# ELECTRONIC POLARIZABILITY, OPTICAL PROPERTIES AND CHEMICAL BONDING OF OXIDE GLASSES

**Vesselin Dimitrov [1], Takayuki Komatsu [2]**

*[1] Department of Silicate Technology, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria*

*[2] Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka-cho, Nagaoka 940-2188, Japan*

# I. INTRODUCTION

- Electronic polarizability of ions demonstrates the easy deformation of their electronic clouds by applying an electromagnetic field. It is closely related to the interionic interactions as well as to many properties of the materials such as refraction, conductivity, ferroelectricity, electro-optical effect, optical basicity along with optical nonlinearity. That is why today's knowledge of the state of polarization of ions in different crystalline and amorphous materials is of significant interest.

The estimation of the electronic polarizability of ions is subject of the so-called **polarizability approach** in materials science, which is well known especially in the field of glass science as done by **Kordes, Fajans, and Kreidl and Weyl and Marboe.** Recently, the polarizability approach has been systematically developed in our current papers concerning the origin of electronic polarizability and optical basicity of simple oxides and oxide glasses **(Dimitrov and Sakka, Dimitrov and Komatsu).**

Three groups of oxides have been proposed taking into consideration their values of oxide ***ion polarizability*** and ***optical basicity***, namely

- **semicovalent predominantly acidic oxides**
- **ionic or basic oxides**
- **very ionic or very basic oxides.**

Four groups of oxide glasses have been established:

- Glasses formed by two glass-forming acidic oxides;
- Glasses formed by glass-forming acidic oxide and modifier's basic oxide;
- Glasses formed by glass-forming acidic oxide and conditional glass-forming basic oxide;
- Glasses formed by two basic oxides.

**Sun** has suggested a **bond energy criterion** for glass formation and has reported comprehensive data on **single bond strength $B_{M-O}$** for various simple oxides based on their **dissociation energy, $E_d$**. The oxides have been divided into three groups, namely

- ***glass-formers***
- ***intermediates***
- ***modifiers***

in accordance with the value of their single bond strength. ***The criterion is simple, that is high value of single bond strength increases a glass forming tendency.***

Recently, we have established that a good correlation exists between electronic polarizability of oxide ions that is optical basicity and single bond strength of many oxides. It was found that an increase of optical basicity corresponds to a decrease of single bond strength of the oxides.

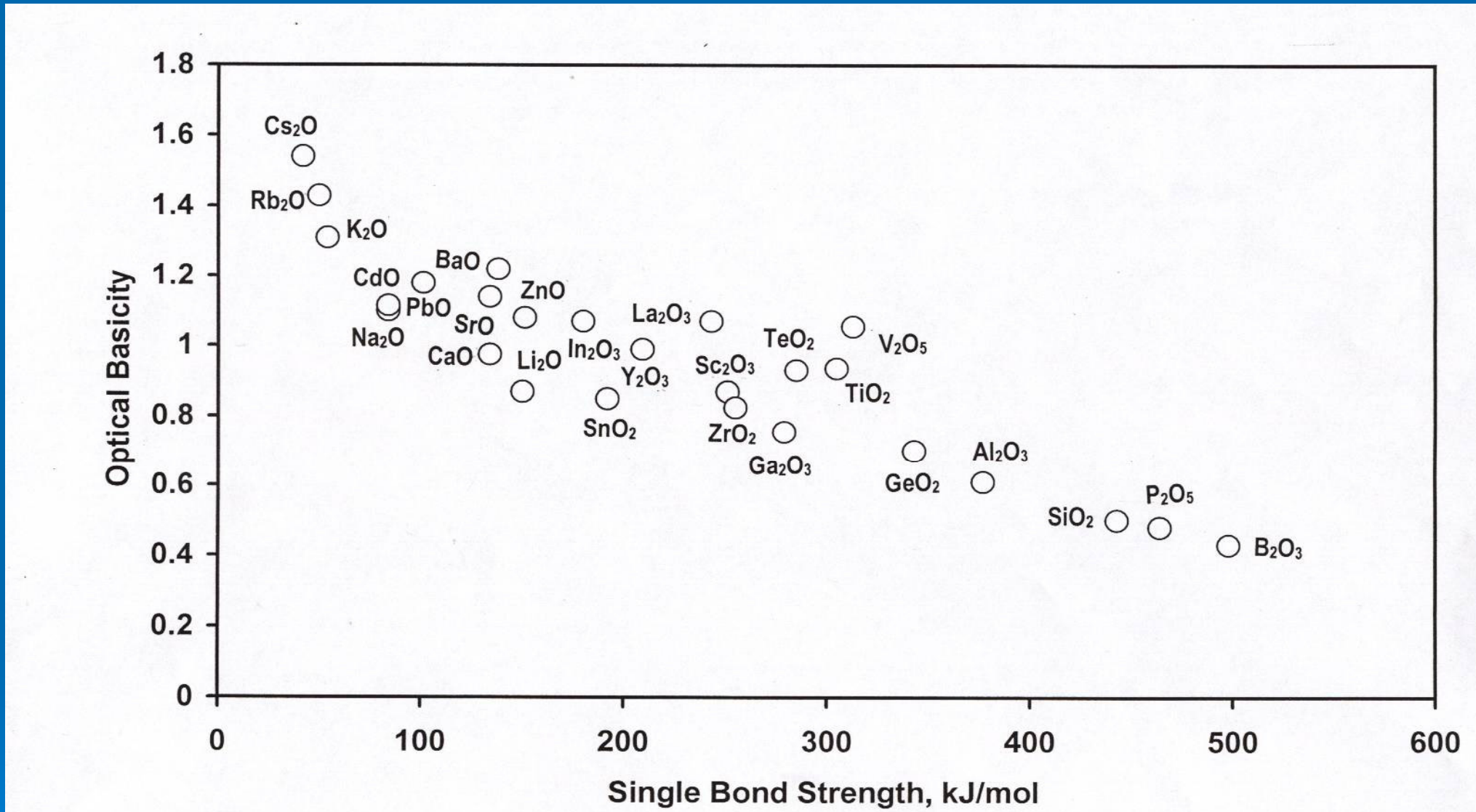



**Fig. 1 Dimitrov and Komatsu**

## PURPOSE

In the present article we have searched for such a relationship between ***optical basicity*** and ***single bond strength*** for series of oxide glasses and discuss about its application in the field of ***nonlinear optical materials***.

