ROUGH ESTIMATION
OF THE NON-LINEAR SUSCEPTIBILITY
IN SOME AMORPHOUS CHALCOGENIDES

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Using generalized Miller's rule and single oscillator model of Wemple and Di Domenico, simple relation is derived for estimation of the non-linear susceptibility ($X^{(3)}$). This relation provides reasonable agreement between the calculated and experimental $X^{(3)}$ values for more than 90 glassy oxides. Prediction of $X^{(3)}$ values for chalcogenide glasses indicates that non-linear susceptibility can reach up to $X^{(3)} \approx 2 \times 10^{-10}$ esu for some telluride glasses.

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Introduction

Amorphous (a) chalcogenides posses interesting optical properties, for example high refractive index (n): $n(\text{a--GeS}_2) \doteq 2.2$ [1], $n(\text{a--As}_2\text{Te}_3) \doteq 3.6$ [2]. Photoinduced changes manifested by photoinduced blue or red (bleaching, darkening) shift of the optical gap (E_g), e.g. [3], photoinduced crystallization, e.g. [4], and photoinduced anisotropy, e.g. [5], are of considerable interest also for possible application of these phenomena to optical memories. Amorphous chalcogenides are also transparent in the mid-infrared spectral region. For example, bulk selenide glasses show good transparency up to 11 μm if the content of oxygen impurities is of ppm order or less, see e.g. [6,7]. There are also some experimental indications that amorphous or glassy chalcogenides have rather high nonlinear optical susceptibility, see e.g. [8,9], and, hence, these materials are promising candidates as non-linear optical elements. The experimental determination of the optical non-linear properties of a material requires rather an elaborate technique, for example Z scan method [10], four wave mixing [11] or optical third harmonic generation [8]. Since these methods are not common in most laboratories, of interest are empirical or semiempirical relations to predict non-linear refractive index ($n(2)$) or non-linear optical susceptibility ($X^{(3)}$) from some linear optical constants of a material.

In this brief communication we shall use some simple semiempirical relations relating $X^{(3)}$ to n in oxide glasses for prediction of $X^{(3)}$ in amorphous chalcogenides.

The Choice of Semiempirical Formula

Several semiempirical formulas were suggested for calculation of $X^{(3)}$ or $n(2)$, see e.g. Phillips and van Vechten [12], Levine [13], Wang [14], Wyne [15], Harrison [16], Fournier and Smitzer [17], Boling et al. [18], Agarwal et al. [19], and Sheik-Bahae et al.[20]. Among formulas presented in Refs [12–20], most widely used in the field of oxide glasses seems to be the formula which relates $n(2)$ to linear refractive index (n) and to the Abbe number introduced by Boling et al. [18]. Of interest is the formula introduced in [20] which relates $n(2)$ to the optical gap ($n(2) \sim E_g^{-4}$) and which can predict $n(2)$ values for both the wide-gap dielectrics and semiconductors, too.

For our purposes – a rough estimation of $X^{(3)}$ in amorphous chalcogenides we shall combine Miller's generalized rule [15] and Wemple–Di Domenico model (W–D) [21]. The reason is that:

(i) Miller's generalized rule is very simple ($X^{(3)} \doteq A(X^{(1)})^4$), this one is physically based, and it gives quite good agreement between predicted and measured $X^{(3)}$ values [14,22].

(ii) Most of relevant experimental data for amorphous chalcogenides (linear refractive index dispersion measured in visible and/or near infrared spectral region) are in literature interpreted using W–D.

(iii) The parameters of W–D, the dispersion energy (E_d) and the energy of effective oscillator (E_0) are related to a "chemistry" of a material; E_d is related to ionicity, anion valency, coordination number, resp., and E_0 is related to some bond energy or "bond gap", or band gap [23].

