Journal of Ovonic Research Vol. 12, No. 6, November-December 2016, p. 309-316

THERMAL STABILITY, LINEAR AND NONLINEAR REFRACTIVE INDICES OF HEAVY TERNARY TELLURITE GLASS

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Heavy glass with composition $90TeO_2/5Bi_2O_3/5Ta_2O_5$(TBT) in mol% based glasses have been prepared by using melt-quenching method. The optical properties and physical parameter of these glass studied with respect to density,ρ, molar volume, V_m, optical packing density, Opd, refractive index, n_0, oxygen molar volume, V_0, electronic polarizability,α_m, molar refraction, R_m, metallization criterion, M (n_0), and third order non-linear optical susceptibility. These glass has highest value of density ρ= 6.2209 $gm\cdot cm^{-3}$,compared with other glass reported . Moreover this glass has advantage optical properties such as: Opd= 72.4, V_m= 30.39 cm^{-3}, V_0=13.81, n_0= 2.295 at 435.84 nm, α_m= 7.08 $Å^3$ and R_m=17.84 $mol^{-1}\cdot cm^3$ at 435.84nm. Thermal characterization of present glass investigation by using (Shimadzu DTA 50). It is found that the glass transition temperature, T_g= 384 ^{0}C, onset crystallization temperature, T_c= 500 ^{0}C, and melting temperature, T_m= 631 ^{0}C and anticrystallization factor, $S = \frac{\Delta T\cdot(T_p - T_c)}{T_g}$. It is found that the addition of heavy oxides $Ta_2O_5$and Bi_2O_3incorporation to TeO_2- based glasses leads to largest refractive index and third order nonlinear optical susceptibility were reported.

(Received October 18, 2016; Accepted December 10, 2016)

Keywords: DTA, Heavy glasses,Density, Linear refractive index

1. Introduction

Heavy metals like that W, Bi, Nb, Pb, and Ta are added to tellurite glasses is studied extensively because such addition seem that show change in optical properties of these glasses. Moreover the tellurite glasses containing heavy metal oxides were found to display a high optical nonlinearity (NLO), which due to its electronic polarizability nature is further characterized by a rapid delay response time [1- 3]. High optical nonlinearity devicesare currently studied for use in telecommunication system which requiredthese glasseshad high third order susceptibility tensor, $\chi^{(3)}$, and nonlinear index. Also the heavy glasses were promising for application in up conversion laser optical materials [4, 5].

The effects of nonlinear optical material are induced by the polarization, P, in a power series expansion of the relation with the applied electric field, E, as follows [6- 8]:

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + ... \qquad (1)$$

Where $\chi^{(1)}$ is the first order of linear susceptibility tensor, $\chi^{(2)}$ is the second order susceptibility and $\chi^{(3)}$ is the third order susceptibility. The linear susceptibility is related the linear refractive index, n_0 , by $\chi^{(1)} = 12.56(n_0^2 - 1)$. We note that the refractive index of bulk material induced to high intense electric field can be computed as follow; $n = n_0 + n_2E^2$, where n_2 is the nonlinear refractive index. The refractive index n2 is related with many physical mechanisms, it can determine as; $n_2 = n_{2(nucl)} + n_{2(el)} + n_{2(electr)} + n_{2(t)}$ where the $n_{2(nucl)}$is nuclear, $n_{2(el)}$electronic, $n_{2(electr)}$electrostrictive and $n_{2(t)}$thermal parts of n_2.

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Besides, the total index of refraction, n, is given by; $n = n_0 + n_2\left\langle E^2 \right\rangle$,where $\left\langle E^2 \right\rangle$ is the time averaged square of the electric field of the incident light beam. The nonlinear refractive index n_2 is related to the third order nonlinear susceptibility χ^3, as follow [9];

$$n_2(w) = 1.7\times10^{-14}(n_0^2+2)^3(n_0^2-1)(\frac{d}{n_0E_s})^2 f(\frac{\hbar w}{E_g}) \qquad (2)$$

Where,

$$\chi^{(3)} = \frac{0.26\times10^{-12} f_l^3(n_w^2-1).d^2.E_s^6}{(E_s^2-E^2)^4} \qquad (3)$$

