STRUCTURA NANO-HETEROGENĂ A STICLELOR OXIDICE▲
NANO-HETEROGENEOUS STRUCTURE OF OXIDE GLASSES

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This communication, having a review character of the works developed in the frame of the department Science and Engineering of the Oxidic Materials and Nano-Materials, begins with a short remembering of the problems of the oxide glass structure in the middle of the last century. A special attention is given to the concept elaborated by Professor Şerban Solacolu under the name quasicrystalline structure of glass. In the current year, a Nobel Prize was given for a theory with a similar name, elaborated for non-crystalline metallic alloys. In the department were studied the ideas concerning the chemical equilibrium in oxidic melts, which determine at high temperatures, the formation of a nano-heterogeneous structure with a certain aggregates distribution theoretically calculable which may be correlated with some properties of the resulted glass. An important progress was realized when an experimental method was elaborated for determining the basicity of these structural elements with the possibility to estimate their compositions and distribution. The principle of the experimental method is presented. The distribution of the nano-heterogeneous elements offers interesting information concerning the structure of glass and make possible correlations with properties. So is outlined the possibility to follow, even at the industrial level, the influences of some components of technology on the structure and properties of the produced glass.

Această comunicare, având un caracter de trecere în revistă a lucrărilor dezvoltate în cadrul departamentului Ştiinţa şi Ingineria Materialelor Oxidice şi a Nano-materialelor, începe cu o scurtă reamintire a problemelor structurii sticlelor oxidice la mijlocul secolului trecut. O atenţie specială se acordă conceptului elaborat de Profesorul Şerban Solacolu sub numele „structura cuasicristalină a sticlelor". În anul curent s-a acordat un Premiu Nobel pentru o teorie cu un nume similar elaborată pentru aliaje metalice necristaline. În department au fost studiate ideile privind echilibrul chimic în topiturile oxidice care determină, la temperaturi ridicate, formarea unei structuri nano-heterogene cu o anumită distribuţie, calculabilă teoretic, a agregatelor, care poate fi corelată cu unele proprietăţi ale sticlei rezultate. Un progres important a fost realizat când a fost elaborată o metodă experimentală pentru determinarea bazicităţii acestor elemente structurale cu posibilitatea de a estima compoziţia lor şi distribuţia. Este prezentat principiul metodei experimentale. Distribuţia elementelor nano-heterogene oferă o informaţie interesantă privind structura sticlei şi face posibilă corelaţia cu proprietăţile. Astfel se evidenţiază posibilitatea de a urmări, chiar la nivel industrial, influenţa unor componente ale tehnologiei asupra structurii şi proprietăţilor sticlei produse.

Keywords: *Professors' Solacolu quasicrystalline structure of glass, studies of glass structure in our department, new SBD method for determination of the nano-heterogeneous aggregates distribution in glass*

1. Introduction

The glass structure is one of the permanent preoccupations of those working in the field of glass science or glass technology. It seems that, approximately in the middle of the last century, the interest in glass structure attains a maximum, remaining, after that, at a high level, in relation with the important technological achievements.

In our Department, this interest results initially in apparition of some scientific books having chapters or being entirely dedicated to glass structural problems. It can be mentioned firstly Physical chemistry of technical silicates published by Professor Dr. Docent Şerban Solacolu corresponding member of the Romanian Academy [1]. This book contains the scientific bases of practically all silicate materials of technical importance. In the glass domain, the structural theories and physical and chemical properties are presented and critically examined. On such basis, Professor Solacolu developed in his book an own concept under the name heterogeneous quasicrystalline glass structure. To the known rules, controlling the chemical compounds formation were added the specific influence of the so-called glass formers and modifiers, which hinder the apparition of correct crystals and the long-range order. The remained different kinds of defects and irregularities confer to structure the heterogeneous quasi-crystalline aspect. Among the new ideas was underlined the important role of the thermal phase equilibrium, studied on complex synthetic high furnace slag. As an example, in figure 1 some results obtained in a six components glass system are shown [2, 3].

