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Nonlinear Optical Properties of TeO_2-Based Glasses: $RO-TeO_2$ (R=Mg, Sr and Ba) Binary Glasses

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The third-order nonlinear optical susceptibilities, $\chi^{(3)}$, of xRO·(100−x)TeO_2 (R=Mg, Sr and Ba) binary glasses have been measured with a special attention to the effect of addition of second component using the third harmonic generation (THG) method. The $\chi^{(3)}$ value obtained is for example, 9×10^{-13} esu for 10BaO·90TeO_2 glass. It is found that the third-order nonlinear optical susceptibilities $\chi^{(3)}$ of alkaline-earth oxide containing TeO_2 glasses decrease drastically with increasing alkaline-earth oxide content, corresponding to the decrease in the polarizability in unit volume. An excellent linear relationship is found to hold between the $\chi^{(3)}$ and $(n_\omega^2+2)^3\cdot(n_\omega^2-1)\cdot E_d/E_0^2$ irrespective of kind of alkaline earth metals.

KEY WORDS: Third-order nonlinear optical susceptibilities/ $\chi^{(3)}$/ Alkaline-earth oxide containing TeO_2 glasses

1. INTRODUCTION

TeO_2-based glasses have attracted much attention as photonic materials.[1-3] TeO_2 itself has been found to be a superior photonic material having a large $\chi^{(3)}$ value of 1.4×10^{-12} esu.[4] The problem of this glass is that only a small piece of glass is produced even by a rapid quenching technique. Therefore, it is absolutely required to add second components in order to obtain a large piece of glass. Fortunately, TeO_2 is known to form a glass with a variety of metal oxides and halides over a relatively wide composition range.[5,6]

In this respect, it is of essence to investigate the influence of addition of each second component on the nonlinear optical properties of TeO_2-based glasses in order to develop glass materials applicable to photonic devices. In this paper, we will deal with the effect of alkaline earth oxide as a second component. Especially, the relationship between $\chi^{(3)}$ and optical parameters is discussed on the basis of semiempirical formula.

2. EXPERIMENTALS

The batch compositions of the binary xRO·(100−x)TeO_2 (R=Mg, Sr and Ba) glasses prepared in this study are shown in Table 1. A 10 g batch of well mixed oxides was melted in a Pt-5% Au crucible at 700–800°C in an ambient atmosphere. The melts were poured into a brass mold and quenched to room temperature. After annealing at 200°C, the glasses were cut into a plate of $10\times10\times2$ mm^3 in size. Both faces were optically polished to eliminate a light scattering

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Table 1. Nonlinear optical properties of xRO·(100−x)TeO_2 (R=Mg, Sr and Ba) binary glasses.

Glass x/mol%	Density /gcm^{-3}	n_ω	$n_{3\omega}$	E_0 /eV	E_d /eV	R_m/V_m	l_c /μm	$T_{3\omega}$ /%	T_ω /%	$I_{3\omega, \text{Sample}}$ /a.u.	$\chi^{(3)}_{\text{exp}}$ /10^{-13}esu
xMgO·(100−x)TeO_2 glasses											
x=10	5.380	2.050	2.106	7.12	22.6	0.516	5.66	79.9	85.7	5.8	5.46
x=15	5.315	2.010	2.063	7.31	22.0	0.503	5.98	82.0	87.5	5.1	4.45
x=20	5.202	2.003	2.053	7.34	21.9	0.501	6.33	79.2	85.3	4.0	3.90
xSrO·(100−x)TeO_2 glasses											
x=10	5.528	2.054	2.118	6.75	21.5	0.518	4.95	74.1	75.9	6.0	7.95
x=15	5.434	2.015	2.073	6.92	20.9	0.505	5.46	74.3	77.4	4.9	6.11
xBaO·(100−x)TeO_2 glasses											
x=10	5.593	2.055	2.119	6.71	21.4	0.518	4.95	78.9	81.2	10.0	9.0
x=15	5.556	2.042	2.106	6.76	21.2	0.556	4.95	79.2	81.0	6.1	6.9
x=20	5.526	2.006	2.063	6.92	20.8	0.526	5.56	79.3	81.6	6.0	5.8

at the surface. The thickness of glasses for THG and transmittance measurement was 1.0±0.05 mm.