Where f_l is the Lorentz field factor $[\frac{(n_w^2+2)}{3}]$, n_w, the refractive index at wavelength *w*, E_s is the Sellmeier gap, E the photonenergy (hν) and d is the bond length between the metal M and oxygen atom ,O, in Å, by the combining Equ. (3) and Equ. (4) it can be determine third order of nonlinearity as follow;

$$\chi^3 = A(n_w^2+2)^3(n_w^2-1)\frac{E_d}{E_s^2} \qquad (4)$$

Where A is a phenomenological constant, we can transform the unit's nonlinear refractive indices as follow [7- 9]:

$$\begin{aligned} n_2(m^2/W) &= (\frac{1}{cn\varepsilon_0})n_2(m^2/V^2) \\ n_2(m^2/V^2) &= \frac{3}{8n}\chi^{(3)}(m^2/V^2) \qquad (5) \\ \chi^{(3)}(m^2/V^2) &= \frac{4\pi}{9\times10^8}\chi^{(3)}(esu) \end{aligned}$$

In the present work, studying the effect of heavy oxide Ta_2O_3 and Bi_2O_3on the thermal and optical properties of TeO_2 based glass.

2. Experimental work

Batches (50 gm) of the glass with composition $90TeO_2$/ $5Bi_2O_3$/ $5Ta_2O_5$ in mol% glass was melted in anPt crucible and heated at a temperature of 950 °C. The melt was allowed to cool to 850 °C and then cast in a graphite mould. Subsequently, the samples were transferred to an annealing furnace and kept at 320 °C for 2 h. Then the furnace was switched off and allowed to cool. From the glassy samples, prisms of the dimension 30x15x15 mm^3 were cut. The prisms were ground and polished using water as liquid component. The prisms were used to measure the linear refractive indices at wavelengths of 643.8, 589.3, 546.1, 479.98 and 435.8 nm. The densities were measured by a helium pycnometer (AccuPyc 1330) with an accuracy of ± 0.03 %.The glass transition temperature (T_g), softening temperature, T_s, the onset temperature of crystallization (T_c), the peak temperature of crystallization (T_p) and the melting temperature (T_m) were obtained by using differential thermal analysis technique (Shimadzu DTA 50). The prepared glass was examined by X-ray diffraction, (Siemens D 6000) using CuK$_\alpha$radiation at 40 kV in the 2θ range from 5 to 90^0.

3. Results and discussions

X- ray diffraction patterns (XRD) of prepared glass 90TeO_2- 5Bi_2O_3- 5Ta_2O_5in mole% and it is found peaks caused by crystalline phases so the sample is in nature of amorphous phase (glass) was shown in Fig. 1. The present glass is transparent with high homogeneity and it has high value of density (ρ= 6.2209 in g.cm^{-3}).The change in the density of the glass attributed by addition of heavy modifier like that Ta_2O_5 and Bi_2O_3 as a constituent elements, hence the present glass has higher density comparing with other tellurite glass like that 75 TeO_2-5 WO_3- 15 Nb_2O_5 - 5 CuO (ρ= 5.3107 gm· cm^3), 75 TeO_2-5 WO_3- 15 Nb_2O_5 - 5 MnO_2 (ρ=5.2937gm· cm^3), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – 5NiO (ρ=5.3388gm· cm^3), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – 5Ag_2O (ρ=5.444gm· cm^3), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – 5ZnO (5.3235gm· cm^3), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – 5MgO (ρ=5.285 gm· cm^3), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – 5TiO_2 (ρ=5.244gm· cm^3), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – 5Na_2O (ρ=5.2178 gm· cm^3) [10].The molar volume, V_m, of the prepared glass related by the density by relation; $V_m = \frac{M}{\rho}$, where M is the molecular weight and ρ is the density and it is equal (V_m= 30.39in cm^3). Also the oxygen molar volume, V_O, related to the molecular weight of sample, it is can be calculated by the relation as follows:

$$V_O = \left(\frac{\sum x_i M}{\rho}\right)\left(\frac{1}{\sum x_i n_i}\right) \qquad (6)$$

where x_i is the molar fraction of component in mol%, i, and n_i is the number of oxygen atoms for each oxide. Besides, the oxygen packing density, Opd, computed from relation as follow;

$$Opd = \frac{100\rho O_i}{M_i} \qquad (7)$$

where O_i is number of oxygen atoms in the constitute of sample. The data of V_m, V_O, are 13.81 cm^3·mol^{-1} and 72.4 gm.atmrespectively, hence,ρ, V_m, V_0 and O.p.d data of the present glasses gives a good information on their structure.