## II. RESULTS AND DICUSSION

### *II.1. Optical basicity and average single bond strength of oxide glasses*

**Duffy** has established a correlation between the **optical basicity, Λ,** and the **electronic polarizability,** $\alpha_{O2-}$, of the oxide ion,

$$\Lambda = 1.67(1 - 1/\alpha_{O2-}) \quad (1)$$

Equation (1) gives a possibility to calculate the **refractive index based optical basicity** $\Lambda(n_o)$ of the medium using data on oxide ion polarizability, $\alpha_{O2-}(n_o)$ obtained by means of the **Lorentz-Lorenz equation**. In fact such basicity can be termed **"experimental"** since for its estimation experimental data on the **refractive index,** $n_o$, and the **density** of oxides or glasses are used.

According to the approach proposed by **Dimitrov** and **Komatsu** the **single bond strength** $B_{M-O}$ of binary glass with general formula $xA_pO_q.(1-x)B_rO_s$ could be expressed by the following equation:

$$B_{M-O} = xB_{A-O} + (1-x)B_{B-O} \quad , \quad (2)$$

where x is the mole fraction of $A_pO_q$, $B_{A-O}$ and $B_{B-O}$ are single bond strengths of M-O in the corresponding individual oxide.

We have calculated the refractive index based on **optical basicity, $\Lambda(n_0)$**, and **single bond strength, $B_{M\text{-}O}$**, of series of binary oxide glasses in the systems:

**$Na_2O$-$B_2O_3$, $Na_2O$-$P_2O_5$, $Na_2O$-$SiO_2$, $Na_2O$-$GeO_2$**

**$La_2O_3$-$P_2O_5$, $PbO$-$SiO_2$,**

**$Li_2O$-$TeO_2$, $Na_2O$-$TeO_2$,**

**$V_2O_5$-$P_2O_5$, $V_2O_5$-$GeO_2$, $PbO$-$V_2O_5$, $SrO$-$V_2O_5$**

**$Sb_2O_3$-$B_2O_3$, $Bi_2O_3$-$B_2O_3$**

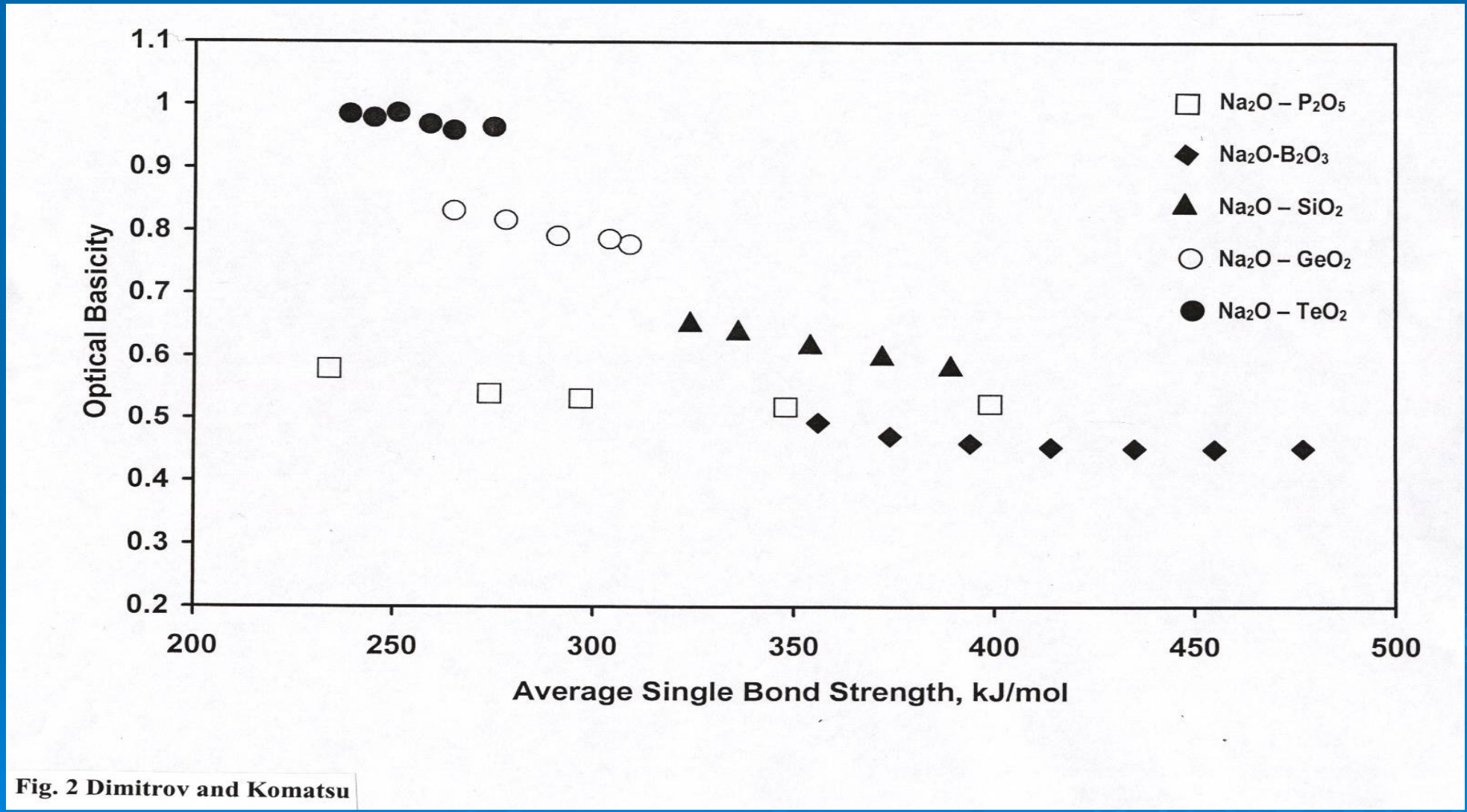
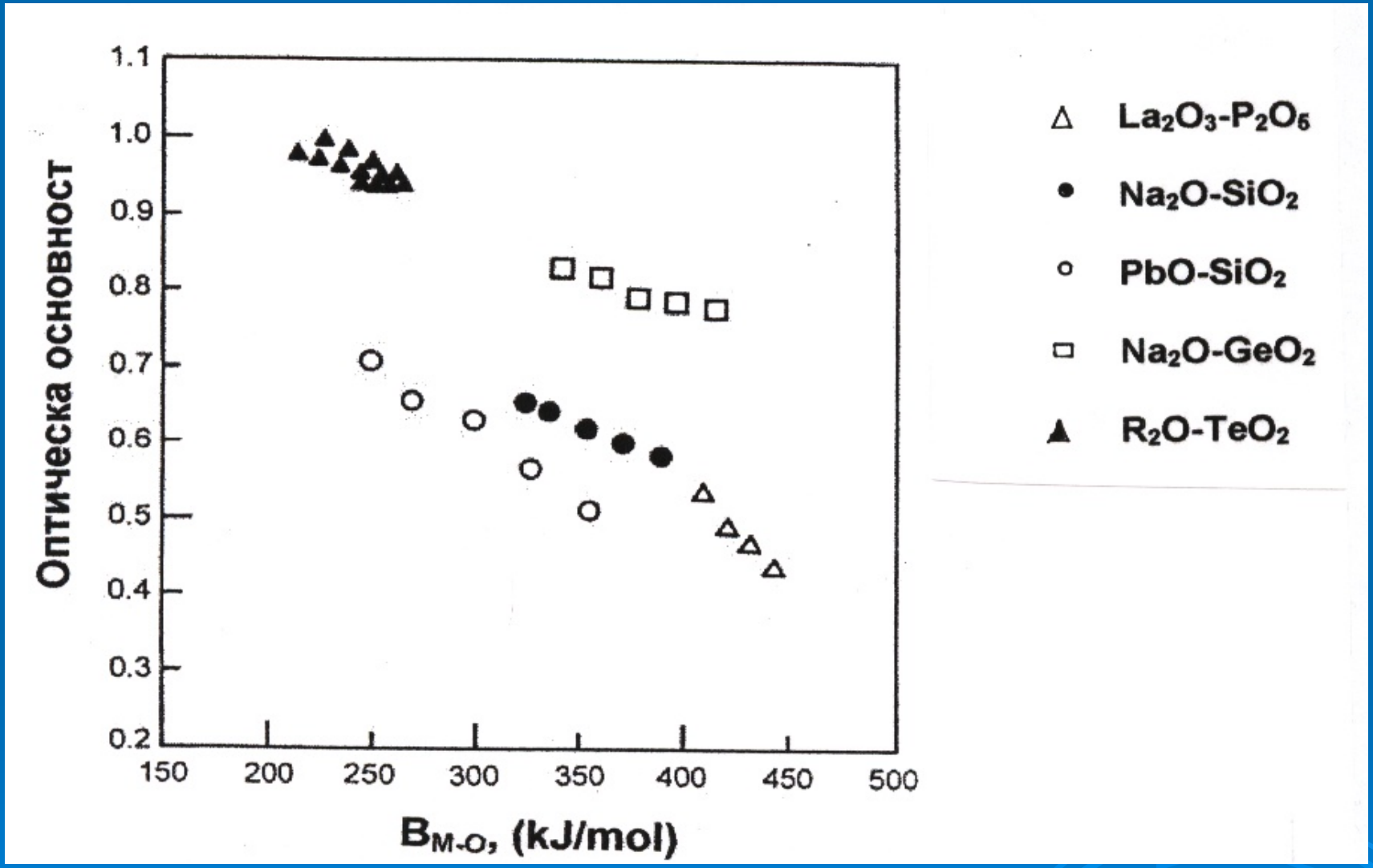



