SEMIEMPIRICAL RELATION BETWEEN NON-LINEAR SUSCEPTIBILITY (REFRACTIVE INDEX), LINEAR REFRACTIVE INDEX AND OPTICAL GAP AND ITS APPLICATION TO AMORPHOUS CHALCOGENIDES

H. Tichá, L. Tichý[a]

University of Pardubice, 532 10 Pardubice, Czech Republic
[a]Joint Laboratory of Solid State Chemistry of the Academy of Sciences of Czech Republic
and the University of Pardubice, 532 10 Pardubice, Czech Republic

Using generalized Miller´s rule and linear refractive index (n), simple relation is suggested for estimation of the non-linear susceptibility ($\chi^{(3)}$) and non-linear refractive index (n_2). This relation provides reasonable agreement between the calculated and experimental $\chi^{(3)}$, n_2 values for more than 90 glassy oxides ($\chi^{(3)}$) and also for 22 optical crystals (n_2). Prediction of $\chi^{(3)}$ and n_2 values for chalcogenide glasses indicates that non-linear susceptibility can reach up to $\chi^{(3)} \cong 2 \times 10^{-10}$ esu for some telluride glasses. Simple semiempirical correlation between n_2 and the optical gap is suggested.

1. Introduction

Amorphous (a) chalcogenides posses interesting optical properties: (i) high refractive index $n(a\text{-}GeS_2) \cong 2.2$ [1], $n(a\text{-}As_2Te_3) \cong 3.6$ [2], (ii) photoinduced changes manifested by blue or red (bleaching, darkening) shift of the optical gap (E_g), e.g. [3], (iii) photoinduced crystallization, e.g. [4], (iv) photoinduced anisotropy, e.g. [5]. 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 order ppm or less, see e.g. [6,7]. Various sulphide and selenide glasses are promising hosts of rare-earths for photonic applications as fibre lasers, optical amplifiers and upconvertors, see e.g. [8,9]. There are some experimental indications that amorphous or glassy chalcogenides have rather high non-linear optical susceptibility, see e.g. [10-14], and, hence, these materials are promising candidates as non-linear optical elements. The experimental determination of the non-linear optical properties of a material requires rather an elaborate technique, for example Z scan method [15], four-wave mixing [16] or optical third harmonic generation [10]. These methods are not common in most of laboratories, and, hence, of interest are empirical or semiempirical relations to predict non-linear refractive index (n_2) or non-linear optical susceptibility ($\chi^{(3)}$) from some linear optical constants of a material.

In this brief communication we shall use some simple semiempirical relations relating $\chi^{(3)}$ to n in oxide glasses for prediction of $\chi^{(3)}$ and n_2 in amorphous chalcogenides.

2. The choice of semiempirical formula and its application

Several semiempirical formulas were suggested for calculation of $\chi^{(3)}$ or n_2 [17-25]. Among formulas presented here [17-25], most widely used in the field of oxide glasses seems to be the formula (38) introduced by Boling et al. [23] which relates n_2 to linear refractive index (n) and to the Abbe number. Important is the formula (7) introduced in [25] 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.

Hajto et al.[26] used Boling´s formula (38), see Ref. [23], for estimation of n_2 values in some chalcogenide glasses. Subsequently, Petkov and Ewen [27] discussed in more detail application of "Boling´s" formula with the Wemple and DiDomenico single oscillator model (W-D) for linear refractive index dispersion and showed that in this case n_2 can be related to some structural parameters of a glass. Independently, Tichý et al. [28] used Miller´s generalized rule [20] in combination with linear refractive index and W-D for estimation of $\chi^{(3)}$ values in some As-Se and Ge-As-Se glasses.

For our purposes – a rough estimation of $\chi^{(3)}$ in amorphous chalcogenides and comparison of $\chi^{(3)}$ and n_2 values of various oxide glasses and single crystals, we shall combine Miller´s generalized rule [20] and low-frequency linear refractive index estimated from Wemple-DiDomenico single effective oscillator model [29]. The reason is that:

(i) Miller´s generalized rule is very simple ($\chi^{(3)} \cong A(\chi^{(1)})^4$, this one is physically based, and it gives quite good agreement between predicted and measured $\chi^{(3)}$ values [19, 30];

(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 that is - E_d is related to an ionicity, anion valency, coordination number, and E_0 is related to some bond energy or „bond gap", or band gap [31].

