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Application of the constant stoichiometry grouping concept to the Raman spectra of $Pb(PO_3)_2$-TeO_2 glasses

I. Apakova [a], O. Yanush [a,*], O. Derkacheva [a], V. Goncharuk [b], I. Maslennikova [b], I. Polyakova [c], A. Anan'ev [d], L. Maksimov [d], T. Markova [a]

[a] St-Petersburg State Technological University of Plant Polymers, I. Chernykh 4, St-Petersburg 198095, Russia
[b] Institute of Chemistry of Far-Eastern Branch of Russian Academy of Sciences, Pr. Stoletiya 159, Vladivostok 690022, Russia
[c] Institute of Silicate Chemistry, Russian Academy of Sciences, 29 Odoevskogo, St-Petersburg 199155, Russia
[d] Research and Technological Institute for Optical Material Science, 36-1 Babushkina, St-Petersburg 192171, Russia

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ABSTRACT

$Pb(PO_3)_2$-TeO_2 glasses in the whole range of glass composition were first obtained and their properties (refractive index, density, T_g and light scattering losses) were determined. Based on the vibrational spectroscopy data a new approach was applied to investigate the interactions of initial oxides in melts resulted in so-called constant stoichiometry groupings (CSGs) formation symbolizing intermediate range order in glasses. Vibrational spectra of glasses are interpreted as a superposition of unchangeable spectral forms (principal spectral components (PSCs)) belonging to CSGs: $PbO \cdot P_2O_5$, $TeO_2 \cdot 2PbO \cdot 2P_2O_5$, $TeO_2 \cdot PbO \cdot P_2O_5$, TeO_2, and possibly $2TeO_2 \cdot PbO \cdot P_2O_5$ and $6TeO_2 \cdot PbO \cdot P_2O_5$. In this work Multivariate Data Analysis has been applied as the independent mathematical tool to decompose Raman spectra of glasses and reveal the number of PSCs. It is shown that application of factor analysis results in the same five PSCs that confirms our data obtained from the CSG concept. This concept allows also the prediction of the existence of unknown compounds, and correspondingly some crystals ($TeO_2 \cdot 2PbO \cdot 2P_2O_5$ and others) were revealed by XRPD of the crystallized glasses. The CSG concept opens the way for elaboration of low scattering glasses as candidates for Raman amplifiers. It is shown that $Pb(PO_3)_2$-TeO_2 glasses with small content of TeO_2 are of interest to photonic technology.

1. Introduction

Tellurite glasses attract considerable interest as promising materials for various bulk, planar and fiber nonlinear optical devices [1–3]. Tellurite glasses, compared to silicate glasses, have a wide transmission region (0.4 mkm–6 mkm [1,4–8]), relatively low phonon energy for an oxide glass ($\approx$800 cm^{-1}) [1], high refractive index ($\geq$2.2 [1,7,9,10]), large non-linearity (non-linear refractive index is two orders of magnitude greater than that of silica [11]), Raman gain, which is around 30 times greater than that of silica [12–14], and a large rare-earth solubility among common oxide glasses [15–18] that are desirable for the application of fiber lasers and amplifiers. Tellurite glasses are technologically important since they are chemically stable, have high homogeneity, uncolored and weather-resistant [19].

In this paper we report a study of $(100-x)(0.5PbO \cdot 0.5P_2O_5)-xTeO_2$ glass series (where x is molar percent TeO_2), that has been less investigated so far [10,20–23]. These glasses, containing heavy metal oxides, have very high Raman cross-section of the bands around 450 cm^{-1} 660 cm^{-1}, and 850–1250 cm^{-1} (the strong band in the spectra of phosphate glasses), and a large spectral bandwidth as compared to fused silica, therefore, they are promising candidates for fiber Raman amplifiers in photonic systems.

Despite that tellurite glasses have been studied for many years, the structure of $(100-x)(0.5PbO \cdot 0.5P_2O_5)-xTeO_2$ glasses has been investigated within the narrow composition ranges. Until the present time, assumptions regarding tellurite glass structure and the identification of IR and Raman bands available in the literature are based mainly on consideration of basic structural units like TeO_4, TeO_{3+1}, TeO_3, and others [7,8,14,20–26].