An estimation of $n(2)$ for amorphous chalcogenides based on Boling's formula in combination with W–D was recently presented by Petkov and Ewen [24]. Independently, Tichý et al. [25] used Miller's generalized rule in combination with W–D for estimation of $X^{(3)}$ in some As-Se and Ge-As-Se amorphous thin films. Within W–D, the linear refractive index dispersion is given by relation [21]

$$n = \left[1 + \frac{E_0 E_d}{E_0^2 - (\hbar\omega)^2} \right]^{1/2} \tag{1}$$

where $E_d = \beta N_c N_e Z_a$. For covalent solids $\beta = 0.34 \pm 0.04\,\text{eV}$, for ionic solid $\beta = 0.27 \pm 0.04\,\text{eV}$, N_c is the coordination number of the nearest neighbour cation to the anion, N_e is the total number of valence electrons per anion, and Z_a is the formal chemical valency of the anion.

The linear optical susceptibility is given by relation

$$X^{(1)} = \frac{(n^2 - 1)}{4\pi} \tag{2}$$

and from (1) and (2) we obtain

$$X^{(1)} = \frac{E_d E_0}{4\pi \left(E_0^2 - (\hbar\omega)^2 \right)} \tag{3}$$

which in the limit $\hbar\omega \to 0$ gives

$$X^{(1)} = \frac{E_d}{4\pi E_0} \tag{4}$$

Using the generalized Miller's rule $X^{(3)} = A(X^{(1)})^4$ [14,15], we obtain

$$X^{(3)} = \frac{A}{(4\pi)^4}\left(\frac{E_d}{E_0}\right)^4 = \frac{A}{(4\pi)^4}\left(n_{(0)}^2 - 1\right)^4 \qquad (5)$$

In order to estimate whether relation (5) gives reasonable result if applied to experimental $X^{(3)}$ and $n_{(0)}$ values, we selected 97 experimental values of $X^{(3)}$ and $n_{(0)}$ of various oxide glasses tabulated in [26]. In Fig.1 the plot of $\log X^{(3)}$ versus $\log\left(n_{(0)}^2 - 1\right)$ indicates reasonable correlation of experimental $X^{(3)}(n_{(0)})$ values within the relation (5) with the slope 4. Estimated A value is $A = 2.3 \times 10^{-10}$ (for $X^{(3)}$ in [esu]) which agrees with A values obtained by Wang [14] for some ionic crystals: $0.6 \times 10^{-10} < A < 2.5 \times 10^{-10}$.
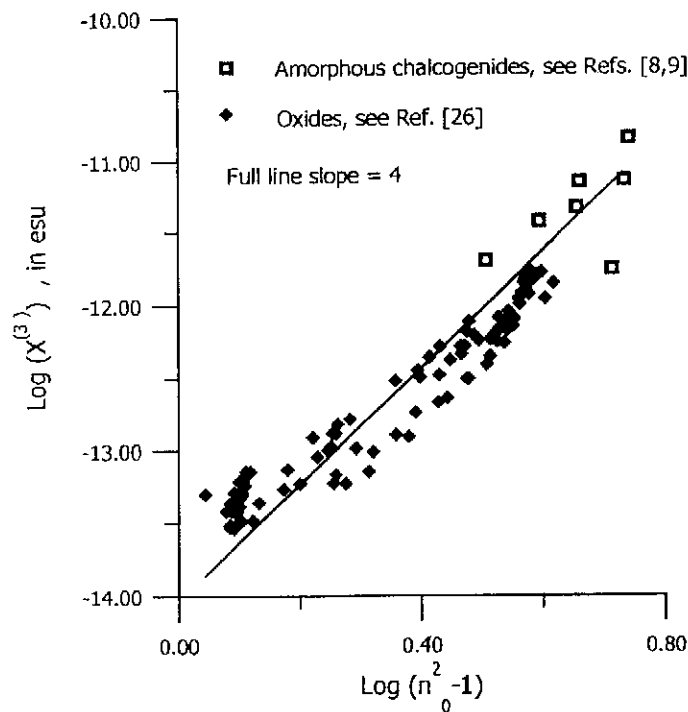

Fig. 1   The dependence of $\log (X^{(3)})$ versus $\log (n_0^2 - 1)$, see relation (5). Points – experimental values; solid line – calculated according to relation (5)