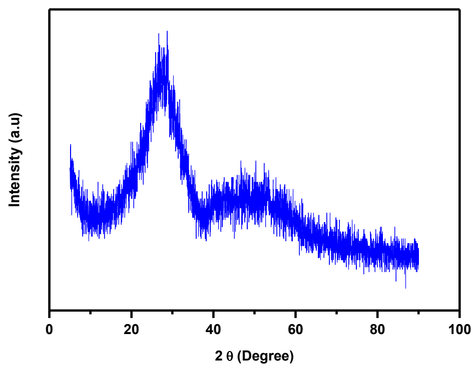

Fig. 1.Show X- ray diffraction patterns of the 90TeO_2-5Bi_2O_3- 5Ta_2O_5 in mol%.

Fig. 2 shows the DTA traces of the prepared glass90TeO_2/ 5Bi_2O_3/ 5Ta_2O_5 in mol% at heating rate of 10K· min^{-1}. From DTA curve it can be determine different characteristic temperatures like thatT_g, T_c, T_p, and T_m in ^{0}C. Thesis data are summarized in Table 1 and the value (ΔT= (T_c- T_g)) has been denote the glass thermal stability. As obtain in Fig. 2, the present glass hasT_g= 384 °C, T_s= 459 ^{0}C, T_c= 521 ^{0}C, T_p= 550 ^{0}C and T_m= 655 ^{0}C. Thermal parameters are very important of prepared glass, anticrystallization,

$$S = \frac{\Delta T \cdot (T_p - T_c)}{T_g} \qquad (8)$$

Table 1. Thermal and optical properties of glass 90TeO$_2$- 5Bi$_2$O$_3$- 5Ta$_2$O$_5$ in mol% have been studied.

Parameters		**at different wavelength (in nm)**				
		435.84	**479.98**	**546.06**	**587**	**643.8**
Density, ρ, (in g·cm^{-3})	6.2209					
Molar volume, V_m, (in cm^3)	30.39					
Oxygen molar volume (in cm^3/mol)	13.81					
Oxygen packing density (in gm.atm)	72.4					
Glass transition temperature,Tg, (^{0}C)	384					
Onset of crystallization temperature, (^{0}C),	521					
Peak of crystallization temperature, (^{0}C)	550					
Melting temperature, (^{0}C)	655					
Anticrystallization factor	10.35					
Glass stability, ΔT,	137					
H factor	0.357					
Refractive index, n_0,		2.295	2.253	2.214	2.1975	2.181
Abbe number, $\upsilon_{d,}$	17					
Molar refraction, R_m, (in cm^3· mol^{-1})		17.84	17.5	17.18	17.04	16.9
Polarizability, α_m, (in Å^3)		7.08	6.95	6.82	6.76	6.7
Metallization criterion, $M(n_0)$		0.413	0.424	0.435	0.439	0.444
Sellmeier energy gap, E_s, (in eV)	6.36					
Dispersion energy, E_d, (in eV)	21.71					
n_2, in 10^{-15} cm^2/W	9.1					
$\chi^{(3)}$ in 10^{-13}esu/ Å^2	4.94					

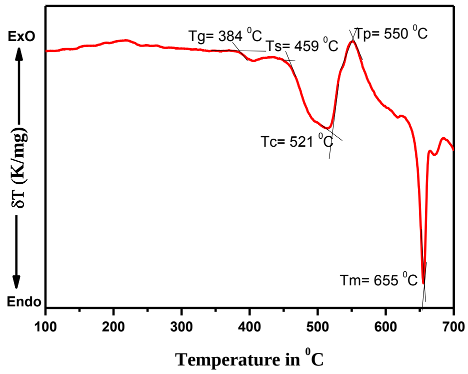

Fig. 2. DTA traces of prepared glass with composition 90TeO$_2$-5Bi$_2$O$_3$- 5Ta$_2$O$_5$ in mol%.

