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# OXIDE GLASSES AND THEIR "STRENGTHENED" OR "WEAKENED" COUNTERPARTS

## Energetical and structural interpretation of thermoanalytical data

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An earlier published concept, showing correlations between the "average lattice energy" of glasses (i.e. their mean molar atomization enthalpy $\Delta_A H$ at 298 K), the network dimensionality $D$ and some properties of different chalcogenide and oxide glasses, was used to interpret the transformation temperatures $T_g$ of glasses containing fluorine or nitrogen instead of oxygen. A plot of $T_g$ *vs.* $\Delta_A H$ allows the comparison of completely different glasses from only one graph. Such a consistent evaluation of composition/property relationships is useful for the further improvement of fluoride and nitride glasses, which are important for applications in optics and telecommunications and as quality-limiting components in silicon nitride-based ceramics.

Since the early work of Goldschmidt [1] it has been known that crystalline fluoroberyllates show remarkable structural similarities to the corresponding silicates (compare, for example, the isomorphism of $Li_2BeF_4$ and $Zn_2SiO_4$), whereas their lowered values of melting temperature, hardness and refractivity are indicative of decreased interactions between the structural units in the lattice. Likewise, many fluoride glasses should represent "weakened" models for analogous oxide glasses. Recently, many thermoanalytical data have been derived for vitreous materials which contain considerable amounts of nitrogen in the oxidation state $-3$ instead of oxygen. Therefore, one is now enabled to ask to what extent such fluoride glasses are "weakened", and such oxynitride glasses are "strengthened" counterparts of oxide glasses.

A direct comparison of selected glass properties as functions of a given composition variation is usually impossible, however, as a consequence of the different stoichiometries and/or of the insufficient congruence of the glass-forming regions for appropriate series of oxide, halide, nitride or other glasses. Therefore, one has to find another variable, which also depends on the chemical composition,

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but in a more generalized way. For example, it could be useful to correlate glass properties, such as transformation temperature $T_g$ or microhardness, with the bond energies between the atoms or the other structural units existing in the glass network. Unfortunately, the calculation and the use of bond energies for energetic calculations is restricted to only a few simple cases [2].

Therefore, some years ago we recommended a concept [3, 4] showing correlations between the "average lattice energy" of glasses (i.e. their mean molar atomization enthalpy $\Delta_A H$ at 298 K), the network dimensionality $D$ and the transformation temperatures $T_g$ or other thermal, mechanical and elastic properties [5, 6] of different, preferentially chalcogenide and oxide glasses.

The great number of thermoanalytical investigations on fluorine or nitrogen-containing glasses now makes it possible to include fluoride and oxynitride glasses in this concept. Both types of materials are of great practical interest: fluoride glasses for applications in optics and telecommunications, oxynitride glasses as quality-limiting components in silicon nitride-based engineering ceramics. For the further improvement of such materials, a consistent evaluation of the composition property relationship is needed for all glasses.

The molar standard atomization enthalpy of a compound in the crystalline ($s$) or vitreous ($v$) state, $\Delta_A H^{\theta}_{A_xB_y}\ldots$, at 298 K may be defined as the internal energy change when one mole of the compound $A_xB_y\ldots$ at standard pressure is converted into defined atoms which are infinitely distant from one another. The molar atomization enthalpies $\Delta H_{(s)}$ or $\Delta H_{(v)}$ can be calculated to a first approximation ($\Delta_A H_1$) from literature data relating to 298 K with the help of a simple thermochemical cycle, using the molar standard atomization enthalpies $\Delta_A H^{\theta}_i$ of the elements $i$ ($i = A, B, C, \ldots$) and the molar standard reaction enthalpies $\Delta_R H^{\theta}_j$ for the formation of the compounds $j$ ($A_xB_y$, $A_yC_z, \ldots$) most probably formed between them:

$$\Delta_A H_1 = \Sigma x_i \cdot \Delta_A H_i - \Sigma x_j \cdot \Delta_R H_j$$

($x_i$ and $x_j$ = mole fractions of elements $i$ and binary compounds $j$).

Below a calculation example is given for a five-component fluorophosphate glass (compare also Fig. 1, series 6):

The glass composition is (in mol% formula units):

$Al(PO_3)_3$ 10; $AlF_3$ 10; $MgFe_2$ 21.6; $CaF_2$ 16.8; $BaF_2$ 41.6.

