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Refractive Index and Nonlinear Optical Properties of Oxide Glasses

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Refractive indexes of multi-component oxide glasses-silica, silicate, borate, aluminate, germanate, tellurite, antimonate, and heavy metal gallate glasses-are presented in the wavelengths range 0.265 to 5.03 μm. Compositional dependence of refractive index and nonlinear optical properties of oxide glasses are investigated. In order to design for the value of refractive index n_d at 0.5876 μm, we calculated ionic refraction, R_i of oxide composing oxide glasses using Lorentz-Lorenz equation. An empirical equation between n_d and R_i was obtained, which enables to predict the value of n_d from the compositional parameter, R_i. Correlation between linear refractive indexes and third order nonlinear susceptibilities $\chi^{(3)}$ are discussed.

1. Introduction

Glass materials play an important roles in realizing wide variety of applications ranging from lenses to optical fiber communication all over the world. They have several practical advantages such as composition diversity, various shapes, and easy mass production at low cost. In the field of optoelectronics and optics, the optical computing systems in the next 21 century require combinations of various forming systems in order to achieve this goal. To develop materials having suitable optical properties, it would, therefore, be desirable to control refractive index as a function of wavelength. The refractive index is especially important to design glasses with various optical properties and is also predominantly influenced by their chemical composition.

Nonlinear optical glasses have attracted much interest since they have high potential for optical devices. In particular, non-resonant nonlinearities have many potential applications such as ultrafast optical switches[1),2)]. For these materials, the nonlinear coefficient is an important property and is closely related to the linear refractive index [3),4)]. For instance, there are empirical relationships between the linear refractive index and third order nonlinear susceptibilities $\chi^{(3)}$; glasses with high linear refractive indexes possess also high $\chi^{(3)}$[4)-6)]. Although this empirical relationship is often used to design crystals and glasses with low refractive index, it has not been applied to oxide glasses with high refractive index such as tellurite glasses. Recently, Yoko et al.[7)-9)] proposed modified Line's equation in order to clarify relationship between third order nonlinear susceptibilities $\chi^{(3)}$ and the linear optical properties. They found that this equation is in good agreement with the observed $\chi^{(3)}$, using the third harmonic generation (THG) method in borate and tellurite glasses. It is expected that glasses which contain high polarizable cation will have a large $\chi^{(3)}$ value. However, correlation between linear refractive indexes and third order nonlinear susceptibilities $\chi^{(3)}$ is not systematically clarified through all of the oxide glasses.

The purpose of this paper to present accurately refractive indexes of oxide glasses: silica, silicate, borate, aluminate, germanate, tellurite, antimonate, and heavy metal gallate (HMG) glasses at various wavelengths from ultraviolet to infrared region using the minimum deviation method [10)]. In order to estimate the refractive index, n_d (He-d line 0.5876μm) of various oxide glasses, a new compositional parameter: ionic refraction, R_i is proposed. Furthermore, oxide glasses with high refractive index is developed for third order nonlinear optical material, and correlation

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Table 1　Glass compositions and optical properties of oxide glasses.

