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New TeO₂ based glasses for nonlinear optical applications: study of the Tl₂O– TeO₂– Bi₂O₃, Tl₂O– TeO₂– PbO and Tl₂O– TeO₂– Ga₂O₃ systems

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Large glass forming domains have been identified at 800°C in the Tl₂O–TeO₂–Bi₂O₃, Tl₂O–TeO₂–PbO and Tl₂O–TeO₂–Ga₂O₃ systems and are presented for the first time. Densities, glass transition (T_g) and crystallisation (T_c) temperatures have been determined. Nonlinear refractive indices of some glasses have been measured at 0.8 and 1.5 μm . Moreover, the relationships between the nature of the modifier oxide and nonlinear optical response of such tellurite glasses have been investigated.

Tellurium dioxide based glasses are promising materials for nonlinear optical applications since they exhibit high linear and nonlinear refractive indices and good visible and infrared transmittance.^(1,2) In particular, our studies within the TeO₂–Tl₂O system have shown that the nonlinear index of thallium tellurite glasses could be from 50 up to 100 times larger than that of SiO₂.⁽³⁾ The origin of this nonlinearity was attributed to the hyperpolarisability of the Te^{IV} atom lone pairs, which as a rule is reinforced by addition of either a second lone pair ion (such as Tl⁺, Bi³⁺, Pb²⁺) or of cations with empty d-orbitals, e.g. Ti⁴⁺ or Nb⁵⁺. From this point of view, numerous studies have been devoted to the knowledge of the relationships between the structure and nonlinear optical response of tellurite glasses.^(3–30)

As thallium tellurite glasses have shown the largest nonlinear indices⁽³⁾ it is now interesting to investigate the effect of addition to such glasses of either an oxide containing a third lone pair ion (PbO or Bi₂O₃) or either an oxide improving their mechanical strength (Ga₂O₃). The aim of this study was to identify the glass

formation domains within the Tl₂O–TeO₂–Bi₂O₃, Tl₂O–TeO₂–PbO and Tl₂O–TeO₂–Ga₂O₃ systems and to determine the densities, glass transition (T_g) and crystallisation (T_c) temperatures of all glassy samples. The third order nonlinearity of some glasses are also under study.

Experimental

Glasses were obtained by melting at 800°C for 1 h appropriate quantities of reagent grade chemicals relevant to the different systems studied: PbO (Aldrich, 99.5%), Bi₂O₃ (Aldrich, 99.9%), Ga₂O₃ (Aldrich, 99.9%), TeO₂ and Tl₂TeO₃ in a sealed gold tube, followed by air quenching of the melts. TeO₂ was prepared by decomposition at 550°C of commercial H₆TeO₆ (Aldrich, 99.9%). Tl₂TeO₃ was synthesised by heating at 350°C for 18 h an intimate mixture of TeO₂ and Tl₂CO₃. Glassy pellets were prepared by melting the same mixtures in platinum crucibles, for 30 min 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 104 K/s). Glass formation domains and crystallised phase compositions were determined by x-ray diffraction (Guinier–De Wolff camera, Cu K α radiation). Glass transition (T_g) and crystallisation (T_c) 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 for 15 s using a 500 g weight mass). Third order nonlinear indexes were measured at 0.8 and 1.5 μm using a Mach-Zehnder interferometer.⁽³⁾

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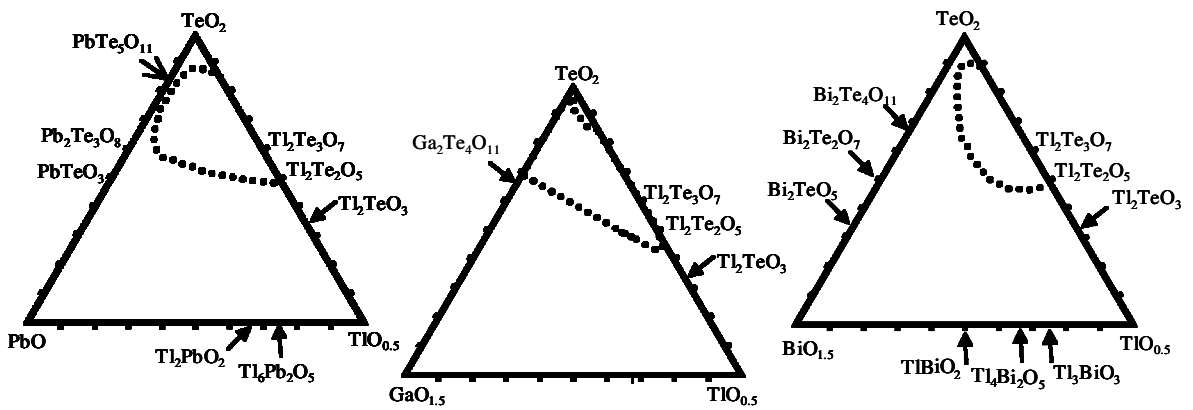