In order to avoid confusion arising from the different numbers of atoms per formula unit (e.g. 13 for $Al(PO_3)_3$, 4 for $AlF_3$), one now has to convert these data into new ones which are valid for formula units containing a fixed number of atoms, e.g. only one atom in the formula unit. We obtain in mol% "normalized" formula

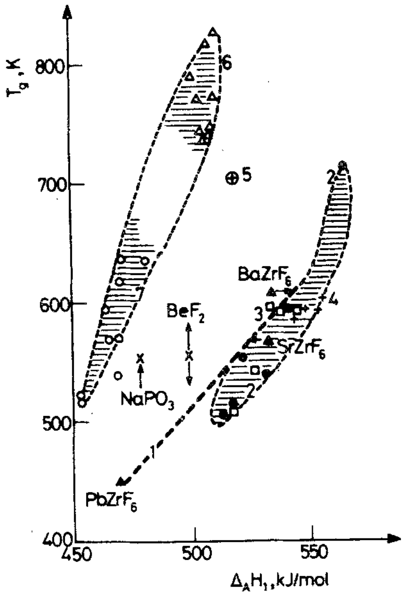

**Fig. 1** Transformation temperatures $T_g$ for selected fluoride and fluorophosphate glasses versus their "average lattice energy" $\Delta_A H_1$

| Number | Symbol | System | Reference |
|---|---|---|---|
| 1 | ▲ | $M^{II}ZrF_6$ (M = Pb, Sr, Ba) | 9 |
| 2 | ● | $MF_4-MF_3$ ($-MF_2$, MF)<br>M = Zr, Th; La; Ba, Eu; Na | 10 |
| 3 | □ | $ZrF_4-ThF_4-BaF_2$ ($-MF_n$)<br>M = Al, Nd; Ca, Pb; Li, Na | 11 |
| 4 | + | $M^{IV}F_4-BaF_2$ ($-LaF_3$)<br>$M^{IV}$ = Zr+Hf+Th | 12 |
| 5 | × | $(CaF_2)_{40}(BaF_2)_{20}(AlF_3)_{40}$ | 13 |
| 6 | △ | $Al(PO_3)_3-M^{II}F_2$ ($-AlF_3$)<br>$M^{II}$ = Mg+Ca+Ba | 14 |
| 7 | ○ | $(NaPO_3)_{50}(BaF_2)_{20}(MF_n)_{30}$<br>$n$ = 2: M = Zn, Cu, Mn, Co, Ni, Mg | 15 |
| $n$ = 3 : | | $n$=3: M = Fe, Ga, Cr | |

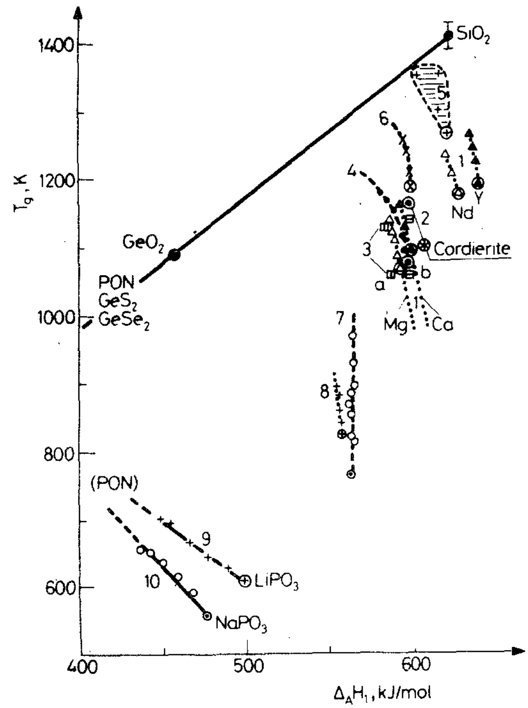

**Fig. 2** Transformation temperatures $T_g$ for selected, nitrogen containing glasses versus $\Delta_A H_1$ (Series 1–8 Si(−Al)−M−O−N, 9–10 P−M−O−N systems; M = metal)