Within W–D, the linear refractive index dispersion is given by relation [29]:

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

where $E_d = \beta N_c N_e Z_a$. For covalent solids $\beta = 0.34 \pm 0.04$ eV, for ionic solids $\beta = 0.27 \pm 0.04$ 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 for isotropic medium, the case of chalcogenide glasses in the first approximation, is given by relation:

$$ \chi^{(1)} = (n^2 - 1)/4\pi , \tag{2} $$

and from (1) and (2) we obtain:

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

which in the limit $\hbar\omega \rightarrow 0$ ($n = n_0$) gives:

$$ \chi^{(1)} = \frac{E_d / E_0}{4\pi} . \tag{4} $$

Using generalized Miller´s rule: $\chi^{(3)} = A(\chi^{(1)})^4$ [19,20] we obtain:

$$ \chi^{(3)} = A/(4\pi)^4 (E_d/E_0)^4 = A/(4\pi)^4 (n_0^2 - 1)^4 . \tag{5} $$

To estimate whether relation (5) gives reasonable result if applied to experimental $\chi^{(3)}$ and n_0 values we selected 97 experimental values of $\chi^{(3)}$ and n_0 of various oxide glasses tabulated in [32]. In Fig.1 the plot log $\chi^{(3)}$ versus log ($n_0^2 - 1$) indicates reasonable correlation of experimental $\chi^{(3)}(n_0)$ values within the relation (5) with the slope 4. Estimated A value is A = 1.7x10^{-10} (for $\chi^{(3)}$ in [esu]) which corresponds with A values obtained by Wang [19] for some ionic crystals: 0.6x10^{-10} < A < 2.5x10^{-10}.

Adair et al. [33] reported nonlinear refractive index for a large number of optical crystals (oxides and halogenides) measured at near one micrometer using nearly degenerate three-wave mixing method. Using both, the relevant E_d, E_0 values taken from [29] and eq. (5), we calculated n_2 values assuming for simplicity [34]:
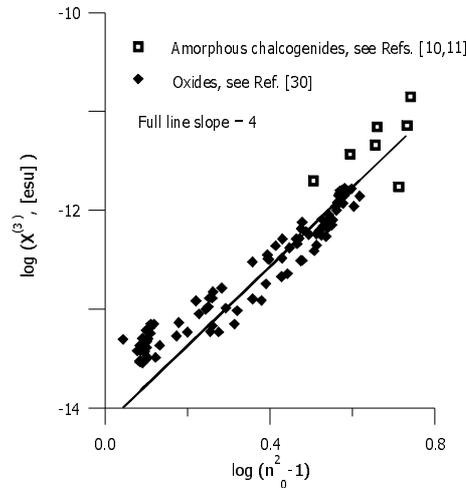
$$ n_2 = 12\pi\chi^{(3)}/n_0 . \tag{6} $$

Fig. 1. The dependence of $\log(\chi^{(3)})$ versus $\log(n^2-1)$. Full symbols-experimental values for oxide glasses [30], open symbols - experimental values for chalcogenide glasses [11], solid line- calculated according to Eq.(3).

Following recommendation suggested by Górski et al. [35] we multiplied the n_2 values reported in [33] by a factor of about 2.3. In Fig.2 are shown calculated values of n_2: $n_2[esu] = 2.6 \times 10^{-13}(E_d/E_0)^4/n_0 = 2.6 \times 10^{-13}(n_0^2 - 1)^4/n_0)$ versus experimental ($2.3\ n_2$) values [33]. In the same figure also experimental n_2 values for some chalcogenide glasses recently reported [12] and n_2 values calculated from experimental $\chi^{(3)}$ values , see [11], using Eq.(6) are shown for reader´s convenience. Taking into consideration four order scale of n_2 values the correspondence between the experimental and calculated values is quite good.
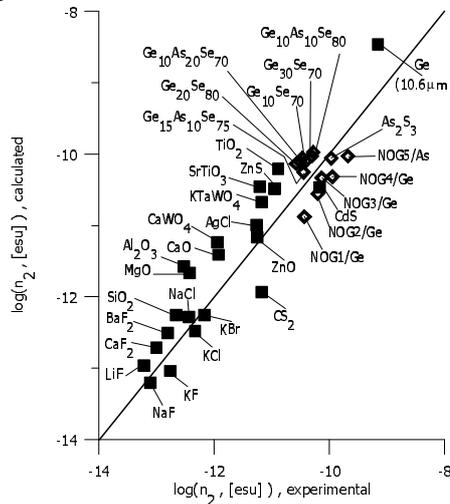

Fig. 2. Calculated n_2 values (Eq.(6)) versus experimental n_2 values, in log-log coordinates. Full symbols, see [31], open symbols - chalcogenide glasses: below line, see [11], above line and CS_2, see [12].