Fig. 2 Dimitrov and Komatsu


Оптическа основност
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
150
200
250
300
350
400
450
500
$B_{M-O}$, (kJ/mol)
$La_2O_3$-$P_2O_5$
$Na_2O$-$SiO_2$
$PbO$-$SiO_2$
$Na_2O$-$GeO_2$
$R_2O$-$TeO_2$

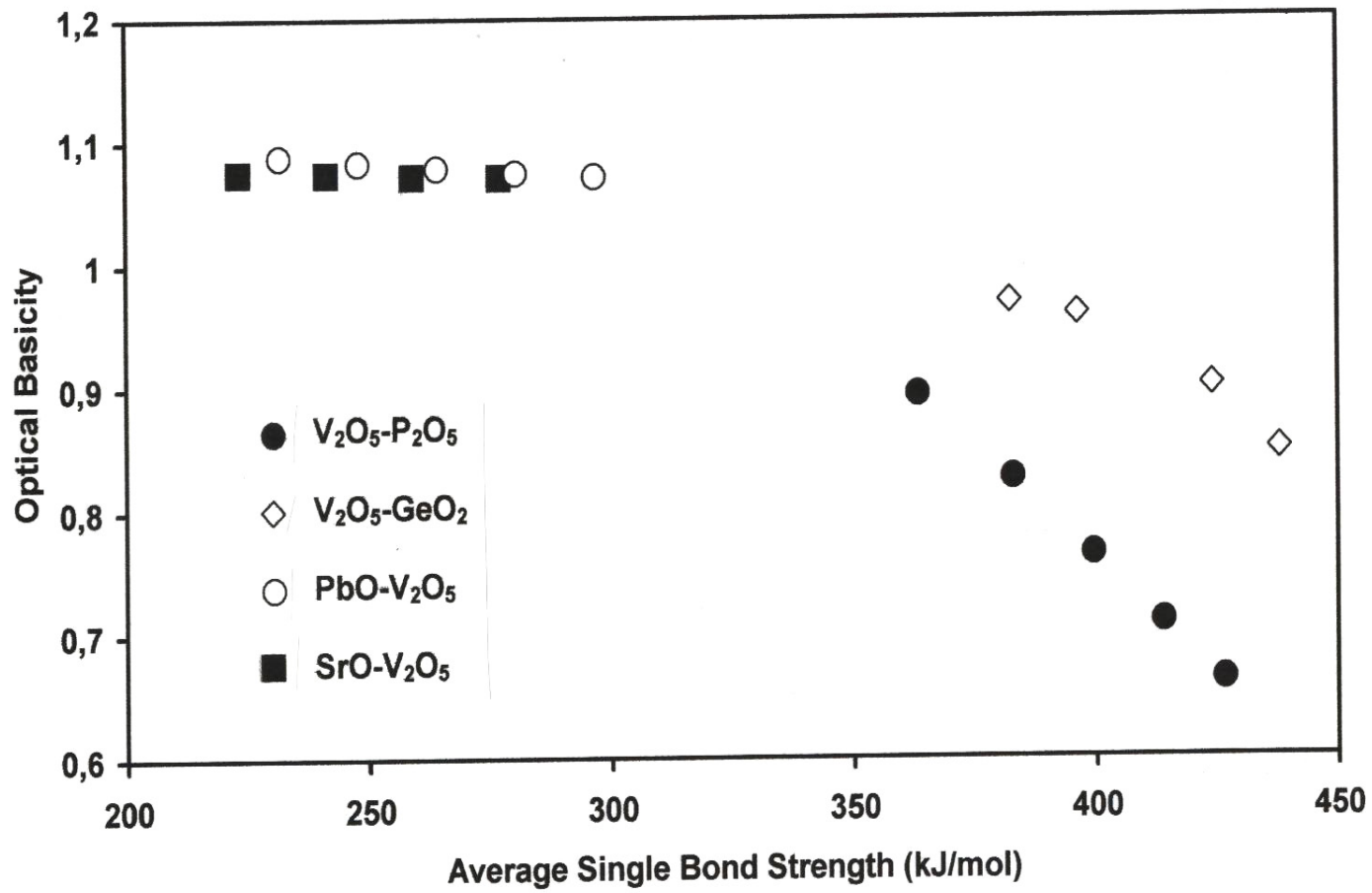
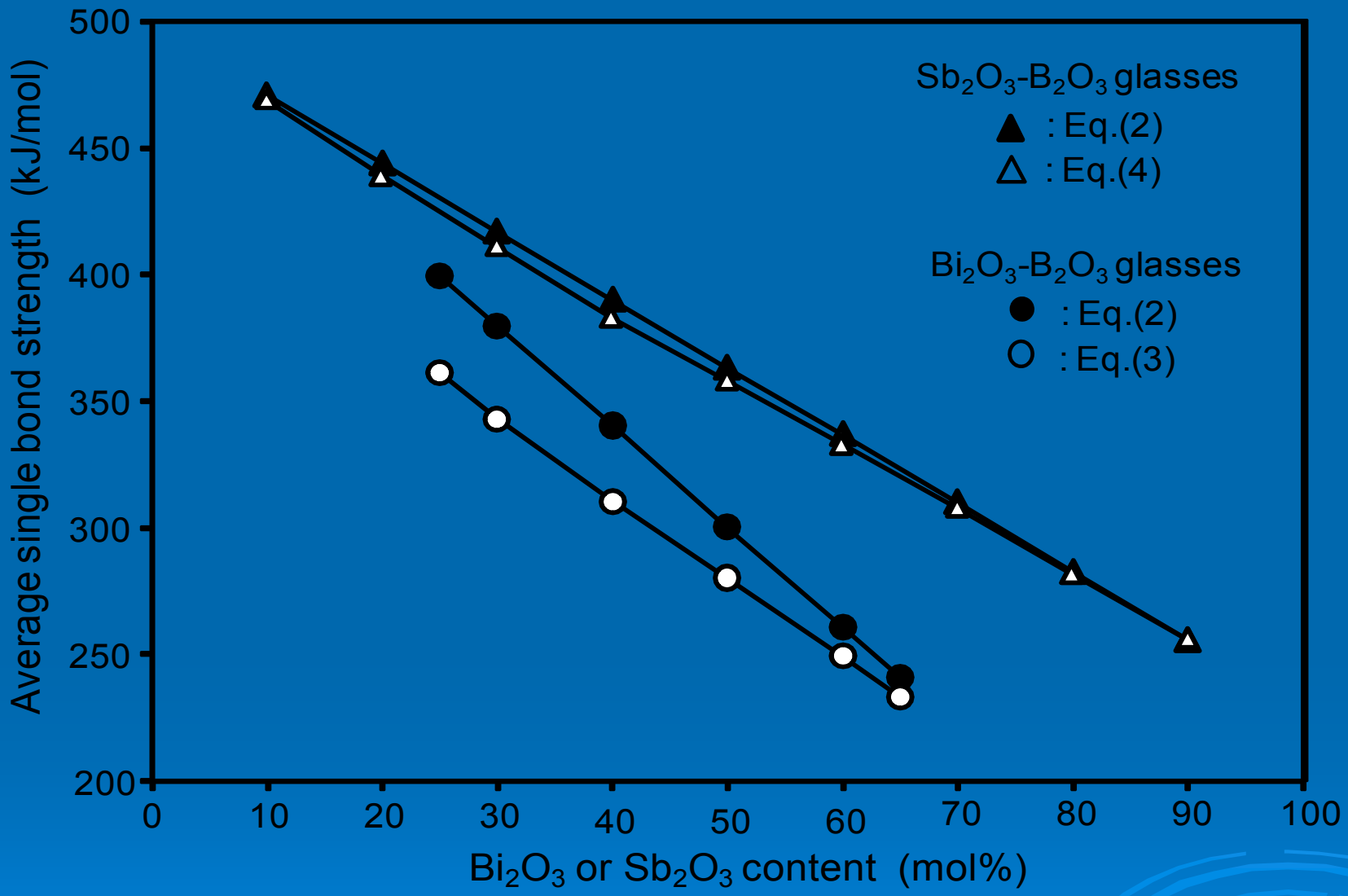
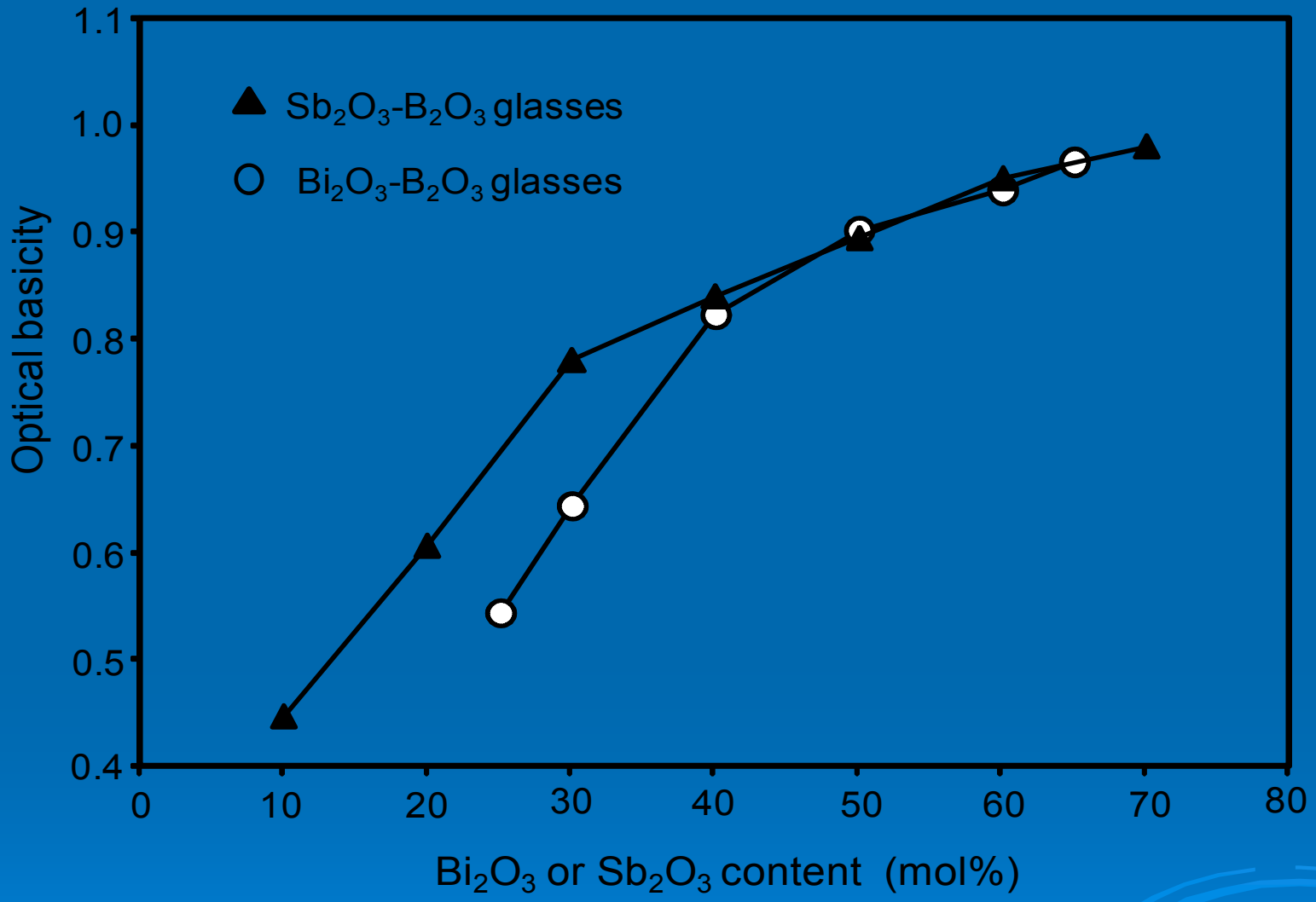
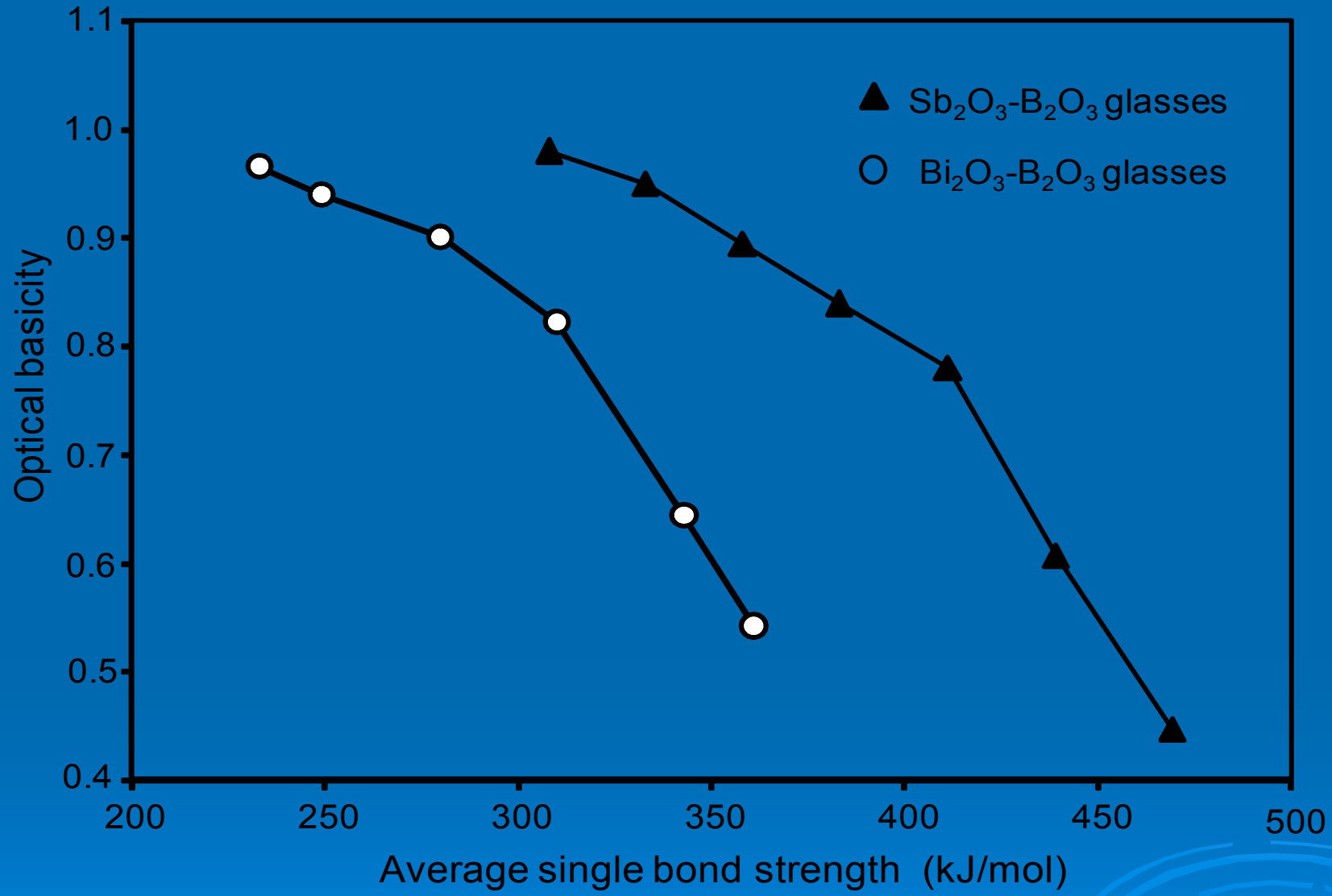