| Number (and reference) | Symbol* | Metal(s) M | $x_N$** | Composition (mol%) for the glasses according to* | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $Al_2O_3$ | $SiO_2$ | $M^{II}O$ | $M_2^{III}O_3$ | $M_2^IO$ | |
| | ▲ | Y | | 14.4 | 60.6 | — | 25.2 | — | — |
| 1 [16] | △ | Nd | 8–9 | | | | | | |
| | ▲ | Ca | | 15.2 | 63.2 | 21.2 | — | - | |
| | △ | Mg | | | | | | | |
| 2 [17] | ⊛ | Mg | 6 | 22.2 | 55.6 | 22.2 | — | — | — |
| 3 [18] | a ◫ | Mg | ≃10 | 12.5 | 50 | 37.5 | — | — | — |
| | b ⊟ | | | 13 | 63 | 24 | — | — | — |
| 4 [19] | ● | Ca | 5.6 | 24 | 40 | 36 | — | — | — |
| 5 [20] | + | Ca | 8.5 | 24 | 72 | — | — | — | 4 $Ca_3N_2$ |
| 6 [21] | × | Ba | 6.8 | 8 | 69 | 23 | — | — | — |
| 7 [22] | ○ | Li + K | 8 | 1.5 | 75 | — | — | 23.5 | — |
| 8 [23] | + | Ca + Na | 4.5 | — | 74 | 10 | — | 16 | — |
| 9 [24] | + | Li | 20.6 | — | — | — | — | 50 | 50 $P_2O_5$ |
| 10 [24] | ○ | Na | 17.7 | | | | | | |

* the first, normally nitrogen-free glasses of the series (with the lowest $T_g$ value) are mostly marked with special symbols

** maximum nitrogen content in mol%, valid for the upper $T_g$ values of the series units:

$$\frac{\mathrm{Al(PO_3)_3}}{13}\ 31.7;\ \frac{\mathrm{AlF_3}}{4}\ 9.76;\ \frac{\mathrm{MgF_2}}{3}\ 15.8;\ \frac{\mathrm{CaF_2}}{3}\ 12.3;\ \frac{\mathrm{BaF_2}}{3}\ 30.44.$$

By inserting the values of $\Delta_A H_j$ calculated previously for each binary compound $j$ from literature data according to the above-mentioned equation:

$$\frac{\mathrm{Al(PO_3)_3}}{13}\ +518;\ \frac{\mathrm{AlF_3}}{4}\ +693;\ \frac{\mathrm{MgF_2}}{3}\ +470;\ \frac{\mathrm{CaF_2}}{3}\ +518;\ \frac{\mathrm{BaF_2}}{3}\ +513$$

(all values in kJ/mol "normalized" formula units), one obtains

$$\Delta_A H_1 = (0.317\cdot 518 + 0.0976\cdot 693 + 0.158\cdot 470 + 0.123\cdot 518 + \\ + 03044\cdot 513)\ \mathrm{kJ/mol} = 526\ \mathrm{kJ/mol}.$$

Such a calculation of the atomization enthalpies of glasses neglects (because of the lack of appropriate thermochemical data) some facts which contribute to the energy balance, e.g.

— the formation of higher than binary compounds;

— the non-ideal mixing of the binary compounds in the solid or in the frozen-in glassy state;

— the small energetic difference between a crystalline and the corresponding glassy phase, caused by the non-equilibrium state of the latter.

For many systems, however, these contributions to the "average lattice energy" are insignificant; the values $\Delta_A H_1$ are often sufficient for the interpretations. Moreover, the reliability of the thermochemical data is sometimes not high enough to justify a further step of approximation in $\Delta_A H$ calculations.

The graphical representation of correlations between the given glass property (here the transformation temperature $T_g$) and the energy $\Delta_A H_1$ now allows the comparison of completely differently composed, one-, two- or multicomponent glasses from only one diagram. To ensure a better survey, two enlarged parts of such a unified diagram are given here; Fig. 1 relates to fluoride, and Fig. 2 to oxynitride and the corresponding nitrogen-free oxide glasses.

The main advantage of such a scheme of classification is that glasses with similar physical characteristics fall into the same region of the diagram. Any data published by different authors on similar glasses can easily be compared. One can foresee the influence of additional components on the property under consideration, which facilitates the interpretation of earlier work, and the planning of further experiments. Moreover, some conclusions seem to be allowed concerning the network structure of the glasses.