The ratio of T_g/T_m, and Hurby's developed $H' = \Delta T/T_g$were calculated.These parameters are ΔT = 137 ^{0}C, S= 10.35, T_g/T_m= 0.586 and H= 0.357 and hence the present glass has high thermal stability compare with other glass system were reported in Ref [4, 5, 11, 12].

The optical parameter such as linear, non-linear refractive index, n_2, molar refraction, molar polarizability and third-order susceptibility $\chi^{(3)}$ are used in fabrication the optical devices from oxide glasses. Here in the present work the linear refractive index, n, of prepared glass was measured at different wavelength are shown in Table 1. The effect of heavy oxide Bi_2O_3 and Ta_2O_5 on the TeO_2 based glass leads to high refractive n= 2.295 at 435.8 nm of prepared sample with composition 90TeO$_2$/ 5Bi$_2$O$_3$/ 5Ta$_2$O$_5$ was obtain. It is related to TeO_4 trigonal bipyramid (tbp) structural units form in the glass matrix. Hence it can be suggested that the glass has high density and TeO_4 consequently it has high refractive index. Moreover other factors effects on the value of refractive index of glass such as; (i) polarizability of the first neighbor ions, (ii) electronic polarizability of the oxide ion, and (iii) optical basicity. The relation between refractive index and molar volume can be estimated as follow;

$$R_m = \frac{V_m \cdot (n_0^2 - 1)}{(n_0^2 + 2)} \tag{9}$$

Where, R_m, is the molar refraction also the relation electronic polarizabilities, α_m, (in $Å^3$) has and n_0 can been calculated by using relation [13]:

$$\alpha_m = \frac{3}{4\pi N}\left(\frac{n_0^2 - 1}{n_0^2 + 2}\right)\frac{M}{\rho} \tag{10}$$

Where N is the Avagadro's number. The values of R_m= 17.84 in $cm^3.mol^{-1}$ and α_m= 7.08 (in $Å^3$) at 435.8 nm for prepared glass, these data are summarized in Table (1). Fig. 3 show the relation between, n_0, and molar polarizability, α_m, (in $Å^3$), at different wave length, it is obtained that n_0 is strongly depend on the, α_m,.Also it is found that the refractive index value strongly depended on the ratio, α_m / V_m, (i.e. the, n, value increase with increasing the ratio α_m / V_m).The present glass $90TeO_2$/ $5Bi_2O_3$/ $5Ta_2O_5$ has (n= 2.295 at 435.8 nm) is highest comparing with other tellurite glass such as 75 TeO_2-5 WO_3- 15 Nb_2O_5 - 5 CuO (n= 2.2898 at 435.8 nm), 75 TeO_2-5 WO_3- 15 Nb_2O_5 - 5 MnO_2 (n= 2.2765 at 435.8 nm), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – 5NiO (2.252 at 435.8 nm), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – $5Ag_2O$ (n= 2.2323 at 435.8 nm), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – 5ZnO (n= 2.2087 at 435.8 nm), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – 5MgO (n= 2.204 at 435.8 nm), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – $5TiO_2$ (n= 2.1875 at 435.8 nm), 75 TeO_2-5 WO_3- 15 Nb_2O_5 – $5Na_2O$ (n= 2.1627 at 435.8 nm). These means that, glass has high density is clear to has high value refractive index depend on the kind of the oxide modifier inter the composition of glass matrix, beside, n_0, is proportional to the inverted mole volume unit and the polarizability of ions in. Other important optical parameters like that metallization criterion, $M(n_0)$, Sellmeier gap, E_s in eV, and dispersion energy, E_d in eV, are summarized in Table (1).The metallization criterion, $M(n_0)$, depend on the basis of linear refractive index and can be calculated from the relation as follow;