Vibrational spectroscopy is one of the most useful experimental techniques available for structural studies of glasses. In Refs. [27–31] it was shown that vibrational spectroscopy is sensitive to the smallest variation of chemical bonds determining properties of glasses and is able to reveal all primary bonds including those that link the polyhedra into larger structural units (intermediate range order structure). The approach has been proposed [27–32] to interpret vibrational spectra (mainly Raman, but also IR) of glasses as a superposition of a relatively small number of unchangeable spectral forms (principal spectral components, PSCs [28]),

* Corresponding author. Tel.: +7 812 786 43 07; fax: +7 812 786 86 00.
E-mail address: O.V.Yanush@inbox.ru (O. Yanush).

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Table 1
Compositions and some properties of the investigated glasses.

TeO_2, mol%	PbO, mol%	P_2O_5, mol%	$^{VV}I_{51}$, rel. un. (for SiO_2: $^{VV}I_{51}=0.49$ $^{VV}I_{440}=1$)	Density d (g/cm^3) at 20 °C		Molar volume V, cm^3/mol (27.3 for SiO_2)	Refractive index n (1.459 for SiO_2)	Glass transition temperature Tg (°C)
				Measured in institute "b"	Measured in institute "d"			
0	50.00	50.00	4.2	4.729		38.6	1.720	322.5
2.52 (2.88)	49.68 (51.11)	47.80 (46.01)	5.3	4.786	4.785	38.0	1.732	
5.19 (5.81)	48.32 (49.15)	46.49 (45.04)	5.6	4.801	4.802	37.8	1.753	316.6
7.95 (8.55)	46.92 (48.22)	45.13 (43.22)	6.1	4.843	4.832	37.3	1.760	
10.92 (10.95)	45.41 (46.51)	43.67 (42.54)	6.3	4.872	4.870	37.0	1.765	323.7
14.03 (14.74)	43.82 (45.75)	42.15 (39.51)	6.8	4.900	4.896	36.6	1.768	
17.39 (18.39)	42.10 (43.82)	40.51 (37.79)	7.3	4.929	4.921	36.2	1.795	352
20.89 (22.31)	40.32 (41.13)	38.79 (36.56)	7.1	4.959	4.909	35.8	1.796	
24.62 (26.20)	38.41 (38.84)	36.96 (34.96)	7.8	4.995	4.987	35.4	1.816	351.3
28.64 (29.73)	36.37 (37.43)	34.99 (32.84)	8.6	5.033	5.039	34.9	1.833	
32.88 (34.78)	34.21 (34.53)	32.91 (31.46)	8.7	5.062	5.077	34.5	1.850	360
37.50 (38.78)	31.86 (31.48)	30.64 (29.67)	10.3	5.111		34.0	1.864	
42.38 (43.77)	29.36 (28.72)	28.25 (27.52)	10.9	5.161	5.156	33.4	1.880	362.9
47.66 (48.01)	26.68 (26.84)	25.67 (25.14)	11.6	5.199	5.216	33.0	1.920	
53.37 (54.68)	23.76 (23.27)	22.87 (22.05)	12.4	5.239	5.265	32.5	1.949	356.9
59.55 (60.89)	20.62 (20.27)	19.84 (18.85)	13.4	5.328	5.317	31.7	1.968	
66.22 (67.48)	17.22 (16.95)	16.56 (15.57)	13.5	5.354	5.363	31.2	1.994	355
73.54 (74.83)	13.49 (13.21)	12.97 (11.96)	14.6	5.430	5.427	30.5	2.034	
81.53 (82.47)	9.42 (9.31)	9.05 (8.22)	16.4 (28)*	5.488	5.484	29.8	2.056	337.4
90.30 (90.92)	4.95 (4.68)	4.75 (4.40)	21.4 (42)*	5.531	5.546	29.2	2.100	322.9

Notes: The results of the analysis are presented in brackets.
* Intensities in brackets are obtained by extrapolation of that for colorless samples.

which add to form the measured spectrum. The number of independent PSCs is determined by the Wallace–Katz technique [33]. These PSCs are interpreted as belonging to the stable products of the interaction of initial oxides, and are called constant stoichiometry groupings (CSGs). For the treatment of vibrational spectra, we hold to the hypothesis that CSGs are 'the smallest particles' which compose the glass, defining its properties [27,32,34].

