Optical basicity, molar volume and third-order nonlinear optical susceptibility of binary borate glasses

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The relationships between optical basicity, molar volume and third-order nonlinear optical susceptibility have been analyzed for binary borate glasses. The qualitative relationships between optical basicity and molar volume are discussed. The quantitative relationships between optical basicity and third-order nonlinear optical susceptibility are established. Our results suggest that the optical basicity parameters from 0.5 to 0.6 consist of the critical range, which separates glasses into two groups, and each group presents specific correlations between optical basicity, molar volume and third-order nonlinear optical susceptibility.

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1. Introduction

Before 1971 in the field of molten salt and glass chemistry, the most general approaches to acid-base behavior was that of Lewis [1]. A Lewis acid is an electron pair acceptor, and a Lewis base is an electron pair donor. It is not quantitative and its application has been restricted. Lux–Flood established the scale of pO^{2-} analogous to pH [2], however, it is not possible for acid-base comparisons to be made over a range of oxyanion systems owing to difficulties in defining thermodynamic oxide ion activities and the effects of redox equilibria involving superoxide formation. In 1971 Duffy and Ingram applied Lewis concept to solvent system [3] , the basicity of the solvent is understood as its ability to share its electrons with an acidic solute. If a suitable metal ion is used as an acid probe for this effect, then through the effects of central-field and symmetry-restricted covalency there should be an expansion of outer orbitals of the probe ions. This expansion can be measured experimentally by s-p transition in probe ions. It is defined as "optical basicity". The establishment of optical basicity made the quantitative comparison of glasses acidity and bacisity possible. Optical basicity is not only the scale of acid-base behavior in glasses, but also the presentation of glass structure and properties [4-6]. In recent years some borate glasses have been considered as promising materials for optical application and draw much more research attentions [7-17]. In our previous work, a general trend of oxide ion polarizability increasing with increasing density has been reported for binary silicate, borate and phosphate glasses [18], the mathematical expressions, between density and third-order NLO susceptibility of binary borate glasses, have also been established [19], afterwards an efficient quantitative relationship among molar polarizability, molar volume and density has been found [20]. In our continuing study, the critical range of optical basicity from 0.5 to 0.6 is found for the binary borate glasses. The intention of the present communication is to provide the different relationships between optical basicity, molar volume and third-order nonlinear optical susceptibility over and below the critical range of optical basicity, respectively.

2. Data on optical basicity, molar volume and third-order nonlinear optical susceptibility

In this communication, the data on cation polarizability α_I, linear refractive n_o at 633nm, density d and third-order nonlinear optical susceptibility $\chi^{(3)}$ are taken from the literatures [21-29]. The molar volume and optical basicity $\Lambda(n_0)$ are obtained from equations (1-3) [25,26,30]. The relative data and calculated results are shown in Table 1. In Table 1 the cation polarizability α_I for B is taken as 0.002 [26], and the atomic weights for B, O, Li, Na, K, Rb, Cs, Ba, Pb, Bi and Sb are taken as 10.81, 16, 6.94, 22.988, 39.102, 85.468, 132.905, 137.34, 207.2, 208.981, and 121.75, respectively [2].

$$\alpha_{O^{2-}}(n_0) = \left[\frac{V_m}{2.52} \square \frac{n_0^2 - 1}{n_0^2 + 2} - \sum \alpha_I \right] (N_{O^{2-}})^{-1} \tag{1}$$

$$\Lambda(n_0) = 1.67[1 - 1/\alpha_{O^{2-}}(n_o)] \tag{2}$$

$$V_m = M_{glass}/d \tag{3}$$

where $\alpha_{O^{2-}}(n_0)$ is oxide ion polarizability for a binary oxide glass with general formula of $xA_pO_q(1\text{-}x)B_2O_3$. $\sum\alpha_I$ denotes the molar cation polarizability given by $xp\alpha_A + 2(1\text{-}x)\alpha_B$ and $N_{O^{2-}}$ denotes the number of oxide ions in the chemical formula given by $xq + 3(1 - x)$. V_m is molar volume, M_{glass} is molar weight given by xM_{ApOq}+(1-x) M_{B2O3} and d density of binary borate glasses.

Table 1. Optical basicity $\Lambda(n_o)$, molar volume V_m and third-order nonlinear optical susceptibility $\chi^{(3)}$ of binary borate glasses.