Composition (mol%)	Density, $\rho/g\cdot cm^{-3}$	Refractive index			$\chi^{(3)}/10^{-14}$ esu
		$n_d/0.5876\mu m$	$n_{3w}/0.633\mu m$	$n_w/1.9\mu m$	
Silica					
Corning 7940	2.20	1.45849	1.45711	1.43950	2.8
Silicate					
$40BaO\cdot 60SiO_2$	3.99	1.6390	1.6359	1.6173	—
$30PbO\cdot 70SiO_2$	4.94	1.778	1.767	1.749	10.7
$40PbO\cdot 60SiO_2$	5.52	1.843	1.833	1.811	20.1
$50PbO\cdot 50SiO_2$	5.97	1.893	1.889	1.859	31.8
$60PbO\cdot 40SiO_2$	6.69	1.984	1.971	1.942	44.2
Borate					
$20BaO\cdot 80B_2O_3$	2.80	1.55927	1.55730	1.53408	4.3
$30PbO\cdot 70B_2O_3$	4.10	1.724	1.717	1.699	8.5
$40PbO\cdot 60B_2O_3$	4.90	1.798	1.789	1.768	15.2
$50PbO\cdot 50B_2O_3$	5.65	1.878	1.867	1.842	21.2
$60PbO\cdot 40B_2O_3$	6.28	1.962	1.954	1.918	40.9
$70PbO\cdot 30B_2O_3$	6.88	2.056	2.049	2.001	72.3
Aluminate					
$65CaO\cdot 35Al_2O_3$	2.88	1.66464	1.66150	1.63878	—
Germanate					
$20Na_2O\cdot 80GeO_2$	4.01	1.68310	1.67942	1.65508	—
Tellurite					
$20Na_2O\cdot 80TeO_2$	4.80	1.9994	1.9888	2.04804	42.8
$20BaO\cdot 80TeO_2$	5.55	2.10053	2.08831	2.02457	51.0
$10Nb_2O_5\cdot 91TeO_2$	5.53	2.20156	2.18627	2.04804	129.2
$20WO_3\cdot 80TeO_2$	5.94	2.19584	2.18157	2.20572	111.0
$20Tl_2O\cdot 80TeO_2$	6.55	2.20572	2.18794	2.10850	—
Antimonate					
Sb_2O_3	5.05	2.003	2.001	1.960	84.0
$20Tl_2O\cdot 80TSb_2O_3$	5.91	2.1814	2.1641	2.0758	—
Heavy metal gallate (HMG)					
$80PbO\cdot 20Ga_2O_3$	7.72	2.2944	2.2734	2.1643	293.0
$40PbO\cdot 40Bi_2O_3\cdot 20Ga_2O_3$	8.12	2.3833	2.3622	2.2455	227.0
$80Bi_2O_3\cdot 20Ga2O_3$	8.44	2.383	2.370	2.271	203.0
$40Tl_2O\cdot 40Bi_2O_3\cdot 20Ga_2O_3$	8.34	2.4921	2.4569	2.3014	—

between linear refractive indexes and third order nonlinear susceptibilities $\chi^{(3)}$ are discussed.

2. Experimental Procedure

All glass samples except for silica were prepared in our laboratory. The preparation process of glass sample were detailed in the previous studies [11),12)]. **Table 1** shows glass compositions in this study. Refractive index was measured with a precision spectrometer (Model GMR-1, Kalnew, Nagano, Japan) at 23℃ in the wavelength range of 0.265 to 5.03 μm. It is important to measure refractive index accurately as a function of wavelength dispersion of glasses. Refractive index is generally measured using a convenient refractometer, (an Abbe, immersion, depth, and ellipsometer methods) or accuracy refractometer (autocollimation and minimum deviation methods) . In particular, the minimum deviation method used in this study is the most powerful technique to obtain the value of refractive index with high accuracy. Note that the quality of optically polished surface must be high in order to measure refractive index as accurate as possible [13)].

The third order nonlinear optical susceptibilities $\chi^{(3)}$ of various oxide glasses: silica, barium borate, lead borate, lead silicate, antimonate, tellurite, and heavy metal gallate glasses (HMG) were investigated by the third harmonic generation (THG) measurement at Institute for Chemical