Fig. 1 V. Dimitrov and T. Komatsu


Average single bond strength (kJ/mol)
500
450
400
350
300
250
200
0
10
20
30
40
50
60
70
80
90
100
Bi2O3 or Sb2O3 content (mol%)
Sb2O3-B2O3 glasses
: Eq.(2)
: Eq.(4)
Bi2O3-B2O3 glasses
: Eq.(2)
: Eq.(3)


1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
Optical basicity
$Sb_2O_3$-$B_2O_3$ glasses
$Bi_2O_3$-$B_2O_3$ glasses
0
10
20
30
40
50
60
70
80
$Bi_2O_3$ or $Sb_2O_3$ content (mol%)


1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
Optical basicity
200
250
300
350
400
450
500
Average single bond strength (kJ/mol)
Sb2O3-B2O3 glasses
Bi2O3-B2O3 glasses

The relationship obtained gives us grounds for making some discussion on the usefulness of the observed correlations. In fact the **refractive index based optical basicity, $\Lambda(n_o)$,** of the glasses is determined on the basis of experimental data on their **refractive index** through a close relation obtained between **basicity** and **oxide ion polarizability**. The **electronic ion polarizability, $\alpha_{O2-}(n_o)$,** represents the polarizability state of an average oxide ion in the glass matrix and its ability to donate electron density to surrounding cations. An increased oxide ion polarizability means a stronger electron donor ability of the oxide ion and vice versa.