The refractive index of each glass was measured over a wide wavelength range from 486 to 1,000 nm by Mizojiri Optical Works model DVA-36VW ellipsometer.

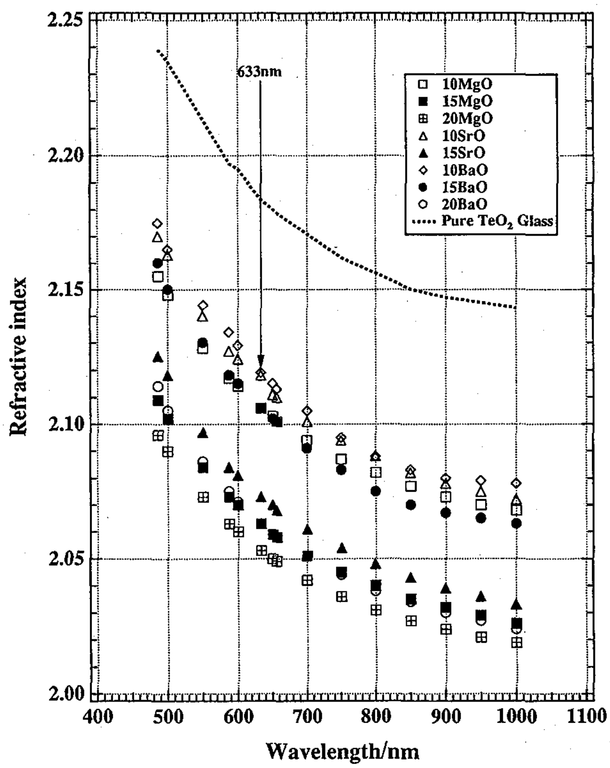

Fig. 1. Variation of refractive index with wavelength in xRO·(100−x)TeO_2 (R=Mg, Sr and Ba) binary glasses.

The transmittance of glasses was determined in the wavelength range from 200 to 2,000 nm by a Hitach model U-3500 spectrophotometer.

The density was measured by the Archimedes method using kerosene as an immersion liquid at 22°C.

The $\chi^{(3)}$ values were determined by the third harmonic generation (THG) method, using a nonlinear optical measurement apparatus assembled by Tokyo Instruments, Inc., Tokyo, Japan. Further details of the THG measurements are described in our previous papers.[2,4,7]

3. RESULTS

As shown in Fig. 1, the refractive indices n of xRO·(100−x)TeO_2 (R=Mg, Sr and Ba) binary glasses are plotted as a function of wavelength ranging from 486 to 1,000 nm. In all