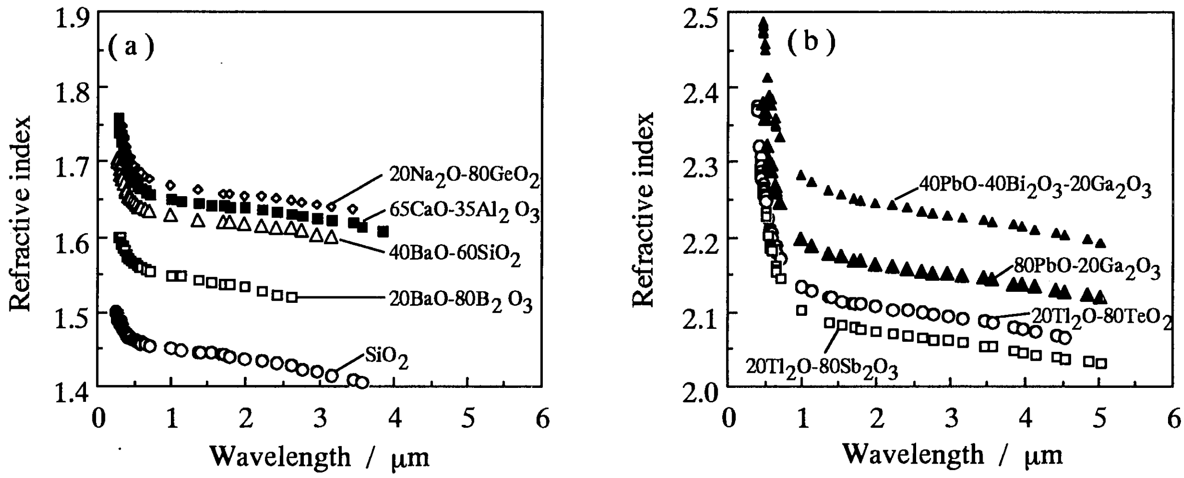


Fig. 1 Refractive index versus wavelength for representative oxide glasses: (a) silica, and silicate, borate, aluminate, germanate, and (b) tellurite, antimonate, and HMG.

Research, Kyoto University, which is described in detail elsewhere [14]. The $\chi^{(3)}$ was calculated by the following expression [15]

$$\chi^{(3)} = \chi^{(3)}_{SiO2} \times \frac{l_{c,SiO2}}{l_c} \sqrt{\frac{I}{I_{SiO2}}} \sqrt{\frac{n_{3w} \cdot n_w^3 \cdot T_{3w,SiO2} \cdot T^3_{w,SiO2}}{n_{3w,SiO2} \cdot n^3_{\omega,SiO2} \cdot T_w^3 \cdot T_{3w}}} \qquad (1)$$

where the subscript of SiO_2 mentions silica glass used standard sample. The subscripts $3w$ (wavelength at 0.633 μm) and ω (wavelength at 1.9 μm) denote the wavelengths of third harmonic and incident waves, respectively. The coherence length of the sample, l_c, was obtained from the fringe patterns [16]. I/I_{SiO2} is the relative third harmonic intensity with respect to SiO_2 glass. The value of transmittance and refractive index of silica glass are as follows: $T_{3w,SiO2}$ = 93.5%, $T_{w,SiO2}$ = 94.7%, $n_{3w,SiO2}$=1.4571 and $n_{w,SiO2}$ = 1.4395. The value of $\chi^{(3)}{}_{SiO2}$=2.8 x 10^{-14} *esu* and $l_{c,SiO2}$ = 18.1 μm were used for the calculation of $\chi^{(3)}$.

In order to investigate the correlation between $\chi^{(3)}$ and optical transition of Pb^{2+}, and Bi^{3+}, reflection spectra in the vacuum ultraviolet region were measured using the SOR of Institute for Molecular Science, Okazaki in Japan as a light source in the region of 2 - 20 eV [17].

3. Results and Discussion

3.1 Refractive indexes of oxide glasses

Fig. 1 shows refractive indexes of (a) silica, silicate, borate, aluminate, germanate and (b) tellurite, antimonate, and HMG glasses as a function of wavelength. The silicate, borate, and aluminate glasses contain oxygen ions and only cations with noble gas structure: Si^{4+}, B^{3+}, Al^{3+}, Na^+, Ca^{2+}, Ba^{2+};[18] the tellurite, antimonate, and heavy metal gallate glasses contain oxygen ions and much amount of high-polarizable cations with non-noble gas structure: [18] Te^{4+}, Sb^{3+}, Pb^{2+}, Bi^{3+}, Tl^+ as network formers or modifiers. For high-refractive index glasses with refractive indexes above 2, n_d increases approximately in the order thallium antimonate glasses < thallium tellurite glasses < HMG glasses. The HMG glass with a composition of $40Tl_2O.40Bi_2O_3.20Ga_2O_3$ has the highest value of n_d = 2.4921 in the oxide glasses.

Table 1 also summarizes some properties: density ρ, n_d, n_{3w}, n_w and $\chi^{(3)}$ of oxide glasses examined in this study. As for high refractive index glasses (n_d > 2) containing highly polarizable cations, the glasses with higher $\chi^{(3)}$ are accompanied by higher refractive index.

