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Zero stress-optic barium tellurite glass

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Abstract

Zero stress-optic glasses are achieved traditionally through a high content of lead oxide or other closely related p-block metal oxide. We have found that the underlying cause for this behavior is the combination of high metallicity and low coordination numbers adopted by compounds such as lead oxide. Here we test this idea by showing that barium tellurite glasses also show zero stress-optic and negative stress-optic response, at very low barium content. This response results from the fact that barium oxide bonds have very high metallicity, and at the same time barium modifies tellurite by lowering the Te coordination number. The two effects together are sufficient to produce zero stress optic response.

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Keywords: Optical properties; Tellurites

1. Introduction

The stress-optic coefficient of glass is the proportionality constant between applied stress and induced birefringence. Of particular technological interest are zero stress-optic glasses, in which, as the name implies, the coefficient vanishes. It is well-known that glasses with high lead oxide content may have zero and even negative stress-optic response [1]; this behavior can also be induced by thallium oxide and bismuth oxide [2–5].

Recently we discovered a remarkably simple correlation between bond length d, metal coordination number N_C, and the stress-optic coefficient, which predicts the existence of a much wider variety of zero stress optic glasses than was previously suspected [6]. We found that glasses with average d/N_C values greater than about 0.5 Å have negative stress optic coefficients, while those with smaller d/N_C are positive. The origin of this correlation is that bonding with high metallicity, that is, large d [7], is favorable for negative stress-optic response, while low coordination numbers are also favorable, as they allow for anisotropic deformations. From this correlation we predicted and then confirmed experimentally that tin(II) phosphates, tin(II) silicates, and antimony borates can generate zero and negative stress-optic glasses.

Both the traditional additives, such as PbO and Bi_2O_3, and the newly discovered additives, including SnO, Sb_2O_3, as well as others we had predicted such as HgO and As_2O_3, have in common that they are metallic or semi-metallic p-block elements, all of which are stable in low valence states and show low coordination numbers because of stereochemically active lone pairs. It is not obvious that the mechanism that leads to zero stress-optic response in these glasses can also yield the same response when a traditional alkali or alkaline-earth additive is used, as these additives always have high coordination numbers. In this report however we show that barium tellurite glasses are also zero stress optic materials, and follow the same correlation trend as the systems we have already reported. They do so, however, because of the coordination number

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reduction of the glass former (TeO_2), not the additive. To compare to a more traditional system, we also present data on lead tellurites.

2. Methods

Glassy TeO_2 was prepared by melting TeO_2 in a platinum crucible for 15 min at 800 °C and quenching between brass plates. Barium tellurite glasses were synthesized from reagent grade $BaCO_3$ and TeO_2. The reagents were melted for 30 min at 800 °C, then quenched into a brass mold heated to 200 °C. The glasses were immediately annealed for 4 h at 290 °C. Lead tellurite glasses were prepared from reagent grade PbO and TeO_2, by melting in a platinum crucible for 30 min at 750 °C, then quenched into a brass mold heated to 200 °C and annealed for 4 h at 325 °C. To perform the photoelastic constant measurement, glasses were cut in order to obtain samples of about $10 \times 5 \times 5$ mm, and two parallel sides were polished. The optical isotropy of each glass was checked before the stress-optic constant measurement by observing the samples through a polarizer.

Raman spectra were acquired on a Bruker RFS100 FT-Raman instrument, operating with an Nd:YAG laser at 235 mW and 1064 nm wavelength. Typically 500 scans were acquired for signal averaging. The stress-optic constant was measured using the quarter-wave plate compensator method using a polarimeter (PS-100 Strainoptic), as detailed elsewhere [8,6].

3. Results

Raman spectra of barium and lead tellurite glasses are shown in Figs. 1 and 2, respectively. The birefringence of barium tellurite glasses and lead tellurite glasses as a function of compressive stress are shown in Figs. 3 and 4. The stress-optic coefficients, derived from Figs. 3 and 4 by linear regression of the data, are listed in Table 1.