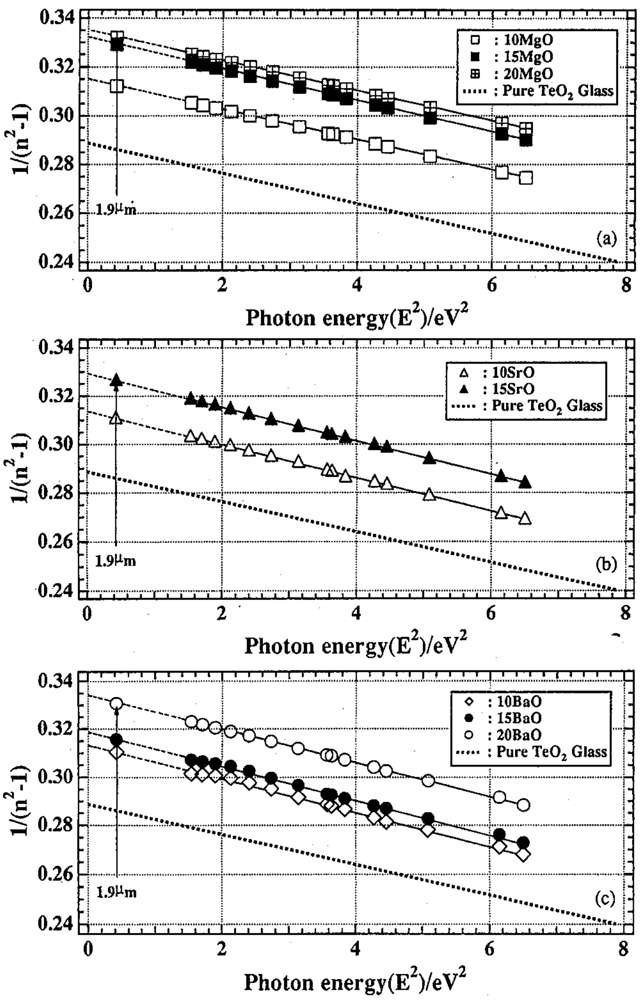

Fig. 2. Dependence of refractive index on photon energy in xRO·(100−x) TeO_2 glasses : (a) R=Mg (x=10, 15 and 20), (b) R=Sr (x=10 and 15) and (c) R=Ba(x=10, 15 and 20).

casees they monotonously decrease with increasing wavelength. Figure 2(a)–(c) show the plots of $1/(n^2-1)$ vs. E^2 according to the following equation proposed by Wemple.[8)]

$$\frac{1}{n^2-1}=\frac{E_0}{E_d}-\frac{E^2}{E_dE_0} \tag{1}$$

where E_d is the dispersion energy and E_0 the excitation energy. Fairly well linear relations between them are observed. The parameters E_0 and E_d obtained from these linear relations are tabulated in Table 1.

Figure 3 shows the refractive indices at 1,900 nm (n_ω) and 633 nm ($n_{3\omega}$) as a function of RO content. For comparison, the values of n_ω and $n_{3\omega}$ of pure TeO_2 glass are also plotted which are cited from ref. 4. In all casees, the addition of RO to TeO_2 reduces the refractive index of TeO_2 glass in the order, BaO>SrO>MgO.

Figure 4(a) and (b) show the composition dependences of the molar volume V_m obtained from density measurements and the molar refraction R_m defined as,[9)]

$$R_m=V_m[(n_\omega{}^2-1)/(n_\omega{}^2+2)] \tag{2}$$

where n_ω is the refractive index. The addition of BaO slightly increases the V_m of TeO_2 glass. The addition of SrO does not seem to change the V_m of TeO_2 glass. The R_m's of TeO_2 decrease with RO content in the order BaO>SrO>MgO. The R_m/V_m, which means the polarizability

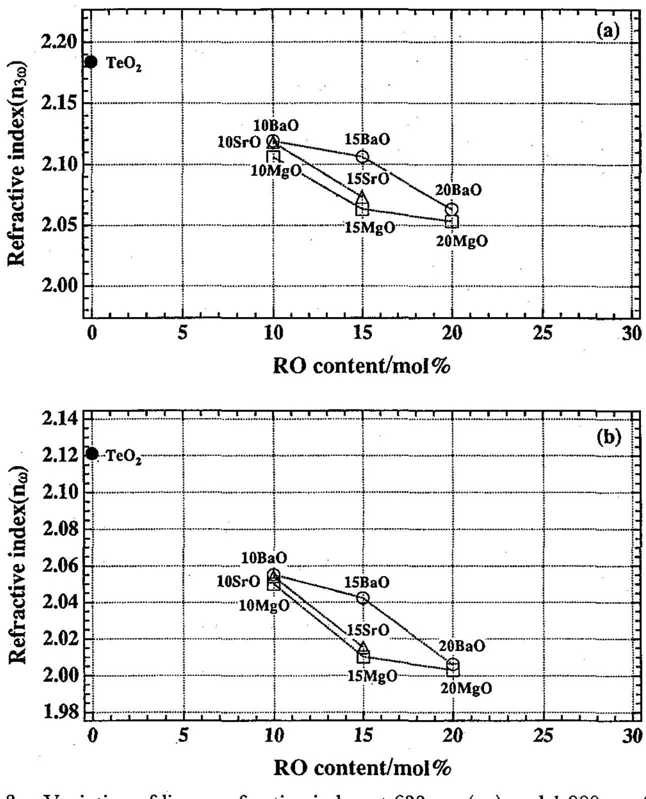

Fig. 3. Variation of linear refractive index at 633 nm (n_ω) and 1,900 nm ($n_{3\omega}$) with RO (R=Mg, Sr and Ba) content in RO-TeO_2 binary glasses.