System (α_I for first oxide)	First oxide mol%	d g /cm^3	n_o 633nm	V_m cm^3/mol	$\Sigma\alpha_I$	$\alpha_{O^{2-}}(n_0)$	$\Lambda(n_o)$	$\chi^{(3)}$
Li_2O-B_2O_3	10	1.962	1.494	33.459	0.0084	1.377	0.458	2.89
(0.024)	20	2.111	1.467	29.215	0.0128	1.232	0.315	3.26
	30	2.229	1.546	25.885	0.0172	1.348	0.431	4.53
	40	2.278	1.559	23.584	0.0216	1.364	0.445	4.76
Na_2O-B_2O_3	10	2.019	1.474	34.104	0.0386	1.345	0.428	2.98
(0.175)	20	2.176	1.431	31.292	0.0732	1.208	0.288	3.17
	30	2.135	1.448	31.535	0.1078	1.351	0.434	3.24
	40	2.353	1.44	28.288	0.1424	1.280	0.365	3.93
	70	2.391	1.442	26.880	0.2462	1.610	0.633	6.58
K_2O-B_2O_3	10	2.022	1.467	35.647	0.1676	1.342	0.426	2.94
(0.820)	20	2.126	1.463	35.060	0.3312	1.346	0.430	3.02
	30	2.265	1.585	33.993	0.4948	1.678	0.674	3.77
Rb_2O-B_2O_3	10	2.252	1.458	36.124	0.2910	1.293	0.378	2.99
(1.437)	20	2.478	1.461	37.564	0.5780	1.351	0.434	3.1
	30	2.838	1.461	36.933	0.8650	1.315	0.400	3.74
Cs_2O-B_2O_3	10	2.407	1.459	37.740	0.5226	1.276	0.361	3.31
(2.595)	20	2.8	1.456	40.021	1.0412	1.260	0.345	3.73
	30	3.229	1.46	41.275	1.5598	1.219	0.300	4.48
BaO-B_2O_3	20	2.822	1.535	30.604	0.3222	1.330	0.415	4.33
(1.595)	30	3.36	1.578	28.195	0.4813	1.347	0.430	5.38
	40	3.776	1.607	27.306	0.6404	1.410	0.485	5.87
PbO-B_2O_3	25	3.769	1.655	28.659	0.9088	1.306	0.391	8.89
(3.623)	30	4.124	1.679	28.054	1.0897	1.297	0.382	10.5
	40	4.917	1.767	26.653	1.4516	1.332	0.416	16
	50	5.648	1.831	25.922	1.8135	1.354	0.436	23.5
	60	6.284	1.89	25.743	2.1754	1.411	0.487	31.8
	70	6.888	1.99	25.715	2.5373	1.582	0.614	50.1
	75	7.207	2.042	25.642	2.7183	1.673	0.672	73.2
Bi_2O_3-B_2O_3	25	5.105	1.871	33.047	0.3800	1.861	0.772	31.9
(1.508)	30	5.443	1.866	34.636	0.4552	1.923	0.801	34.7
	40	6.256	1.978	36.470	0.6056	2.174	0.902	51.5
	50	6.932	2.08	38.631	0.7560	2.435	0.984	63.4
	60	7.428	2.088	41.387	0.9064	2.590	1.025	81.3
	65	7.627	2.186	42.906	0.9816	2.836	1.081	118
Sb_2O_3-B_2O_3	10	2.394	1.451	38.349	0.1147	1.328	0.412	4.96
(1.111)	20	2.93	1.667	38.906	0.2254	1.841	0.763	10.6
	30	3.406	1.708	39.984	0.3361	1.950	0.814	16.4
	40	3.994	1.81	39.652	0.4468	2.114	0.880	30.2
	50	4.369	1.865	41.328	0.5575	2.287	0.940	35.6
	60	4.474	1.895	45.317	0.6682	2.555	1.016	44
	70	4.731	1.922	47.545	0.7789	2.716	1.055	51.5
	80	4.887	1.997	50.568	0.8896	3.041	1.121	65.4
	90	5.073	2.001	53.087	1.0003	3.180	1.145	76.2

3. Correlations between optical basicity, molar volume and third-order nonlinear optical susceptibility

On the basis of Table 1, we have plotted the data on optical basicity $\Lambda(n_o)$, the molar volume V_m and third-order nonlinear optical susceptibility $\chi^{(3)}$ respectively in Figs. 1 and. 2, where M_2O denote Li_2O, Na_2O, K_2O, Rb_2O and Cs_2O.

Table 2. The expressions between third-order nonlinear optical susceptibility $\chi^{(3)}$ and optical basicity $\Lambda(n_o)$.