Figure 1. Crystalline phases and glass formation domains, at 800°C, within the Tl_2O - TeO_2 - PbO , Tl_2O - TeO_2 - Ga_2O_3 and Tl_2O - TeO_2 - Bi_2O_3 systems

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 $\approx -10^\circ C$).

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 $T_c - T_g$) of the different glassy samples have been reported else-

where.⁽³¹⁻⁴⁾ In this paper we shall concentrate on the effects resulting from the addition of Bi_2O_3 , PbO or Ga_2O_3 to the 60 TeO_2 .40 $TlO_{0.5}$ (mol%) compositional glass which has shown a large value of third order nonlinearity. The variations with composition of the density, glass transition and crystallisation temperatures, with respect to the modifying oxide content, are depicted in Figure 2. The densities increase as expected 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 maintains it constant whereas addition of Ga allows significant increase. Addition of Bi_2O_3 , PbO or Ga_2O_3 to the (mol%) 60 TeO_2 .40 $TlO_{0.5}$ glass improves the Vickers hardness of samples: 60 TeO_2 .40 $TlO_{0.5}$; $H_v = 206 \text{ g}/\mu\text{m}^2$; 90(60 TeO_2 .40 $TlO_{0.5}$).10 $GaO_{1.5}$; $H_v = 275 \text{ g}/\mu\text{m}^2$; 90(60 TeO_2 .40 $TlO_{0.5}$).10 $BiO_{1.5}$; $H_v = 250 \text{ g}/\mu\text{m}^2$; 90(60 TeO_2 .40 $TlO_{0.5}$).10 PbO ; $H_v = 254 \text{ g}/\mu\text{m}^2$. The largest value of hardness is obtained with Ga_2O_3 addition.

Nonlinear optical properties

Third order nonlinearities of some glassy tellurite samples, measured at 0.8 and 1.5 μm , are reported, respectively, in Table 1. For comparison, the values measured for a standard glass SF59 (Schott fabrication) are also given. It is worth noting that the nonlinear properties of such glasses are higher than that of a lead silica glass and clearly depend of the nature of the modifier oxide, Table 1, Figure 3. The third order nonlinearity increases with the linear polarisability of the added cation. Thallium tellurite glasses (at least up to 40 mol% $TlO_{0.5}$ concentration) exhibit the highest nonlinearity and gallium tellurite glasses show the lowest. 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 ion (such as Bi^{3+} or Pb^{2+}) or either a d^{10} cation (such as Ga^{3+}) to 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 strengthens the mechanical properties of glasses, reduces their third order nonlinearities. The increasing concentration of PbO within thallium