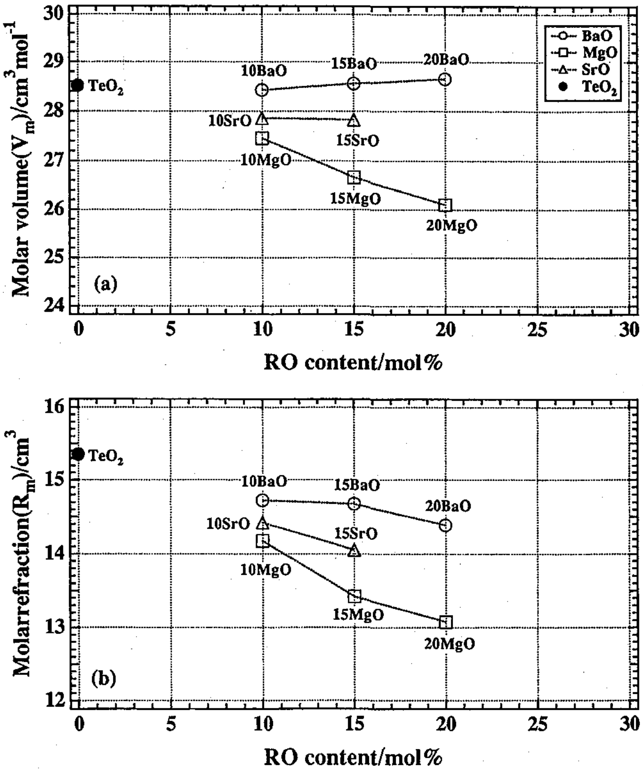

Fig. 4. Composition dependences of (a) Molar volume (V_m) and (b) Molar refraction(R_m) in xRO·(100−x)TeO_2(R=Mg, Sr and Ba) binary glasses.

per unit volume, is plotted against RO contents in Fig. 5. In each of glass systems, the values decrease with RO contents.

The third-order nonlinear optical susceptibilities, $\chi^{(3)}$, determined from the third harmonic generation intensity $I_{3\omega}$ are shown in Fig. 6. In all cases, the $\chi^{(3)}$ values decrease with RO content in the order BaO>SrO>MgO.

4. DISCUSSION

The addition of alkaline earth oxides, MgO, SrO and BaO, has been found to decrease both the refractive index and $\chi^{(3)}$ of TeO_2 glass. It is therefore concluded that although these oxide components have a positive effect in that they extend the glass forming region of TeO_2-based glasses to a considerable extent, they do not improve the linear and nonlinear optical properties of TeO_2-based glasses at all.

Fig. 7 shows a relation between the $\chi^{(3)}$ and n_ω. It is interesting to note that the $\chi^{(3)}$ values are much lower in MgO-TeO_2 glasses than in SrO and BaO-TeO_2 glasses even though their n values are the same. In the latter two glass systems, they have almost the same $\chi^{(3)}$ values when the n values are the same. Figure 8 shows a relation between the $\chi^{(3)}$ and $(R_m/V_m)^4$. Although the $\chi^{(3)}$ increase with increasing $(R_m/V_m)^4$, a unique straight line can not be fitted to the data,