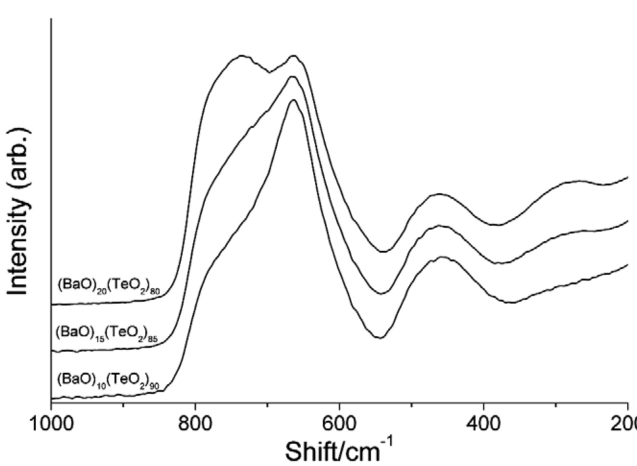

Fig. 1. Raman spectra of barium tellurite glasses.

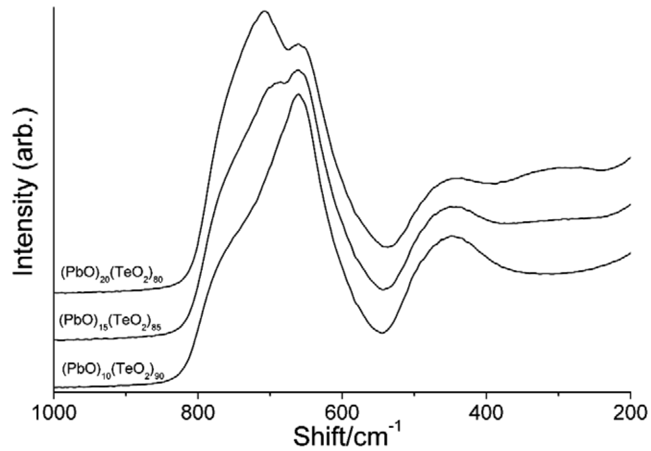

Fig. 2. Raman spectra of lead tellurite glasses.

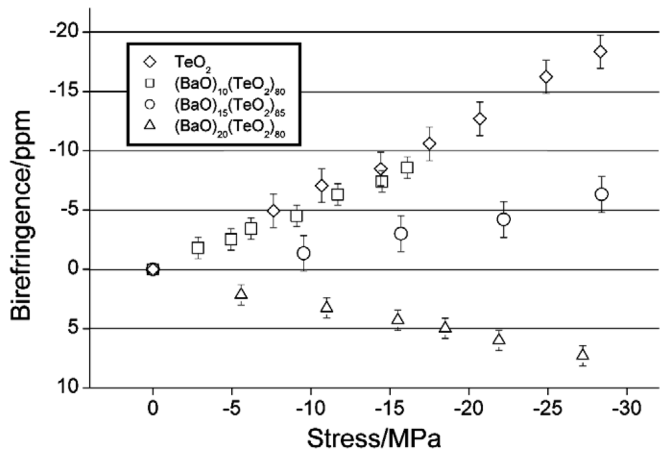

Fig. 3. Birefringence as a function of compressive stress in barium tellurite glasses.

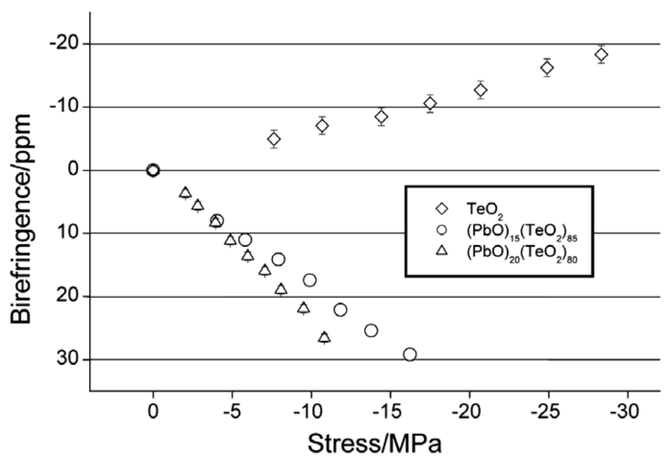

Fig. 4. Birefringence as a function of compressive stress in lead tellurite glasses.