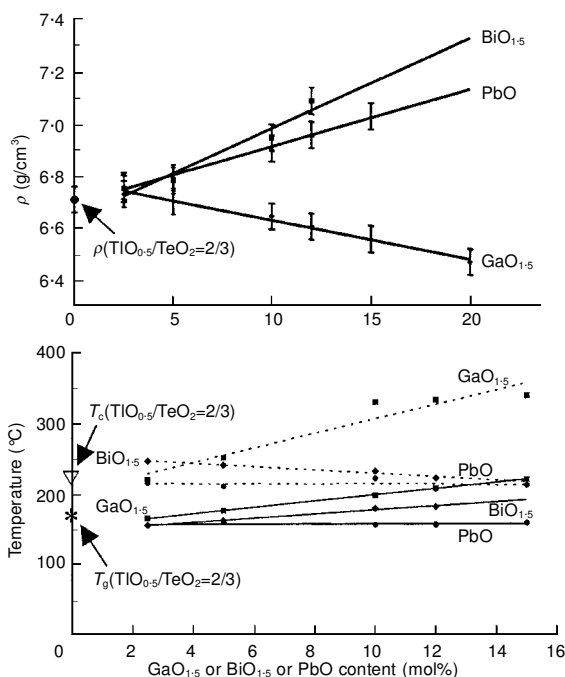


Figure 2. Evolution of the densities (ρ), the glass transition T_g (—) and the crystallisation temperatures T_c (----) of an initial compositional glass 60 TeO_2 .40 $TlO_{0.5}$ (mol%) with respect to the modifying oxide content

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 LPCM laboratory of Montpellier (P. Charton and P. Armand collaborations))

Glassy samples (mol%)	$\chi^{(3)}$ (m^2/V^2) 10^{23} ($\pm 10\%$)	Reference
(a)		
SF59 (60PbO.40SiO ₂)	234	*
56TeO ₂ .24TiO _{0.5} .20PbO	567	+
80TeO ₂ .10TiO _{0.5} .10PbO	231	+
70TeO ₂ .10TiO _{0.5} .20PbO	320	+
85TeO ₂ .10TiO _{0.5} .5PbO	366	+
75TeO ₂ .10TiO _{0.5} .15PbO	418	+
57TeO ₂ .38TiO _{0.5} .5PbO	562	+
66.5TeO ₂ .28.5TiO _{0.5} .5PbO	580	+
63TeO ₂ .27TiO _{0.5} .10PbO	498	+
59.5TeO ₂ .25.5TiO _{0.5} .15PbO	473	+
66.5TeO ₂ .28.5TiO _{0.5} .5PbO	580	+
56TeO ₂ .24TiO _{0.5} .20PbO	567	+
57TeO ₂ .38TiO _{0.5} .5PbO	562	+
51TeO ₂ .34TiO _{0.5} .15PbO	510	+
76TeO ₂ .19TiO _{0.5} .5PbO	427	+
72TeO ₂ .18TiO _{0.5} .10PbO	390	+
68TeO ₂ .17TiO _{0.5} .15PbO	433	+
64TeO ₂ .16TiO _{0.5} .20PbO	433	+
85TeO ₂ .15PbO (+1% B ₂ O ₃)	348	+
80TeO ₂ .20PbO (+1% B ₂ O ₃)	370	+
85TeO ₂ .15BaO	323	–
85TeO ₂ .15TiO ₂	396	–
90TeO ₂ .10TiO ₂	422	–
82TeO ₂ .18GaO _{1.5}	227	–
75TeO ₂ .25TiO _{0.5}	482	+
60TeO ₂ .40TiO _{0.5}	476	+
50TeO ₂ .50TiO _{0.5}	294	+
85TeO ₂ .15NbO _{2.5}	351	+
58TeO ₂ .36TiO _{0.5} .5BiO _{1.5}	632	+
54TeO ₂ .36TiO _{0.5} .10GaO _{1.5}	445	+
58.5TeO ₂ .39TiO _{0.5} .2.5GaO _{1.5}	360	+
(b)		
SF59	62	*
54TeO ₂ .36TiO _{0.5} .10GaO _{1.5}	148	+
54TeO ₂ .36TiO _{0.5} .10PbO	194	+
59TeO ₂ .36TiO _{0.5} .5BiO _{1.5}	194	+

tellurite glasses does not significantly affect their nonlinearities, Figure 4. In comparison, for PbO contents in the range 5–20 mol%, the third order nonlinearity is practically constant at about 400 10^{-23} m^2/V^2 for a ratio of $\text{TlO}_{0.5}/\text{TeO}_2=1/4$ and about 550 10^{-23} m^2/V^2 for a ratio of $\text{TlO}_{0.5}/\text{TeO}_2=3/7$.

Discussion

Comparison of the third order nonlinearities of glassy samples has been difficult since up to now they were obtained by various techniques and at wavelengths more or less close to the fundamental absorption, thus leading to some discrepancies between values measured for the same material.