$$M(n_0) = \frac{(n_0^2+2)-(n_0^2-1)}{(n_0^2+2)} \tag{11}$$

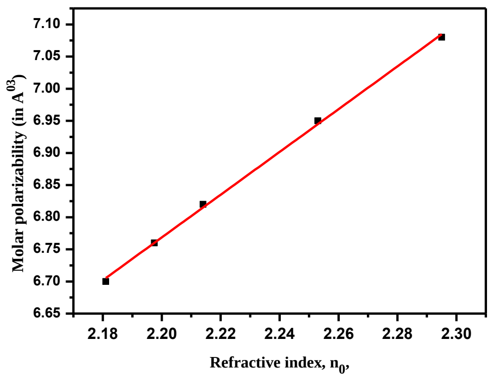

Fig. 3. Relation between refractive index, n_0, and electronic polarizability in A^{03} at different wavelength of glass with composition $90TeO_2$-$5Bi_2O_3$- $5Ta_2O_5$ in mol%.

From previous literature it is found that oxides had large refractive index with small energy gap possesses small value of M (n_0) hence the nature of metallic and non metallic of bulk glass can classified into condition as; when $R_m/V_m < 1$ (non-metal) and $R_m/V_m > 1$(metal).

Moreover the value of metallization criterion depends on the value of optical energy gap of glasses. This means that when the metalalizationn criterion increase leads to increase in the optical energy gap. The present glass have high refractive index with smallest value of optical gap with small value of $M(n_0)$= 0.413 at 435.8 nm these means that it has broadband of conduction and valence band. Fig.4 show the relation between refractive index,n_0, and metallization criterion, $M(n_0)$ at different wave length. The Sellmeier gap energyE_s , is the dispersion energy,E_d, and linear refractive index depends on wavelength by the relation as follow:

$$n^2(\nu) - 1 = \frac{E_s E_d^2}{E_s E_d - E^2} \qquad (12)$$

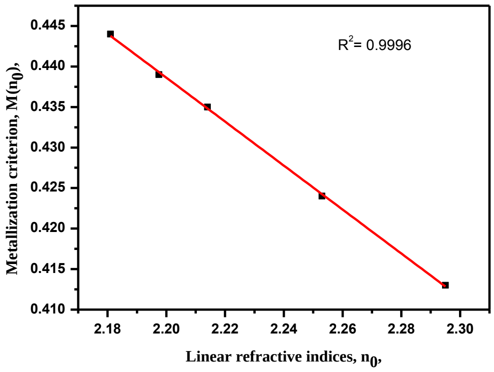

Fig. 4. Relation between refractive index, n_0, and metallization criterion, M (n_0) at different wavelength of glass with composition 90TeO_2-5Bi_2O_3- 5Ta_2O_5 in mol%.

Fig.5 shows a plot of $1/(n^2(\nu)-1)$ versus E^2 $(h\nu)^2$of prepared glass. From the linear relation it can be determine values of E_s and E_d are obtained (see Table 1). In the present glass obtain that E_d= 21.71 eV and E_s= 6.36 eV values, if the decrease in dispersion energies with the composition this means that the decrease in the covalent bond in glass matrix. The third order nonlinear susceptibilityof empirical Miller's, depend on the linear refractive indices and linear optical susceptibility $\chi^{(1)}$determine by the relation as follow:

$$\chi^{(3)}(n_0) = \left[\frac{(n_0)^2 - 1}{4\pi}\right]^4 x10^{-10}$$
$$\chi^{(1)} = \left[\frac{(n_0)^2 - 1}{4\pi}\right] \qquad (14)$$

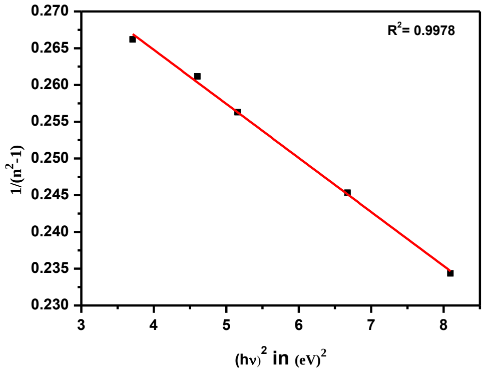

Fig. 5.show the relation between 1/(n^2- 1) versus $h\nu$ in $(eV)^2$ of glass with composition 90TeO_2-5Bi_2O_3- 5Ta_2O_5 in mol%.

