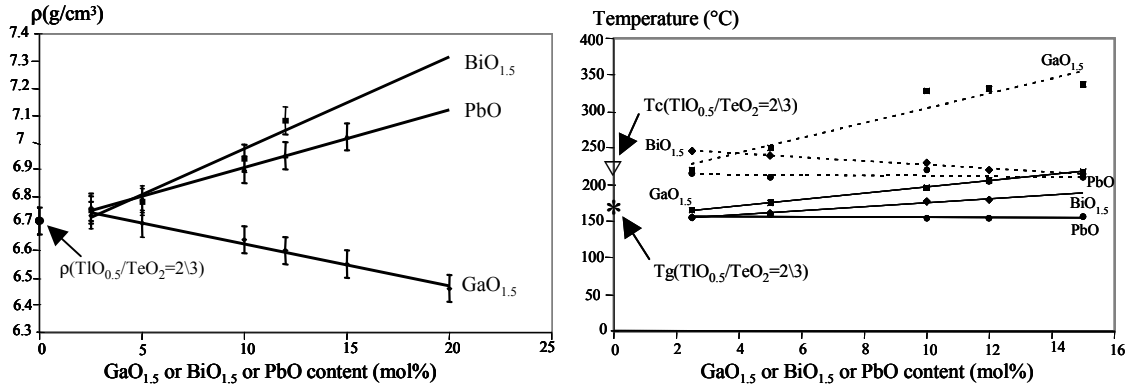

Figure 2: Evolution of the densities (ρ), the glass transition (Tg) and the crystallisation temperatures (Tc) of a initial compositional glass 60mol%TeO_2-40mol%$TlO_{0.5}$ with respect to the modifying oxide content

Nonlinear optical properties

Third order nonlinearities of some glassy tellurite samples, measured at 0.8 μm and 1.5 μm, are reported respectively in Table 1. As an indication, the values measured for a standard glass SF59 (Schott fabrication) are also given. It is worth noting that the non-linear properties of such glasses are higher than that of a lead-silica glass and clearly dependent of the nature of the modifier oxide (Table 1, figure 3). The third order nonlinearity increases with the linear polarizability of the adding cation. Thallium tellurite glasses (at least up to 40 mol% of $TlO_{0.5}$ concentration) exhibit the highest nonlinearity and gallium tellurite glasses show the lowest one. Intermediate nonlinearities have been obtained with lead, niobium, barium and titanium tellurite glasses. The contribution of a third modifying oxide, either a third lone pair holder (such as Bi^{3+} or Pb^{2+}) or either a d^{10} cation (such as Ga^{3+}) on the third order nonlinearity is illustrated in figure 3. Addition of PbO or Bi_2O_3 improves the nonlinear properties whereas addition of Ga_2O_3, even if it strengths the mechanical properties of glasses, decreases the values of their third order nonlinearities. The increasing concentration of PbO within thallium tellurite glasses does not affect significantly their nonlinarities.

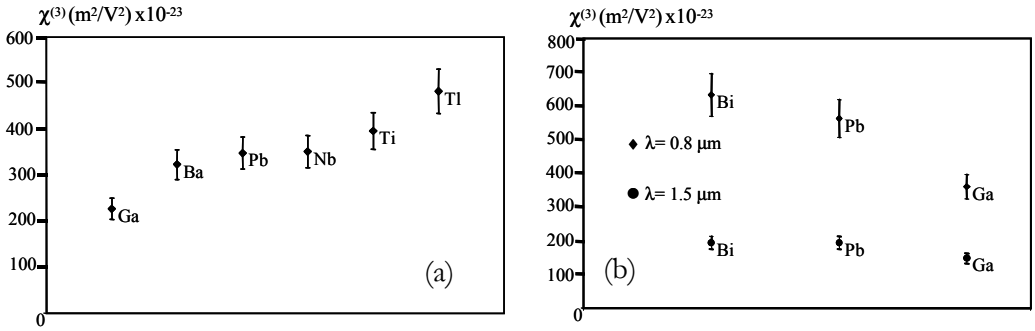

Figure 3: (a) Evolution of the χ(3) third order nonlinear indexes at 0.8 μm with respect to the nature of the modifying oxide added to a 85mol%TeO_2-15mol%MO_x (M=Ga, Pb, Nb, Ti, Tl) neighbouring glass composition; (b) Evolution of the third order nonlinearity at 0.8 μm and 1.5 μm with respect to the nature of the modifying oxide added to a thallium tellurite glass with constant composition ($TlO_{0.5}/TeO_2 \approx 2/3$)

As example for PbO contents in the range 5 – 20 mol%, the third order nonlinearity is practically constant and about 400 10^{-23} m^2/V^2 for a ratio of $TlO_{0.5}/TeO_2$=1/4 and about 550 10^{-23} m^2/V^2 for a ratio of $TlO_{0.5}/TeO_2$=3/7.