On the other hand, the **single bond strength ,$B_{M-O}$**, proposed by **Sun** gives us another view to make an interpretation of the basicity in terms of **thermodynamics** since, as was pointed out above, **$B_{M-O}$** is based on the **dissociation energy** of the oxides.

***Therefore, the usefulness of the observed correlations resides in the prediction of bulk optical basicity in each system of given composition using well known data reported by Sun on $B_{M-O}$ in simple oxides.***

From point of view of chemical bonding more acidic silicate, borate and phosphate glasses possess large $\mathbf{B_{M\text{-}O}}$ **(480-320 kJ/mol)** which implies participation of an average oxide ion in more covalent **M-BO (bridging oxygen)** bonds such as **B-O-B, P-O-P, Si-O-Si.** The smallest values of $\mathbf{B_{M\text{-}O}}$ of about **250 kJ/mol** are obtained for basic **tellurite and bismuthate** glasses. These values are assumed to support the formation of more ionic **Te-O…Na+, Te-O-Te and Bi-O-Bi** chemical bonds.

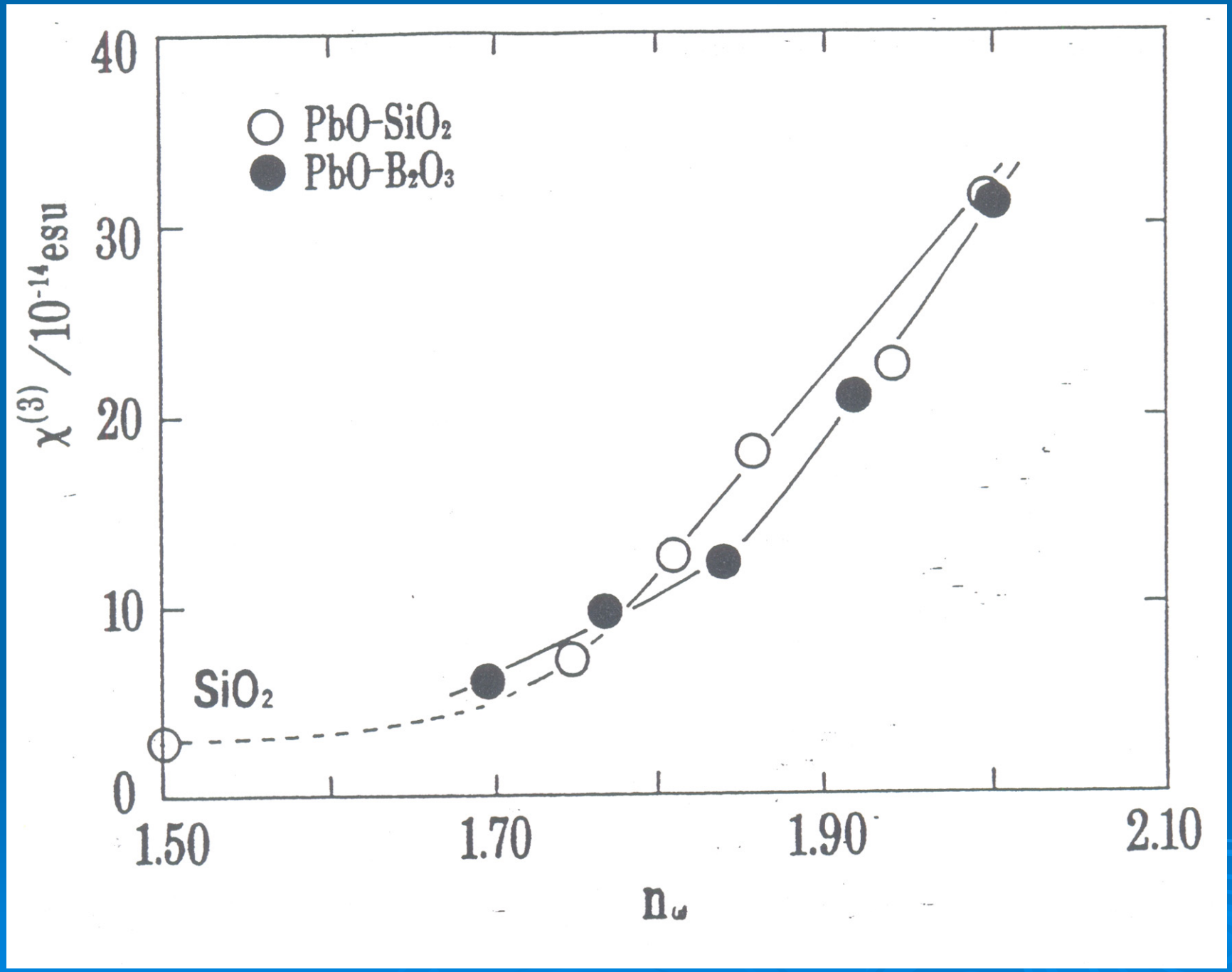
## *II. 2. Dependence of nonlinear optical properties on optical basicity and single bond strength of the glasses*