Fluoride glasses are generally characterized by a low dimensionality $D$ of the glass network, and also (compare $\mathrm{BeF_2}$ (Fig. 1) with $\mathrm{SiO_2}$ (Fig. 2)) by lowered values of $\Delta_A H_1$. According to this, they are really "weakened" counterparts of oxide glasses. However, it is not easy to separate the influences of the two factors ($D$ and $\Delta_A H_1$) on $T_g$ or on other properties, especially in the case of fluoride glasses, where the structure/property correlations are strongly influenced by Coulombic forces, which increase in a complex manner the dimensionality of the island, chain or layer structures characteristic of glasses with nonpolar covalent bonds.

Nevertheless, the low $T_g$ value of glassy $BeF_2$ speaks in favour of a sharing of at least a proportion of the tetrahedral $BeF_4$ groups by edges; in this case, chain fragments would be formed in the glass structure, instead of the three-dimensional network which is characteristic of crystalline $BeF_2$ and which results from tetrahedra connection through corners.

A similar structure, chain fragments of edge-shared fluorozirconate polyhedra, held together by Coulombic interaction with the metal ions, was proposed for the fluorozirconate glasses of lead, strontium and barium (Fig. 1, series 1). For such an "isostructural series", the temperatures $T_g$ increase with increasing values of $\Delta_A H_1$. Some other examples of a possible structural interpretation of thermoanalytical data will be given in a forthcoming publication [7].

In the case of oxynitride glasses (Fig. 2), the substitution of divalent oxygen by threefold-coordinated nitrogen results in an increase of the effective dimensionality of the glass network, even in cases where, even in the nitrogen-free "parent glass" (compare, for example, cordierite in Fig. 2), a high connectivity (i.e. a high number of network bonds that link each repeat unit in the glass network) is achieved. Therefore, in spite of the slight decrease of $\Delta_A H_1$, the $T_g$ values increase considerably with the nitrogen content of the glasses, even for the relatively low degrees of substitution of oxygen by nitrogen attained so far. Consequently, the assumption is justified that glasses containing nitrogen in the network are "strengthened" counterparts of similarly composed oxide glasses.

The glass with the highest nitrogen content (33.3 mol%) seems to be vitreous phosphorus oxynitride, PON, for which not only the transformation temperature $T_g \simeq 915$ K, but also thermochemical data were recently published [8], which allow calculation of an approximate value of $\Delta_A H_1 \simeq 320$ kJ/mol. The relatively high $T_g$ value is in accordance with the assumption that the cristobalite-like structure of the crystalline compound PON also exists in the vitreous state.

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**Zusammenfassung** — Ein früher publiziertes Konzept, das Zusammenhänge zwischen der mittleren Gitterenergie von Gläsern (d. h. ihrer mittleren molaren Atomisierungsenthalpie $\Delta_A H$ bei 298 K), der Netzwerk-Dimensionalität $D$ und einigen Eigenschaften verschiedener Chalkogenid- und oxidgläser darstellt, wurde zur Deutung der Glasumwandlungstemperatur $T_g$ von Fluorid- und Nitridgläsern verwendet. Eine Aufzeichnung von $T_g$ über $\Delta_A H$ erlaubt, sehr verschiedene Gläser in einem Diagramm zu vergleichen. Eine derartige widerspruchsfreie Auswertung der Beziehungen zwischen Zusammensetzung und Eigenschaften ist nützlich zur Verbesserung von Fluorid- und Nitridgläsern, die Anwendungen in der Optik und bei der Datenübertragung finden oder in Keramiken auf Siliciumnitrid-Basis qualitätsbegrenzende Bestandteile sind.

**Резюме** — Ранее опубликованные общие представления, показывающие корреляции между «средней энергией решетки» стекол (т. е. их средняя молярная энтальпия атомизации $\Delta_A H$ при 298 К), размерностью $D$ сетки и некоторыми другими свойствами различных халькогенидных и оксидных стекол, были использованы для интерпретации температур стеклообразования $T_g$ стекол, содержащих фтор и азот вместо кислорода. График в координатах $T_g - \Delta_A H$ показал сравнение полностью различных стекол на основе только одного графа. Такая последовательная оценка взаимосвязей состав — свойство является полезной для дальнейшего улучшения фторидных и нитридных стекол, нашедших важное применение в оптике и телесвязи, а также как компоненты для получения керамики на основе нитрида кремния.