4. Discussion

The two glass families studied here, barium tellurite and lead tellurite, are both known in the literature [9,10]. Figs. 1

Table 1
Stress-optic coefficients C in Brewsters for tellurite glasses

Composition	C/Brewsters
TeO_2	0.64(6)
$(BaO)_{10}(TeO_2)_{90}$	0.52(5)
$(BaO)_{15}(TeO_2)_{85}$	0.20(2)
$(BaO)_{20}(TeO_2)_{80}$	−0.27(3)
$(PbO)_{10}(TeO_2)_{90}$	<0
$(PbO)_{15}(TeO_2)_{85}$	−1.82(18)
$(PbO)_{20}(TeO_2)_{80}$	−2.33(23)

The error estimate in C is based on calibrating the measurement method against commercial glasses of known stress-optic response. A precise measurement of C for $(PbO)_{10}(TeO_2)_{90}$ was not possible, but C was clearly negative under compression.

and 2 show the Raman spectra of the samples we prepared, showing typical behavior [11,12,9,13,10]. In particular, the bands at 275 and 735 cm^{-1} show increasing amounts of 3 and '3 + 1' coordinate Te, as modifier is added. Presumably, at the low concentrations studied here, both Ba and Pb act primarily as modifiers, with high coordination numbers. This behavior is invariably found for barium, and also for lead when present below 40%.

In terms of the empirical correlation parameter d/N_C, TeO_2 has a value of about 0.5 Å and crystalline BaO has a value of about 0.46 Å. The combination of both would in general not be expected to yield glasses with negative stress optic response, because their average cannot be above the 0.5 threshold. This expectation is borne out in barium phosphate glasses, in which phosphate (P_2O_5) has a d/N_C value of 0.40 Å, and indeed, barium phosphate glasses are known to have small but positive stress optic coefficients [14]. Moreover, glassy TeO_2 exhibits positive stress-optic response (Table 1). As the Raman spectra show, however, in tellurites the N_C number for tellurium decreases as modifier is added. Indeed, Table 1 shows that a barium tellurite glass with about 17.5 mol% BaO would have $C = 0$. Using an average Te–O bond length of 2.0 Å and d/N_C of 0.46 Å for the BaO component, the critical 0.5 Å threshold would be reached for a Te–O coordination number of about 3.9. This value in turn corresponds to about 10% TeO_3 units and the rest TeO_4. Certainly, photoelastic measurements are not the appropriate way to measure coordination numbers, but it is reassuring that the model is consistent with coordinations which are in broad agreement with those estimate from Raman spectra. In the case of the lead tellurites, because PbO is already a negative photoelastic material and TeO_2 is so close to threshold, the model predicts that all lead tellurite glasses should have negative stress optic response, as in fact they do (Table 1).

5. Conclusions

There are two primary conclusions from this study. First, d/N_C correctly predicts the stress optic behavior even when changes in it arise from changes in the glass former structure, as opposed to the more usual case of the property of the added modifier. Secondly, both barium tellurite and lead tellurite are glass systems with tunable stress optic response. The barium tellurite case is particularly interesting because it can form a strictly zero stress-optic glass that is lead-free. Recent environmental legislation prohibits the use of lead in a variety of products, and so searching for lead-free alternatives is important. Barium tellurite glasses when suitably modified may be useful as replacements for lead silicates, due to their high intrinsic index of refraction, durability, and transparency.

Acknowledgements

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