In Table 1 are summarized 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 $\chi^{(3)}$ values which could be expected for amorphous chalcogenides. From Table 1, it is evident that calculated $\chi^{(3)}$ values are comparable with experimental $\chi^{(3)}$ values, see Fig.1 and [10,11]. Hence, using equation (5), the non-linear optical susceptibility can be estimated from linear refractive index (n_0) and/or from average oscillator energy (E_0) and dispersion energy (E_d) of the Wemple-Di Domenico single oscillator model.

Table 1. Chemical composition and the values of the single oscillator energy (E_0), the dispersion energy (E_d), the linear refractive index (n_0), relevant references, calculated non-linear susceptibility ($\chi^{(3)}$) and non-linear refractive index (n_2), resp., for various amorphous chalcogenides. [$n_0 = (E_d/ E_0 + 1)^{1/2}$; $\chi^{(3)}$, calc., see Eq.(5); n_2, calc., see Eq. (6)].

Chemical composition	E_0 [eV]	E_d [eV]	n_0	Ref.[No]	$\chi^{(3)}$, calc. [esu]	n_2, calc. [esu]
$As_{38}S_{62}$	5.3	21.8	2.26	36	1.96×10^{-12}	3.26×10^{-11}
$As_{40}S_{60}$	6.0	25.2	2.28	37	2.13×10^{-12}	3.51×10^{-11}
$Ge_4As_{36}S_{60}$	6.5	25.7	2.23	37	1.67×10^{-12}	2.83×10^{-11}
$Ge_{15}As_{25}S_{60}$	6.5	26.4	2.25	37	1.86×10^{-12}	3.11×10^{-11}
$Ge_{25}As_{15}S_{60}$	6.4	26.8	2.28	37	2.1×10^{-12}	3.47×10^{-11}
$Ge_{36}As_4S_{60}$	6.3	27.4	2.31	37	2.44×10^{-12}	3.98×10^{-11}
$As_{41}Se_{59}$	3.59	23.0	2.72	28	1.15×10^{-11}	1.59×10^{-10}
$As_{40}Se_{60}$	4.7	28.0	2.64	37	8.6×10^{-12}	1.23×10^{-10}
$Ge_{10}As_{30}Se_{60}$	4.5	23.2	2.48	37	4.83×10^{-12}	7.33×10^{-11}
$Ge_{22}As_{18}Se_{60}$	4.44	22.2	2.45	37	4.27×10^{-12}	6.57×10^{-11}
$Ge_{36}As_4Se_{60}$	4.6	24.2	2.50	35	5.23×10^{-12}	7.88×10^{-11}
$Ge_{40}Se_{60}$	3.7	16.0	2.31	37	2.39×10^{-12}	3.9×10^{-11}
$Ge_{10}Sb_{30}Se_{60}$	3.5	20.2	2.60	37	7.58×10^{-12}	1.1×10^{-10}
$Ge_{25}Sb_{15}Se_{60}$	4.10	23.3	2.59	37	7.12×10^{-12}	1.04×10^{-10}
$Ge_{35}Sb_5Se_{60}$	3.8	20.4	2.52	37	5.67×10^{-12}	8.47×10^{-11}
$Ge_{50}S_{50}$	4.12	23.4	2.58	38	7.11×10^{-12}	1.04×10^{-10}
$Ge_{33..3}S_{66.6}$	5.45	19.76	2.15	39	1.18×10^{-12}	2.07×10^{-11}
$As_{16}Te_{84}$	2.07	27.04	3.75	2	1.99×10^{-10}	2.0×10^{-9}
$As_{30}Te_{70}$	2.25	28.22	3.68	2	1.68×10^{-10}	1.72×10^{-9}
$As_{40}Te_{60}$	2.325	28.05	3.61	2	1.45×10^{-10}	1.51×10^{-9}
Te	2.3	27	3.43	40	1.30×10^{-10}	1.42×10^{-9}