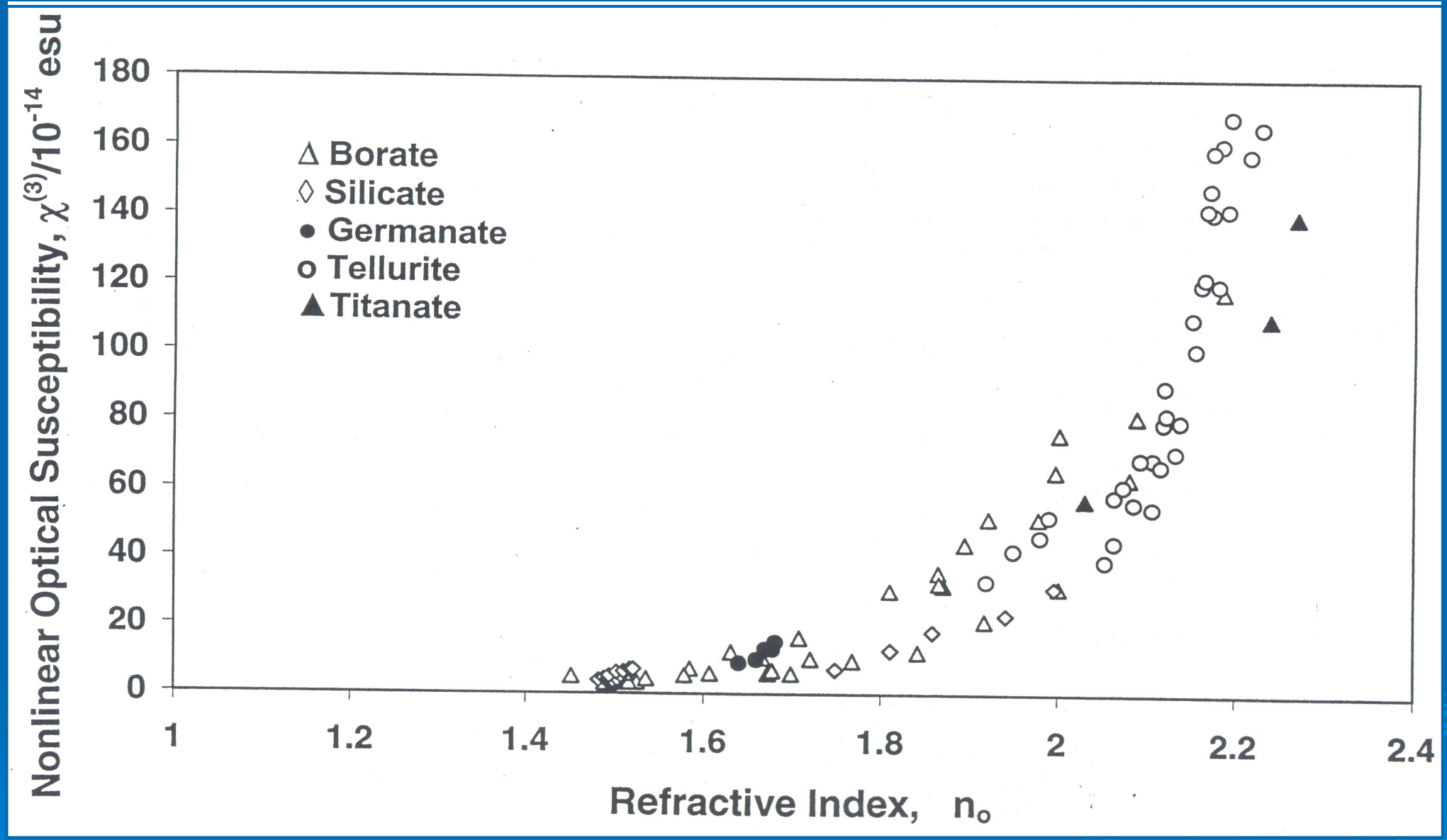
Since the optical nonlinearity is caused by ***electronic polarization*** of the glass upon exposure to intense light beams, ***polarizability*** is one of the most important properties which govern the ***nonlinearity response*** of the glass.

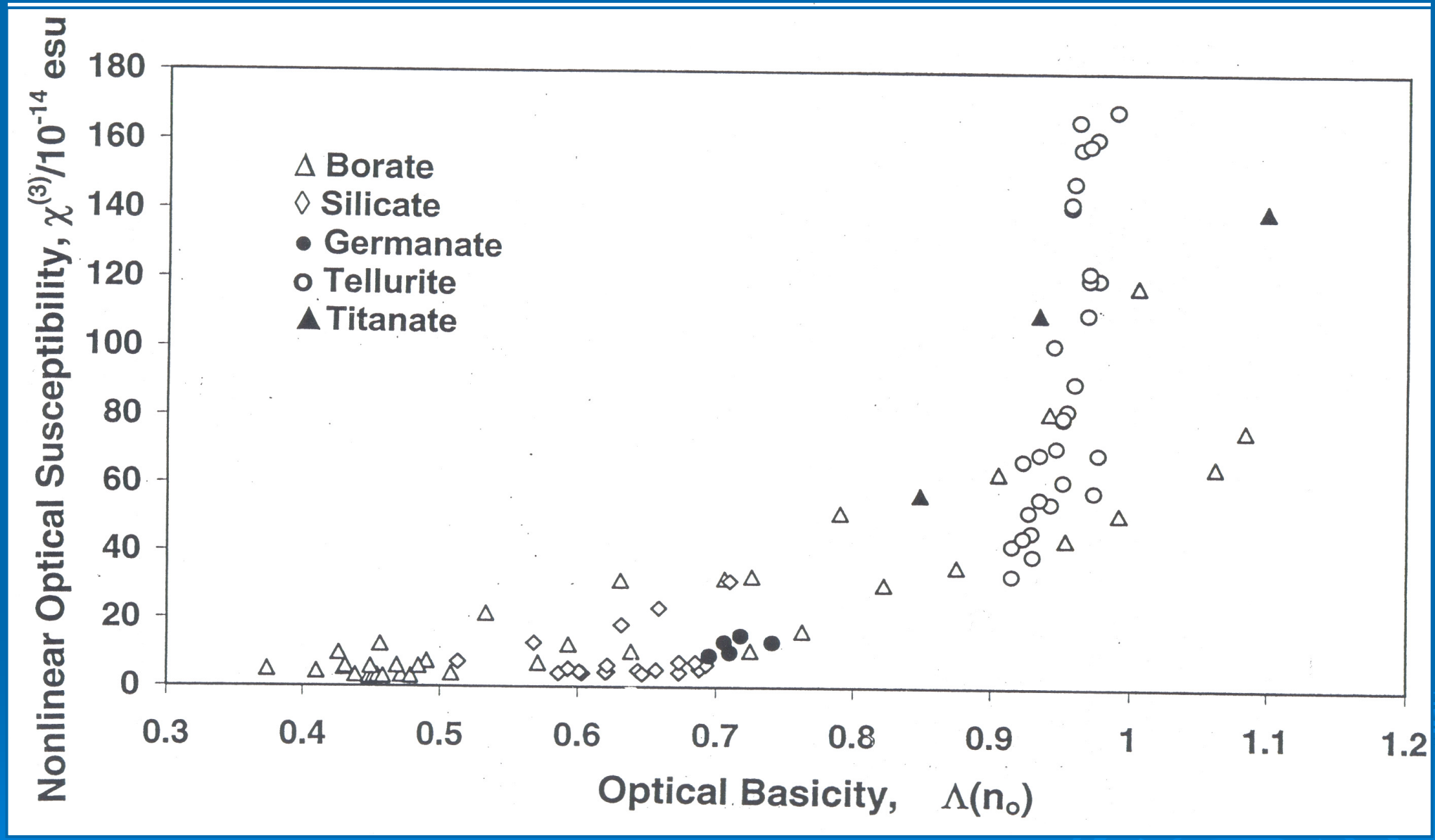
$$\mathbf{P} = \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \ldots \qquad (3)$$