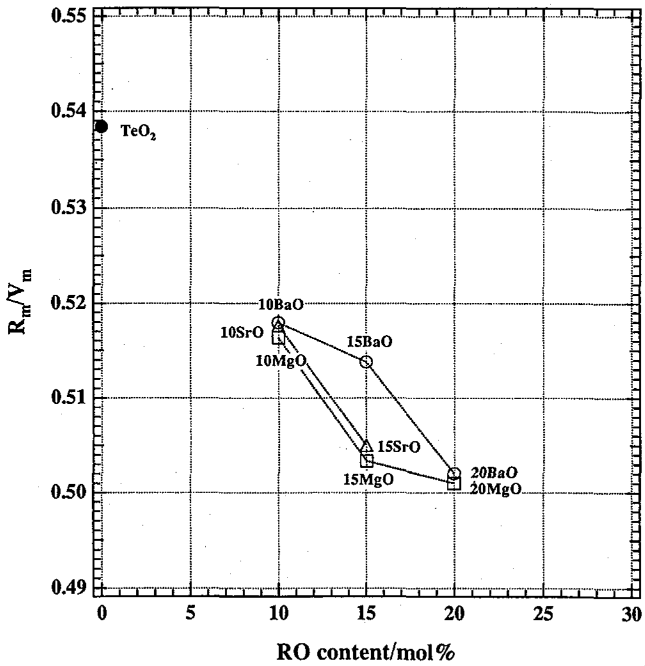

Fig. 5. Polarizability per unit volume (R_m/V_m) of xRO·$(100-x)TeO_2$ (R=Mg, Sr and Ba) binary glasses as a function of RO content

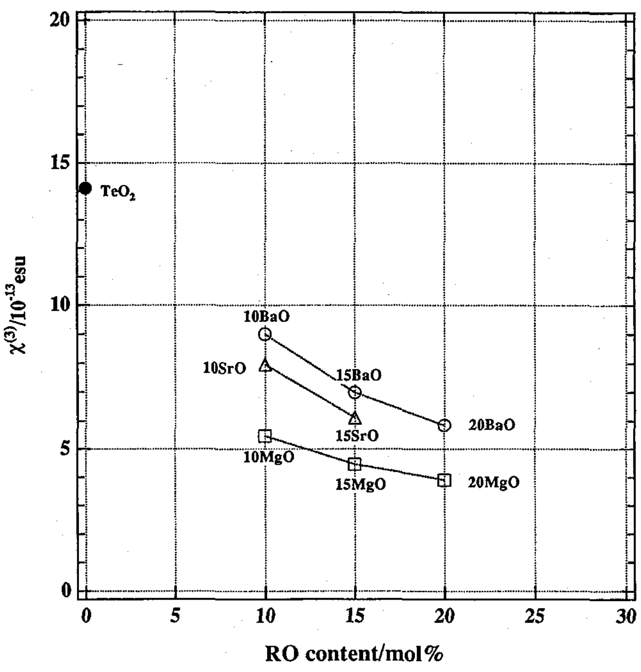

Fig. 6. The third-order nonlinear optical susceptibility $\chi^{(3)}$ of xRO·$(100-x)$ TeO_2 (R=Mg, Sr and Ba) binary glasses as a function of RO content.

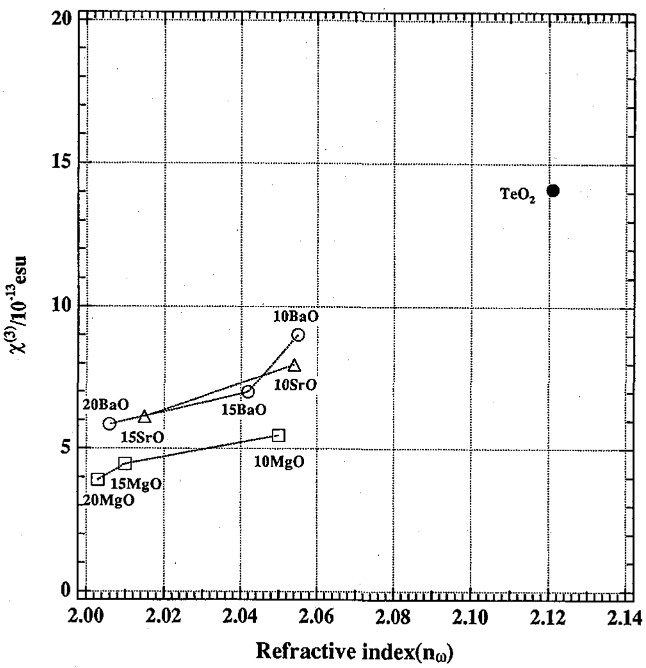

Fig. 7. Relationship between the $\chi^{(3)}$ and linear refractive index (n_ω).

indicating that the generalized Miller's rule[10,11] does not strictly hold in these glasses. It should be also noted that the MgO-TeO_2 glasses exhibit a different behavior from other glasses just like in Fig. 7.