Refractive index, n is given in terms of the density ρ, the average molecular weight M, and the molar refraction R using the Lorentz-Lorenz formula [19]

$$\frac{n^2-1}{n^2+2}\cdot\frac{M}{\rho}=R \qquad (2)$$

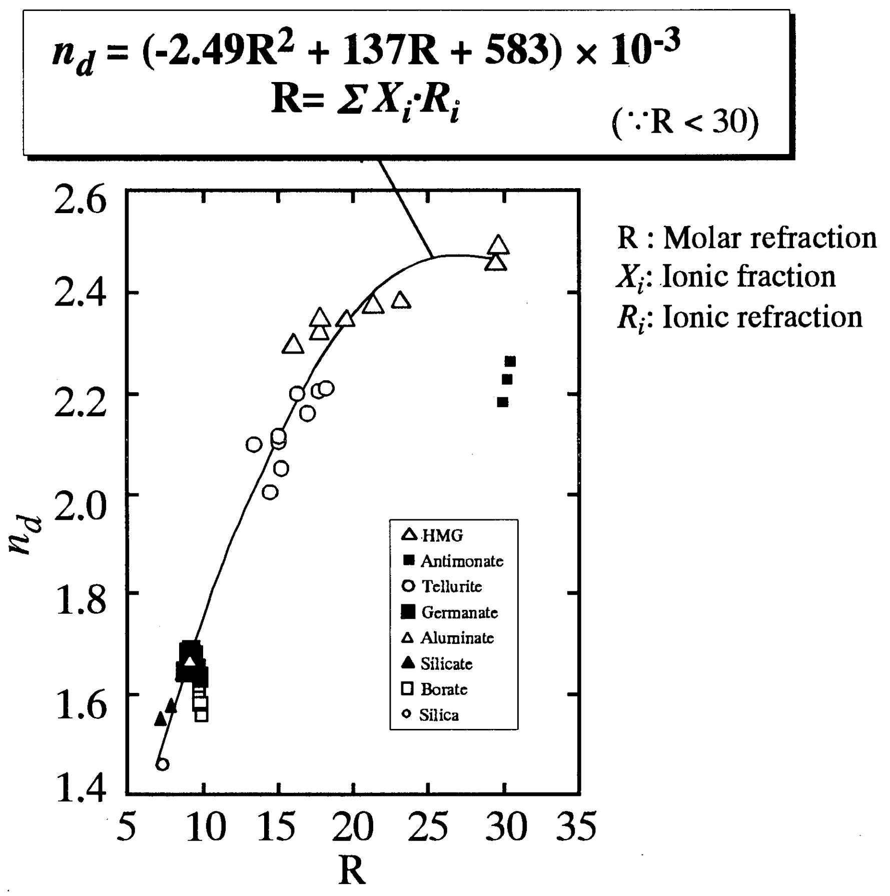
The formula indicates that refractive index is affected by two factors, that is, the packing and the polarization of a glass. Refractive index, n increases as molar volume, M/ρ decreases and ionic polarizabilities of glass constituents increase. Ionic refraction, R_i was calculated using the following additive formula:

$$R=\sum_i X_i \cdot R_i \qquad (3)$$

The R_i was calculated from molar refraction, R and ionic fraction, X_i on the assumption that the R_i of the oxygen remain constant with variation of composition [19]. The author used this parameters as ionic polärizability to develop oxide glasses with high refractive index. **Fig. 2** shows relationship between refractive index, n_d and calculated molar refraction, R. Also the ionic refraction, R_i value previously reported19) are also shown in **Fig. 2**. From this **figure**, the following an empirical equation was obtained

$$n_d = (2.49R^2 + 137R + 583) \times 10^{-3} \ (R<30) \qquad (4)$$

This equation indicates that the compositional parameter R_i is useful to design the glasses except for antimonate with high refractive index.



Ion	R_i
B^{3+}	0.05
Si^{4+} *	0.08
Li^{+} *	0.12
Al^{3+} *	0.14
Mg^{2+} *	0.26
Na^{+} *	0.47
Ta^{5+}	0.69
Ca^{2+} *	1.39
Y^{3+} *	1.70
K^{+} *	2.24
Sr^{2+} *	2.59
Ge^{4+}	2.60
Ga^{3+}	3.60
Ba^{2+} *	4.73
O^{2-}	6.95
Pb^{2+}	8.50
Nb^{5+}	9.20
Sb^{3+}	9.50
Te^{4+}	9.60
Ti^{4+}	10.0
Bi^{3+}	11.7
Tl^{+}	13.5

*Ref. 19

Fig. 2 The relationship between refractive index, nd and molar, R in oxide glasses.