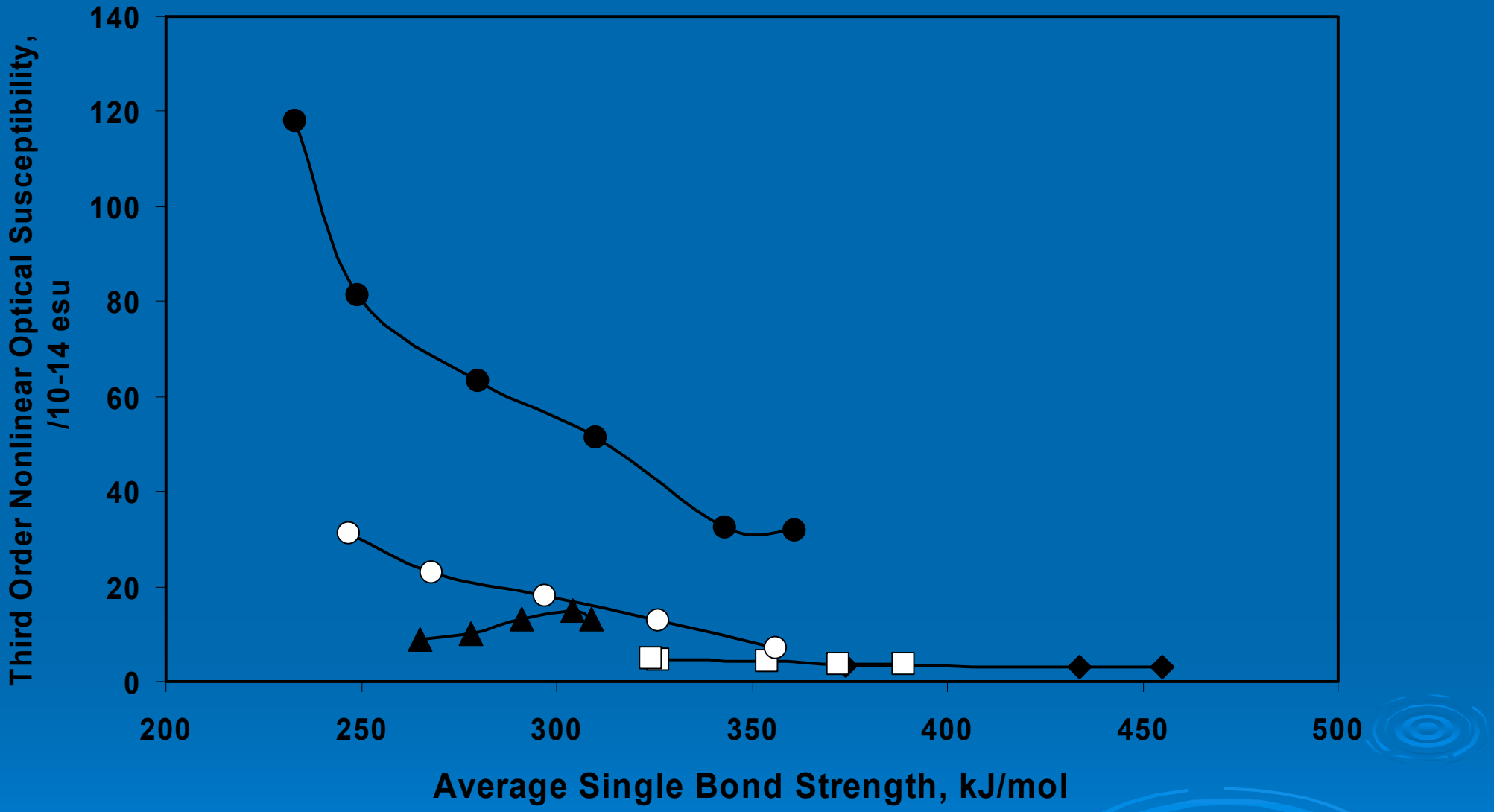
$$\mathbf{P} = \chi^{(1)}\,\mathbf{E} + \chi^{(2)}\,\mathbf{E}^2 + \chi^{(3)}\,\mathbf{E}^3 + \ldots, \qquad (4)$$

where $\chi^{(1)}$ is the linear optical susceptibility and $\chi^{(2)}$ and $\chi^{(3)}$ are second and third order nonlinear optical susceptibilities.


40
30
20
10
0
○ PbO-SiO₂
● PbO-B₂O₃
SiO₂
χ(3) /10-14esu
1.50
1.70
1.90
2.10
nω


Nonlinear Optical Susceptibility, $\chi^{(3)}/10^{-14}$ esu
180
160
140
120
100
80
60
40
20
0
1
1.2
1.4
1.6
1.8
2
2.2
2.4
Refractive Index, $n_o$
Borate
Silicate
Germanate
Tellurite
Titanate


Nonlinear Optical Susceptibility, $\chi^{(3)}/10^{-14}$ esu
180
160
140
120
100
80
60
40
20
0
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
Optical Basicity, $\Lambda(n_o)$
Borate
Silicate
Germanate
Tellurite
Titanate


Third Order Nonlinear Optical Susceptibility, /10-14 esu
140
120
100
80
60
40
20
0
200
250
300
350
400
450
500
Average Single Bond Strength, kJ/mol

# Conclusions

- The established correlation between optical basicity and single bond strength for many oxide glasses gives an opportunity to predict the trend of optical basicity in different glass-forming systems using data on single bond strength of the simple oxides.

- Glasses of high optical nonlinearity have to be searched among glasses with high refractive index, high optical basicity, and small single bond strength.

# THANK YOU FOR YOUR ATTENTION