The analysis of the intensities of the PSCs, which are extracted from the Raman spectra by the technique described in Ref. [28], makes it possible to calculate the composition dependences of the molar fraction of each CSG. This information enables to explain, calculate and predict compositional dependences of the refractive index, density, structural thermal expansion coefficient (STEC), the fraction of four coordinated boron atoms, Kerr coefficient and other properties of binary and ternary

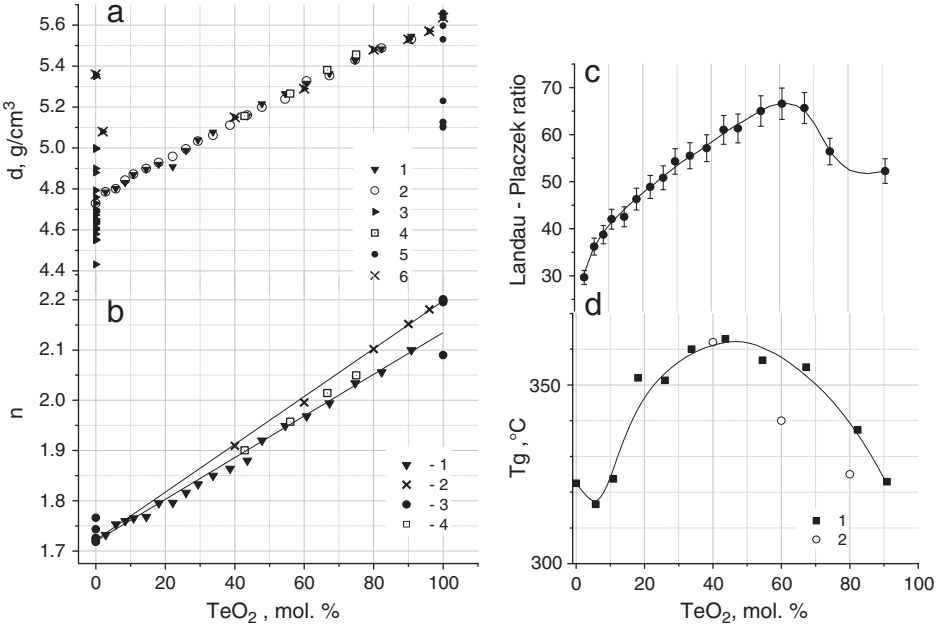

Fig. 1. Glass composition dependences of density d (a), refractive index n (b), Landau–Placzek ratio (c) and glass transition temperature T_g (d) for $(100-x)(0.5PbO \cdot 0.5P_2O_5)-xTeO_2$ glasses (Table 1). Points are experimental data and lines are guides to the eye. a: 1, 2 — experimental results, this work (obtained in Research and Technological Institute for Optical Material Science (St-Petersburg) and in the Institute of Chemistry of Far-Eastern Branch of Russian Academy of Sciences (Vladivostok) correspondingly), 3 — experimental data for $Pb(PO_3)_2$ from the literature [40], 4 — experimental data obtained by N.V. Ovcharenko, 5 — experimental data for TeO_2 from the literature [40], and 6 — experimental data obtained by H. Bürger [40]; b: 1 — experimental results, this work (refractive index at $\lambda=632.8$ nm), 2 — experimental data obtained by H. Bürger (refractive index at $\lambda=546.07$ nm) [40], 3 — experimental data for $Pb(PO_3)_2$ and TeO_2 from the literature [40], and 4 — experimental data obtained by N.V. Ovcharenko (refractive index at $\lambda=643.85$ nm) [10]; and d: 1 — experimental results, this work; and 2 — experimental data obtained by H. Bürger [40].