To obtain glasses with higher refractive index, the optimum composition is readily selected for the following conditions: highly polarizable cations are incorporated into a unit volume of the glass as many as possible as network formers or network modifiers in the glass. HMG glasses [20] containing much amount of highly polalizable Pb^{2+}, Bi^{3+}, and Tl^{+} ions are consistent with the above condition. It is found that the enhancement of refractive index by containing the large amount of Tl_2O was larger than that of PbO and Bi_2O_3 from **Fig. 2**.

3.2 Correlation between linear refractive index and third order optical susceptibilities $\chi^{(3)}$

In this section, correlation between linear refractive index and third order optical susceptibilities $\chi^{(3)}$ are discussed. There are several theoretical equation to estimate $\chi^{(3)}$ from linear refractive index or optical susceptibility $\chi^{(3)}$ [21),22)]. The empirical Miller's rule [23)] is generally available for non-resonant wavelength region as

$$\chi^{(3)} = (\chi^{(1)})^4 \times 10^{-10}\, esu = (n_w^2 - 1/4\pi)^4 \times 10^{-10}\, esu, \quad (5)$$

that shows the higher the refractive index, the larger value of $\chi^{(3)}$. **Fig. 3** shows the relationship between linear refractive index and third order optical susceptibilities $\chi^{(3)}$ in various oxide glasses: silica, barium borate, lead borate, lead silicate, antimonate, tellurite, and HMG glasses. A HMG glass ($40Tl_2O$-$40Bi_2O_3$-$20Ga_2O_3$) posses the highest refractive index, suggesting a high $\chi^{(3)}$. But, because of high absorption around 0.633 μm, the determination of $\chi^{(3)}$ was not successful by the THG method. The $\chi^{(3)}$ increases approximately with increasing linear refractive index. The largest $\chi^{(3)}$ value shows 2.93 x 10^{-12} esu for the $80PbO$-$20Ga_2O_3$ glasses, which is about 100 times larger than that of silica glass. For the silica, lead silicate, barium-, lead-borate glasses with refractive indexes below 2, as the value of $\chi^{(3)}$ is applied to empirical *Eq.*(5). However, the relationship is not the same for the antimonate, tellurite, and HMG glasses with refractive indexes above 2. Therefore, an attempt was made to propose an empirical relationship for oxide glasses with high refractive index above 2 as follows

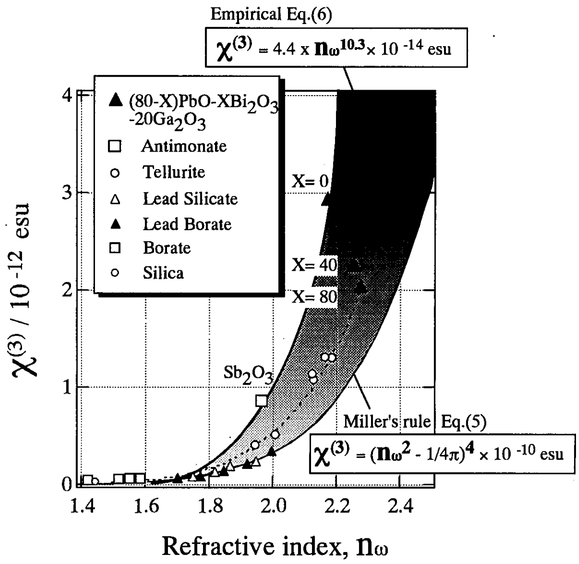


Fig. 3 Third order nonlinear susceptibility $\chi^{(3)}$ of oxide glasses as a function of linear refractive index at 1.9μm