Glassy samples	$\chi^{(3)}$ (m^2/V^2) 10^{-23} (±10%)	Reference
SF59 (60PbO-40SiO_2)	234	*
56TeO_2-24$TlO_{0.5}$-20PbO	567	+
80TeO_2-10$TlO_{0.5}$-10PbO	231	+
70TeO_2-10$TlO_{0.5}$-20PbO	320	+
85TeO_2-10$TlO_{0.5}$-05PbO	366	+
75TeO_2-10$TlO_{0.5}$-15PbO	418	+
57TeO_2-38$TlO_{0.5}$-05PbO	562	+
66.5TeO_2-28.5$TlO_{0.5}$-05PbO	580	+
63TeO_2-27$TlO_{0.5}$-10PbO	498	+
59.5TeO_2-25.5$TlO_{0.5}$-15PbO	473	+
66.5TeO_2-28.5$TlO_{0.5}$-05PbO	580	+
56TeO_2-24$TlO_{0.5}$-20PbO	567	+
57TeO_2-38$TlO_{0.5}$-05PbO	562	+
51TeO_2-34$TlO_{0.5}$-15PbO	510	+
76TeO_2-19$TlO_{0.5}$-05PbO	427	+
72TeO_2-18$TlO_{0.5}$-10PbO	390	+
68TeO_2-17$TlO_{0.5}$-15PbO	433	+
64TeO_2-16$TlO_{0.5}$-20PbO	433	+
85TeO_2-15PbO (+1%B_2O_3)	348	+
80TeO_2-20PbO (+1% B_2O_3)	370	+
85TeO_2-15BaO	323	-
85TeO_2-15TiO_2	396	-
90TeO_2-10TiO_2	422	-
82TeO_2-18$GaO_{1.5}$	227	-
75TeO_2-25$TlO_{0.5}$	482	+
60TeO_2-40$TlO_{0.5}$	476	+
50TeO_2-50$TlO_{0.5}$	294	+
85TeO_2-15$NbO_{2.5}$	351	+
58TeO_2-36$TlO_{0.5}$-05$BiO_{1.5}$	632	+
54TeO_2-36$TlO_{0.5}$-10$GaO_{1.5}$	445	+
58.5TeO_2-39$TlO_{0.5}$-2.5$GaO_{1.5}$	360	+

(a)

Glassy samples	$\chi^{(3)}$ (m^2/V^2) 10^{-23} (±10%)	Reference
SF59	62	*
54TeO_2-36$TlO_{0.5}$-10$GaO_{1.5}$	148	+
54TeO_2-36$TlO_{0.5}$-10PbO	194	+
59TeO_2-36$TlO_{0.5}$-05$BiO_{1.5}$	194	+

(b)

Table 1: Third order nonlinearities of some glasses measured at (a) 0.8 µm and (b) 1.5 µm (* commercial glass, + glasses prepared in our institute, - glasses prepared in LPMC laboratory of Montpellier (P. Charton and P. Armand collaborations))

Discussion and conclusion

The comparison of the third order nonlinearities of glassy samples is not evident since up to now they were obtained by various techniques and at wavelengths more or less close to the fundamental absorption, leading to some discrepancies between values measured for the same material. However the influence of both the nature and the concentration of the modifying oxides has been clearly demonstrated. It is now well established that increasing content of modifying oxides within the TeO_2 glassy matrix leads generally to a progressive

depolymerisation of the glassy network induced by a progressive transformation of the TeO_4 disphenoids into TeO_3 trigonal pyramids through an intermediate asymmetric TeO_{3+1} polyhedron (excepted with TiO_2 which does not change the structural units). Ab-initio calculations of the two molecular diagrams of $(TeO_4)^{4-}$ and $(TeO_3)^{2-}$ units have shown that the linear polarizability of the TeO_4 disphenoids was about 20 times higher than that of TeO_3 trigonal groups. Therefore it is reasonable to think that insertion of modifiers should lead to a decrease of the non-linear optical properties. Such an evolution is observed within Nb_2O_5, WO_3 or Ga_2O_3 tellurite glasses. On the other hand, such phenomenon is not observed at all with addition of Tl_2O. Such behaviour is certainly related to the high stereochemical activity of the lone pair of thallium atoms which induced strong polarizability of thallium-oxygen groups. The contribution of the lone pairs of thallium atoms seems to compensate, at least up to 40 mol% of $TlO_{0.5}$ content, the decrease of the polarizability associated to the depolymerization of the tellurium oxide glassy network. Ab-initio polarizability calculations of thallium-oxygen units are now in progress in order to confirm such hypothesis. In conclusion, thallium tellurite glasses (containing less than 40 mol% of $TlO_{0.5}$) present the highest third order nonlinearities and are very promising materials for non linear optical devices. However, addition of d^0 or d^{10} shell metal ions, such as Ga^{3+}, Nb^{5+}, W^{3+}, facilitates the elaboration of glasses presenting a largest glass transition temperature (in the range 300-370°C with respect to 120-250°C for thallium tellurite glasses) and a high thermal stability (Tc-Tg about 100°C with respect to 50°C for thallium tellurite glasses) but disfavours the nonlinear optical properties. Addition of a third lone pair holder (Bi^{3+}, Pb^{2+}) to thallium tellurite glasses improves the third order nonlinearity but does not increase the physical properties of glasses (thermal stability, mechanical strength), whereas the addition of Ga_2O_3, even if it induces a decrease of the third order nonlinearity, allows to improve the feasibility of glasses and to increase their thermal stability.

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