3. The correlation between n_2 and the optical gap

It was suggested by Wemple and DiDomenico [29] and by Ke. Tanaka [41] that W-D effective oscillator energy (E_0) relates to the optical gap (E_g). According to W-D the relation between E_g and E_0 can be expressed in the form $E_0 \approx 1.5 E_t$, where E_t is the lowest direct band gap. According to Ke. Tanaka for amorphous chalcogenides it is approximately valid $E_0 \cong 2 E_g$. For a broad interval in E_g values: 0.18 (InSb) $\leq E_g$ (eV) $\leq$ 13.6 eV (LiF) we examined the empirical correlation between E_g and E_0, see Fig. 3.
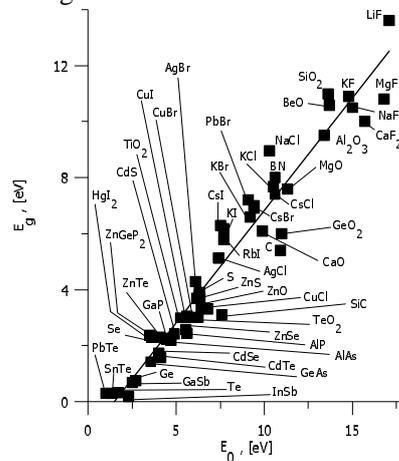

Fig. 3. The empirical corelation between E_g values and E_0 values for various solids. Full symbols- experimental values, full line - empirical correlation: $E_g = 0.8E_0 - 1.2$. The E_0 values were taken from Refs.[29,40], the E_g values were taken from Refs.[42,43].

From this figure it is evident that within examined scale of E_g, E_0 values, the correlation $E_0(E_g)$ can be expressed in the form: $E_0 = 1.25 (1.2 + E_g)$, and hence really $E_0 \sim E_g$. Using this proportionality and relations (5,6) one obtains approximately $n_2 \sim B/E_g^4$. Fortunately the errors introduced by neglecting the E_d changes with the chemical composition and taking simple proportionality $E_0 \sim E_g$ cancels each other and consequently the correspondence between n_2 and E_g^{-4} shown in log n_2 versus log E_g coordinates in Fig.4 is quite reasonable. The full line in Fig.4 corresponds to the semiempirical relation $n \sim B/E_g^4$ for $B = 1.26 \times 10^{-9}$ [esu eV^4] where n_2 is in esu units and Eg is in eV units. The region of predicted and also measured n_2, E_g values for chalcogenide glasses is marked by shaded eclipse.
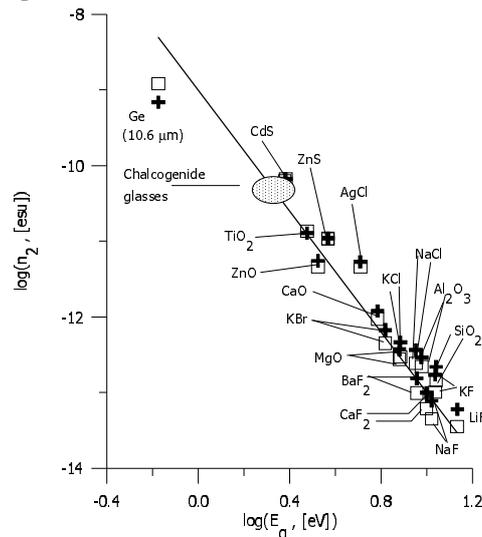

Fig. 4. log(n_2) versus log(E_g) dependence. The n_2 values multiplied by 2.3, see text, taken from Ref.[33] are marked by **+,** the n_2 values calculated using Eqs.(5,6) are marked by □, the full line with the slope = 4 corresponds to $n_2 \cong B/E_g^4$. The E_g values are taken from Ref. [43]. The shaded eclipse indicates the region of amorphous chalcogenides.

4. Conclusion

Simple semiempirical relation based on generalized Miller´s rule allows an estimation of non-linear susceptibility ($\chi^{(3)}$) and non-linear refractive index (n_2) from linear refractive index and/or from the dispersion energy and the energy of effective oscillator of the Wemple-Di Domenico model. For a number of various glasses and optical crystals suggested relation indicates reasonable correspondence between calculated and experimental $\chi^{(3)}$ and n_2 values. Its application to chalcogenide glasses confirms that these materials could reach, in agreement with experimental results [10-14], rather high $\chi^{(3)}$, n_2 values. For a broad range of n_2 and E_g values the semiempirical relation was found in the form $n_2(esu) \cong B/E_g^4$. Amorphous and glassy chalcogenides have rather high values of n_2 and, hence, they are very interesting materials for some non-linear optical applications.

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