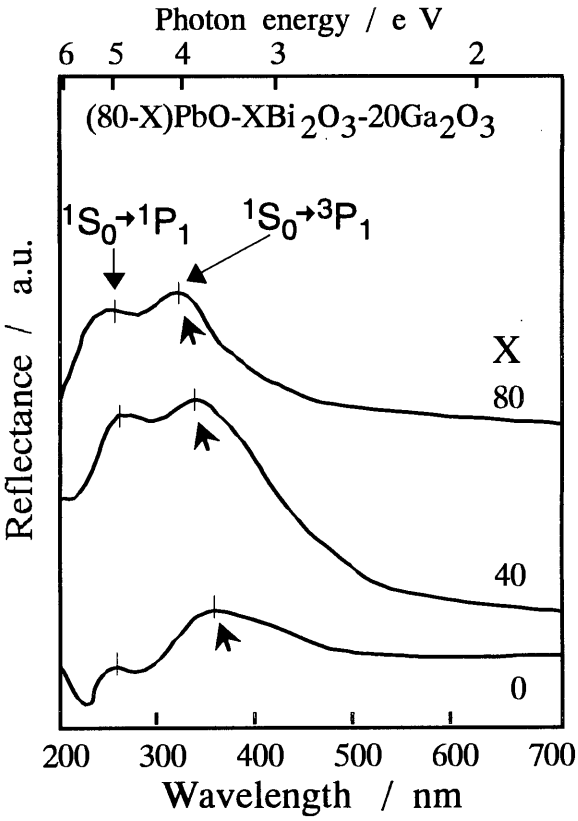


Fig. 4 Reflection spectra of (80−X) PbO-XBi_2O_3-$20Ga_2O_3$ glasses.

$$\chi^3 \geqq 4.4 \times n_w^{10.3} \times 10^{-14}\ esu. \quad (6)$$

Meanwhile, as Bi_2O_3 is substituted for PbO (constant 20 *mol*% Ga_2O_3), refractive index increases and the value of $\chi^{(3)}$ decreases. The author explains this phenomenon in terms of the ultraviolet reflection spectra. **Fig. 4** shows the ultraviolet reflection spectra of (80-X) PbO-XBi_2O_3-$20Ga_2O_3$ glasses. The resonance energies of the 80PbO-$20Ga_2O_3$ glass (X=0) are found at 3.5 and 5.0 *eV*, which are attributed to the $^1S_0 \rightarrow {}^3P_1$ and $^1S_0 \rightarrow {}^1P_1$ transitions of the Pb^{2+} ion, respectively[24),25)]. The $^1S_0 \rightarrow {}^3P_1$ transitions of Pb^{2+} ion are slightly shifted to high energy side, when Bi_2O_3 is substituted for PbO (X=0 to 80). It is indicated that the resonance energy of the B_i^{3+} ions found at 4.0 and 5.0 eV, which are attributed to the $^1S_0 \rightarrow {}^3P_1$ and $^1S_0 \rightarrow {}^1P_1$ transitions of the Bi^{3+} ion, respectively[26)]. On the other hand, the $^1S_0 \rightarrow {}^1P_1$ transition of the Pb^{2+} and Bi^{3+} ion at 5*eV* is essentially unchanged irrespective of PbO and Bi_2O_3 contents. The value of $\chi^{(3)}$ for 80PbO-$20Ga_2O_3$ are larger than those for $80Bi_2O_3$-$20Ga_2O_3$, indicating that enhancement by the optical transition occur from $^1S_0 \rightarrow {}^3P_1$ orbitals of Pb^{2+} ion. The value of $\chi^{(3)}$ for antimonate glass is larger than those of lead-silicate, -borate and alkali-tellurite glasses with similar refractive indexes. It is probably due to the variation of bond style in glass structure such as covalency or ionicity[27)]. Furthermore, it is necessary for investigating from the viewpoint of the glass structure such as the covalent character of Sb-O[28)] and Te-O bond, and theoretical electronic band structure of antimonate and tellurite glasses.

4. Conclusions

The variations of refractive indexes with wavelength in the region from 0.265 to 5.03 μm are presented for oxide glasses: silica, silicate, borate, aluminate, germanate, tellurite, antimonate, and heavy metal gallate glasses. To estimate refractive index, n_d, the compositional parameter: ionic refraction, R_i was calculated from measured refractive index and density using the Lorenz-Lorentz equation. The empirical equation between refractive index, n_d and molar refraction, R_i was obtained as $n_d = (2.49R^2 + 137R + 583) \times 10^{-3}$ (R<30).

The largest $\chi^{(3)}$ value shows 2.93×10^{-12} esu for the 80PbO-$20Ga_2O_3$ glasses, which is about 100 times larger than that of silica glass. Empirical Miller's rule was applied to oxide glasses with refractive indexes below 2: silica, lead silicate, barium-, lead-borate glasses, that is, $\chi^{(3)}$ value was dependent on the eighth power of refractive index, n^8. For the oxide glasses with refractive indexes above 2: antimonate, tellurite, and heavy metal gallate glasses, an attempt was made to propose an empirical relationship, $\chi^{(3)} \geqq 4.4 \times n^{10.3} \times 10^{-14}$ *esv*, based on the measured refractive index and $\chi^{(3)}$.

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