The glass $90TeO_2$/ $5Bi_2O_3$/ $5Ta_2O_5$ have largest value of measured third order of nonlinear indices by method DFWM [4], the present glass has $\chi^{(3)}_{me.} = 4.94 \cdot 10^{-13}$ esu, and also it have largest value of polarizability 7.08Å^3 . The value of third order nonlinear susceptibility, $\chi^{(3)}_{me.}$, of present sample are in the order as follows; 90TeO2/ $5Bi_2O_3$/ $5Ta_2O_5$> $85TeO_2$/ $5Nb_2O_5$/ 5ZnO/ $5TiO_2$> $68TeO_2$/ $5Nb_2O_5$/ 20ZnO/ 7PbO > $85TeO_2$/ $5Nb_2O_5$/ 5ZnO/ $5Ag_2O$ > $90TeO_2$/ $5Nb_2O_5$/ 5ZnO/ 0.4CdS > $88TeO_2$/ $12Nb_2O_5$/ 0.5CdS > $68TeO_2$/ $5Nb_2O_5$/ 20ZnO/ $7Na_2O$ [4, 10, 14].The ions with lone pair of electrons in the valence shell of the Te^{4+}, Bi^{3+} and transition element ions has empty d^0 atomic orbital like that Ta^{5+}leads to increase in optical nonlinearity. Because the field strength of these transition metalsare very small with very high oxide ion polarizability moreover oxides Ta_2O_5 and Bi_2O_3 posse high coordination number toward oxide ions with low O 1s binding energy. Hence this explain; the glass $90TeO_2$/ $5Bi_2O_5$/ $5Ta_2O_5$ (sample 4) have the largest value of polarizability, higher nonlinear indices and higher third order nonlinear susceptibility. It is found that relation of the third order nonlinear susceptibility, $\chi^{(3)}$, measured by using THG technique of the binary tellurite glasses with the molar polarizibility, α_m, and showed that the $\chi^{(3)}$ increase with increasing, α_m, .Dimitrov and Sakka [15] estimated that the simple oxides such as PbO, Ta_2O_5, Nb_2O_5, CdO have large nonlinear refractive indices which posses a metallization criterion value in the range 0.35 –0.45, otherwise B_2O_3 and SiO_2oxide have a small value of nonlinear refractive indices posses large value of metallization criterion are in range from 0.5 to 0.7. As the same case the binary tellurite glass composition containing Nb_2O_5, TiO_2, Ta_2O_5, WO_3, MoO_3, and Bi_2O_3[15, 16] have large value of nonlinear indices where posses a metallization criterion in valuethe range 0.42- 0.5 range. The present glass posses value metallization criterions $M(n_0)$= 0.413 at 435.8 nm which is a good agreement with reported value in binary glasses. Hence, it can be conclude that the refractive index and third order nonlinear susceptibility, $\chi^{(3)}_{me.}$ decrease with increasing the metallization criterion $M(n_0)$.

Finally, the prepared glass has high refractive indices and evaluated third order nonlinear optical susceptibility values observed in Bi_2O_3, Ta_2O_5 inter in TeO_2 based glass matrix, indicate that these glasses can be use for optical devices applications.

4. Conclusions

The incorporation of heavy oxide Ta_2O_5 and Bi_2O_3 into TeO_2 based glass has been synthesized. The thermal properties and optical properties of this glass have been obtained by measuring DTA and the linear refractive indices, n_0.

It is found that this glass has high density value ρ= 6.2209 in g.cm^{-3} with high thermal stability parametersΔT = 137 ^{0}C and S= 10.35. Moreover these glass has large glass transition temperature, Tg= 384 with large linear refractive index. Moreove the glass $90TeO_2$/ $5Bi_2O_3$/ $5Ta_2O_5$ has high value of third order of nonlinear indices, $\chi^{(3)}_{me.} = 4.94 \cdot 10^{-13}$ esu, and also it has high value of polarizability 7.08 Å^3

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