As stated above, $\chi^{(3)}$ of MgO-TeO_2 glasses is much smaller than that of SrO-TeO_2 and BaO-TeO_2 glasses. This may reflect that MgO-TeO_2 glasses have unit structures different from SrO or BaO-TeO_2 glasses. In fact, Sekiya *et al.*[12] reported based on the Raman spectroscopy that the structural units contained in SrO and BaO-TeO_2 glasses are very similar to each other, while those in MgO-TeO_2 glasses are quite different from the case for SrO and BaO-TeO_2 glasses. In SrO- and BaO-TeO_2 glasses, isolated structural units, such as $Te_2O_5^{2-}$ and TeO_3^{2-} ions, coexist with a continuous network composed of tellurium-oxygen polyhedra. In MgO-TeO_2 glasses, the coordination state of tellurium atom changes in analogy with the case of BaO-TeO_2 glasses, but a new structural unit, $(Te_3O_8^{4-})_n$, found in $Pb_2Te_3O_8$, $Nb_2Te_3O_{11}$, $Mg_2Te_3O_8$ and $Zn_2Te_3O_8$, is formed in high MgO content glasses.

Figure 9 shows a relation between the$\chi^{(3)}$ and the term $(n_\omega^2+2)^3\cdot(n_\omega^2-1)\cdot E_d/E_0^2$ [2], which was originally derived by Lines[13~14] based on the bond orbital theory[15~16] and modified by the present authors[2,4]. A good linear relationship between two is observed. A discrepancy, as in Fig. 7 and 8, is not observed in this case. These means that the relation in Fig. 9 is more universal than the relations between the$\chi^{(3)}$ and n or $(R_m/V_m)^4$, and useful to predict the $\chi^{(3)}$ value from these measurable parameters, n, E_d and E_0.

5. CONCLUSION

Linear and nonlinear optical properties of xRO$\cdot$(100$-x$)TeO_2 (R=Mg, Sr and Ba) glasses

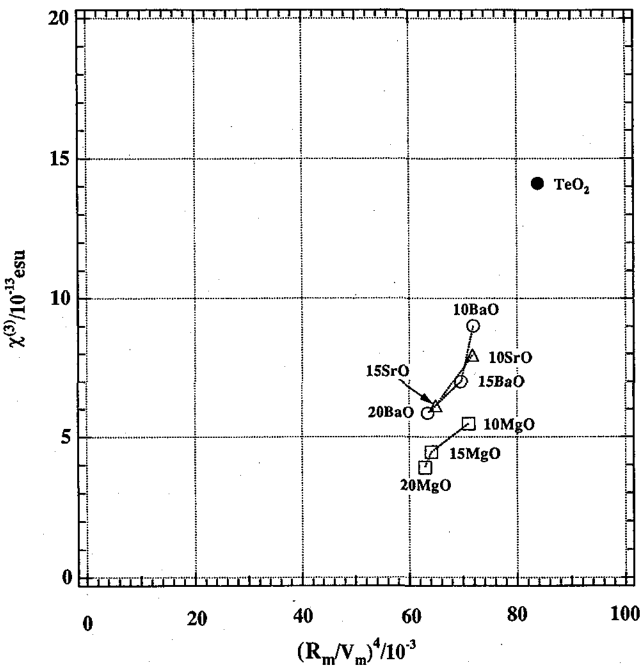

Fig. 8. Relationship between the $\chi^{(3)}$ and $(R_m/V_m)^4$.