Table I Chemical composition, the single oscilator energy (E_0), the dispersion energy (E_d), the linear refractive index (n_0), relevant references, and calculated non-linear susceptibility ($X^{(3)}$)

Chemical composition	E_0, eV	E_d, eV	n_0	Ref. (No)	$X^{(3)}_{calc.}$, esu
$As_{38}S_{62}$	5.3	21.8	2.26	27	2.65×10^{-12}
$As_{40}S_{60}$	6.0	25.2	2.28	28	2.88×10^{-12}
$Ge_4As_{36}S_{60}$	6.5	25.7	2.23	28	2.26×10^{-12}
$Ge_{15}As_{25}S_{60}$	6.5	26.4	2.25	28	2.51×10^{-12}
$Ge_{25}As_{15}S_{60}$	6.4	26.8	2.28	28	2.84×10^{-12}
$Ge_{36}As_4S_{60}$	6.3	27.4	2.31	28	3.31×10^{-12}
$As_{41}Se_{59}$	3.59	23.0	2.72	25	1.56×10^{-11}
$As_{40}Se_{60}$	4.7	28.0	2.64	28	1.16×10^{-11}
$Ge_{10}As_{30}Se_{60}$	4.5	23.2	2.48	28	6.53×10^{-12}
$Ge_{22}As_{18}Se_{60}$	4.44	22.2	2.45	28	5.78×10^{-12}
$Ge_{36}As_4Se_{60}$	4.6	24.2	2.50	28	7.08×10^{-12}
$Ge_{40}Se_{60}$	3.7	16	2.31	28	3.23×10^{-12}
$Ge_{10}Sb_{30}Se_{60}$	3.5	20.2	2.60	28	1.03×10^{-11}
$Ge_{25}Sb_{15}Se_{60}$	4.10	23.3	2.59	28	9.64×10^{-12}
$Ge_{35}Sb_5Se_{60}$	3.8	20.4	2.52	28	7.68×10^{-12}
$Ge_{50}S_{50}$	4.12	23.4	2.58	29	9.62×10^{-12}
$Ge_{33.3}S_{66.6}$	5.45	19.76	2.15	30	1.60×10^{-12}
$As_{16}Te_{84}$	2.07	27.04	3.75	2	2.69×10^{-10}
$As_{30}Te_{70}$	2.25	28.22	3.68	2	2.27×10^{-10}
$As_{40}Te_{60}$	2.325	28.05	3.61	2	1.96×10^{-10}
$As_{55}Te_{45}$	2.42	28.21	3.56	2	1.71×10^{-10}
Te	3.178	32.7	3.36	2	1.04×10^{-10}
Te	2.848	30.82	3.44	2	1.27×10^{-10}

$$n_0 = \left(\frac{E_d}{E_0} + 1 \right)^{1/2}, \ X^{(3)}_{calc.}, \text{ see Rel. (5)}$$

Estimation of $X^{(3)}$ for Some Representative Chalcogenide Glasses

Table I summarizes chemical compositions and parameters of W–D single oscillator model for some typical chalcogenide thin films. We selected chemical compositions in rather broad interval in linear refractive index to show possible scale of $X^{(3)}$ values which could be expected for amorphous chalcogenides. From Table I it is evident that calculated $X^{(3)}$ values are comparable with experimental $X^{(3)}$ values, see Fig.1 and Refs [8,9]. We conclude that using equation (5), the non-linear optical susceptibility can be estimated from average oscillator energy (E_0) and dispersion energy (E_d) of the Wemple–Di Domenico single oscillator model. Since E_0 relates to the optical gap, one can expect that $X^{(3)}$ will increase with a decrease in the gap. Simultaneously, $X^{(3)}$ depends on E_d that is on the formal valency of anion, on the average coordination number of cation to the anion, and on the number of valence electrons per anion. Consequently, Rel. (5) gives some possibility of the chemical composition tailoring with respect to $X^{(3)}$ value.

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