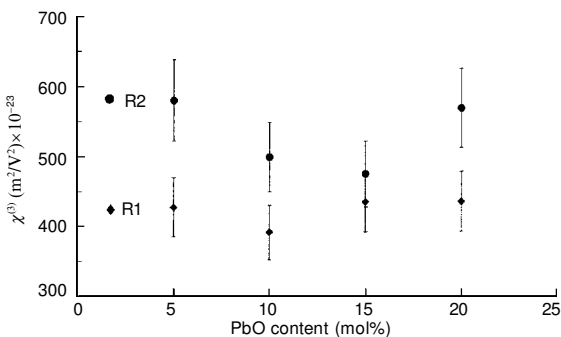


Figure 4. Evolution of the $\chi^{(3)}$ third order nonlinear indexes at 0.8 μm with respect to the PbO content added to a TeO_2 - $\text{TlO}_{0.5}$ glass (with respectively $\text{R1}=\text{TlO}_{0.5}/\text{TeO}_2=1/4$ and $\text{R2}=\text{TlO}_{0.5}/\text{TeO}_2=3/7$)

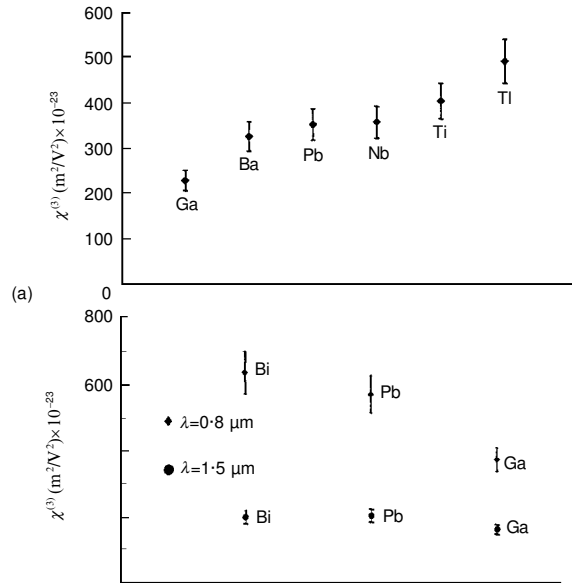


Figure 3. (a) Evolution of the $\chi^{(3)}$ third order nonlinear indexes at 0.8 μm with respect to the nature of the modifying oxide added to a $85\text{TeO}_2.15\text{MO}_x$ (mol%) ($M=\text{Ga}, \text{Pb}, \text{Nb}, \text{Ti}, \text{Tl}$) neighbouring glass composition; (b) Evolution of the third order nonlinearity at 0.8 and 1.5 μm with respect to the nature of the modifying oxide added to a thallium tellurite glass with constant composition ($\text{TlO}_{0.5}/\text{TeO}_2=2/3$)

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^(3–26) (except with addition of B_2O_3 or TiO_2 , which does not change the structural units).^(27–30) *Ab initio* calculations of the two molecular diagrams of $(\text{TeO}_4)^{4-}$ and $(\text{TeO}_3)^{2-}$ units have shown that the linear polarisability of the TeO_4 disphenoids was about 20 times higher than that of TeO_3 trigonal groups.⁽³⁵⁾ Therefore, it is reasonable to think that insertion of modifiers should lead to a decrease of the nonlinear optical properties. Such an evolution is observed within Nb_2O_5 , WO_3 or Ga_2O_3 tellurite glasses. On the other hand, such a phenomenon is not observed 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 polarisability of thallium oxygen groups. The contribution of the lone pairs of thallium atoms seems to compensate, at least up to 40 mol% $\text{TlO}_{0.5}$ content, the decrease of the polarisability associated to the depolymerisation of the tellurium oxide glassy network. *Ab initio* polarisability calculations of thallium oxygen units are now in progress in order to confirm such a hypothesis.

Conclusion

Thallium tellurite glasses (containing less than 40 mol% $\text{TlO}_{0.5}$) present the highest third order nonlinearities and are very promising materials for nonlinear optical

devices. However, addition of d^0 or d^{10} shell metal ions, such as Ga^{3+} , Nb^{5+} , W^{6+} , 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 ($T_c - T_g$ about 100°C with respect to 50°C for thallium tellurite glasses) but disfavors 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 the improvement of the feasibility of glasses and to increase their thermal stability.

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