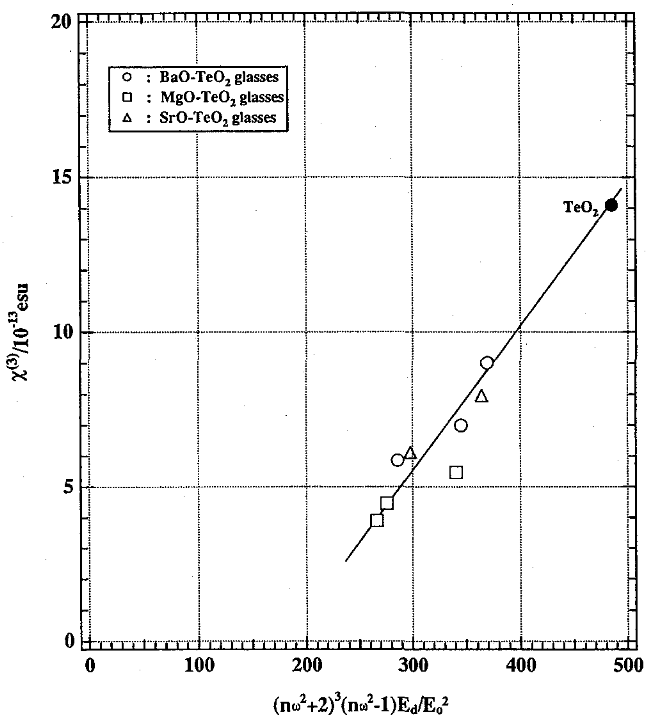

Fig. 9. Relationship between the $\chi^{(3)}$ and the term $(n_\omega{}^2+2)^3 \cdot (n_\omega{}^2-1) \cdot E_d/E_0{}^2$.

have been measured. The results obtained are summarized as follows.

(1) Alkaline earth oxides, such as MgO, SrO and BaO deteriorate both the linear and nonlinear optical properties of TeO_2 glasses, although they extend the glass forming region.

(2) The structure of MgO-TeO_2 glasses may possibly be different from that of SrO- and BaO-TeO_2 glasses which have a basically similar structure to each other and both contain isolated structural units of $Te_2O_5^{2-}$ and TeO_3^{2-}. The difference in glass network structure is reflected on the linear relationship between the $\chi^{(3)}$ and linear refractive index or $(R_m/V_m)^4$.

(3) The modified Lines relationship, $\chi^{(3)} \propto (n_\omega^2+2)^3 \cdot (n_\omega^2-1) \cdot E_d/E_0^2$, was found to hold for the alkaline earth tellurite glasses irrespective of the kind of the alkaline earth metal.

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REFERENCES

(1) S.H. Kim, T. Yoko, F. Miyaji and S. Sakka, Proc. Int. Conf. on Sci. and Tech. of New Glasses, Ed. S. Sakka and N. Soga, Tokyo, The Ceramic Society of Japan, 187 (1991).
(2) S.H. Kim, T. Yoko and S. Sakka, *J. Am. Ceram. Soc.*, **76**, 865 (1993).
(3) H. Nasu, Y. Ibara and K. Kubodera, *J. Non-Cryst. Solids*, **110**, 229 (1989).
(4) S.H. Kim, T. Yoko and S. Sakka, *J. Am. Ceram. Soc.*, **76**, 2486 (1993).
(5) W. Vogel, H. Burger, B. Muler, G. Zerge, W. Muler and K. Forkel, *Silikattechnik*, **25**, 205 (1974).
(6) M. Imaoka and T. Yamazaki, *J. Ceram. Soc. Jpn.*, **76**, 160 (1968).
(7) V.V. Dimitrov, S.H. Kim, T. Yoko and S. Sakka, *J. Ceram. Soc. Jpn.*, **101**, 59 (1993).
(8) S.H. Wemple, *J. Chem. Phys.*, **67**, 2151 (1977).
(9) M.B. Volf, Chemical Approach to Glass, in Glass Science and Technology, 7, Elsevier, 43 (1984).
(10) C.C. Wang, *Phys. Rev. B*, **2**, 2045 (1970).
(11) E.M. Vogel, M.J. Weber and D.M. Krol, *Phys. and Chem. of Glasses*, **32**, 231 (1991).
(12) T. Sekiya, N. Mochida and A. Ohtsuka, *J. Non-Cryst. Solids*, **144**, 128 (1992).
(13) M.E. Lines, *Phys. Rev. B*, **41**, 3372 (1990).
(14) M.E. Lines, *Phys. Rev. B*, **43**, 978 (1991).
(15) W.A. Harrison, *Phys. Rev. B*, **8**, 4487 (1973).
(16) W.A. Harrison, *Phys. Rev. B*, **14**, 702 (1976).