System	$\Lambda(n_o) < 0.5$	$\Lambda(n_o) > 0.6$
$M_2O(BaO)$-B_2O_3	$\chi^{(3)}=3.9543\Lambda(n_o)+2.1962$	$\chi^{(3)}=-68.537\Lambda(n_o)+49.964$
PbO-B_2O_3	$\chi^{(3)}=224.86\Lambda(n_o)-76.874$	$\chi^{(3)}=400.94\Lambda(n_o)-196.15$
Bi_2O_3-B_2O_3		$\chi^{(3)}=246.14\Lambda(n_o)-164.88$
Sb_2O_3-B_2O_3		$\chi^{(3)}=0.3724\ e^{4.6915\Lambda(no)}$

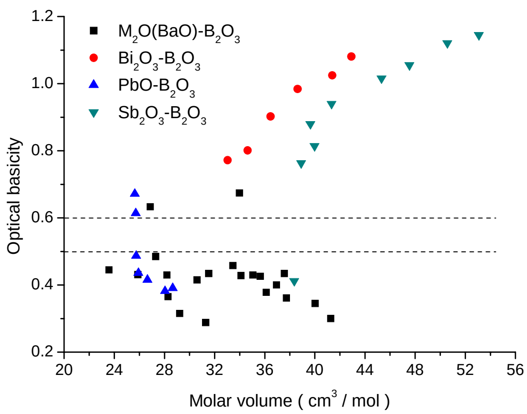

Fig. 1. Optical basicity as a function of molar volume.

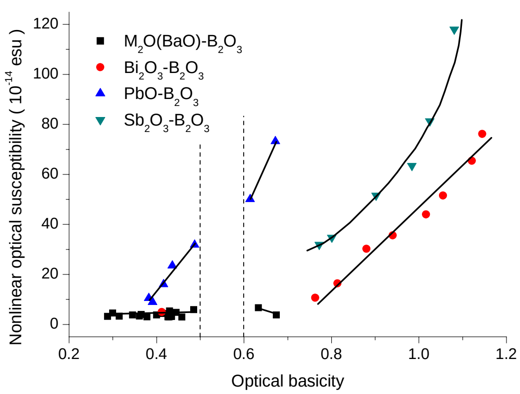

Fig. 2. Third-order nonlinear optical susceptibility as a function of optical basicity.

Fig.1 shows different qualitative trends between $\Lambda(n_o)$ and V_m across the optical basicity range from 0.5 to 0.6. $\Lambda(n_o)$ decreases with increasing V_m as $\Lambda(n_o)<0.5$, and $\Lambda(n_o)$ increases with increasing V_m as $\Lambda(n_o)>0.6$. Fig. 2 presents different quantitative relationships between $\chi^{(3)}$ and $\Lambda(n_o)$ across the optical basicity range from 0.5 to 0.6. For $M_2O(BaO)$-B_2O_3 glasses, $\chi^{(3)}$ increases with increasing $\Lambda(n_o)$ as $\Lambda(n_o) < 0.5$, and $\chi^{(3)}$ decreases with increasing $\Lambda(n_o)$ as $\Lambda(n_o)>0.6$. For PbO-B_2O_3 glasses $\chi^{(3)}$ increases more rapidly with increasing $\Lambda(n_o)$ as $\Lambda(n_o)>0.6$ than that as $\Lambda(n_o) < 0.5$. For Bi_2O_3-B_2O_3 glasses $\chi^{(3)}$ increases linearly with increasing $\Lambda(n_o)$ as $\Lambda(n_o)>0.6$. For Sb_2O_3-B_2O_3 glasses $\chi^{(3)}$ increases exponentially with increasing $\Lambda(n_o)$ as $\Lambda(n_o)>0.6$. The quantitative expressions between $\chi^{(3)}$ and $\Lambda(n_o)$ for the investigated binary borate glasses are estimated by the least squares method and listed in Table 2. Further researches are needed to find the critical value in the specific range of optical basictiy from 0.5 to 0.6 and the relationships between the critical range and glass structure.

4. Conclusions

For the investigated binary borate glasses (totaling 9 glass systems and 43 glass compostions), the optical basicity range from 0.5 to 0.6 is critical, which separates glasses to two groups, which present different correlations between optical basicity, molar volume and third-order nonlinear optical susceptibility. Optical basicity presents a decrease trend with increasing molar volume as optical basicity is smaller than 0.5, optical basicity has a increases trend with increasing molar volume as optical basicity is larger than 0.6. For Sb_2O_3-B_2O_3 glasses third-order nonlinear optical susceptibility increases exponentially with increasing optical basicity. For Bi_2O_3-B_2O_3 glasses third-order nonlinear optical susceptibility increases linearly with increasing optical basicity. For PbO-B_2O_3 glasses, third-order nonlinear optical susceptibility increases linearly with increasing optical basicity, and as optical basicity is larger than 0.6 it increase more rapidly than that as optical basicity is smaller than 0.5. For $M_2O(BaO)$-B_2O_3 glasses third-order nonlinear optical susceptibility increases linearly with increasing optical basicity as optical basicity is smaller than 0.5 and decreases linearly with increasing optical basicity as optical basicitoy is larger than 0.6. These results will promote to search for the structural reason of these optical property changes, and will contribute a lot to the search for glass material with larger third-order nonlinear optical susceptibility.

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