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▲ Lucrare prezentată la / *Paper presented at:* Consilox XI

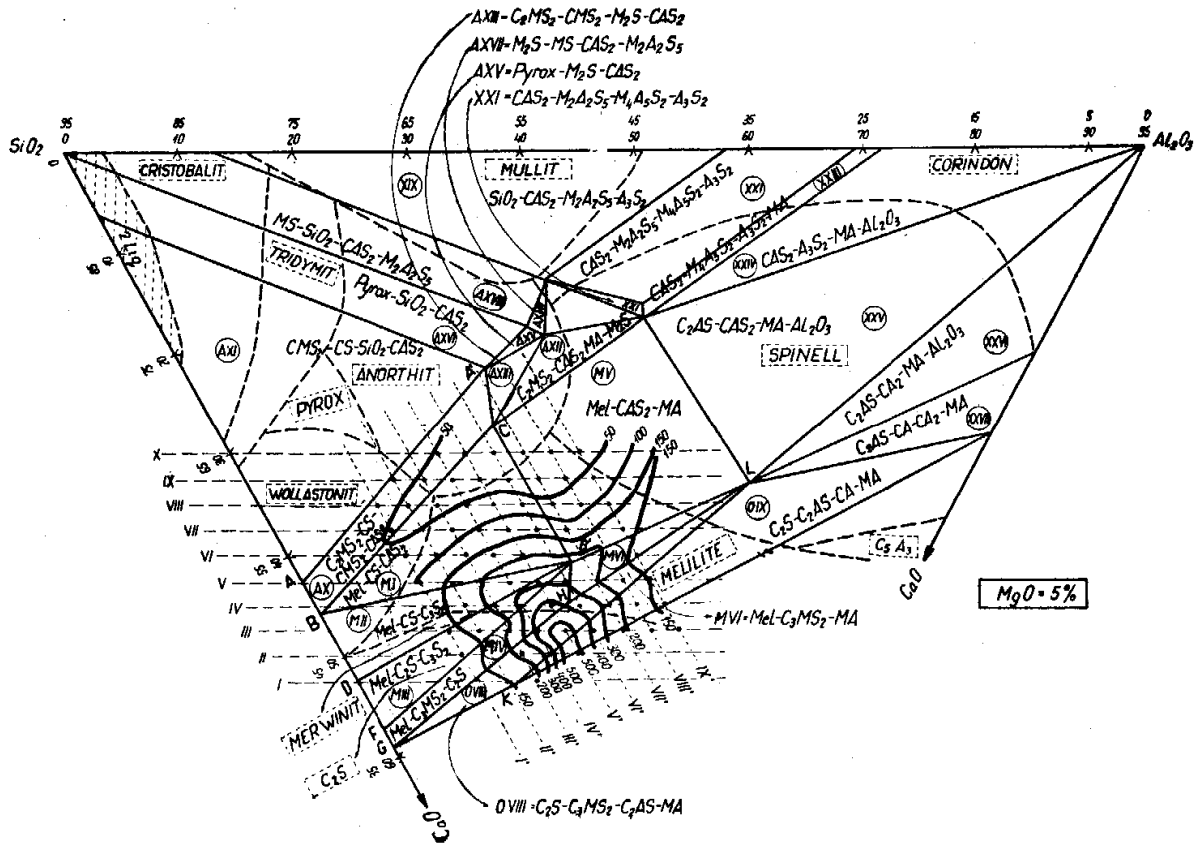

Fig. 1 - An example of equal strength curves of cements with sinthetic glassy high furnace slags, obtained in this thermal equilibrium system [2]/*Un exemplu de curbe de egală rezistență a cimenturilor cu zguri de furnal înalt vitroase sintetice, obținute în acest sistem de echilibru termic.*

The ideas presented in the book mentioned above and many experimental results, were published in Romanian and English and at least in two European journals in 1958 [2] and in 1964 [4] and were used in works of doctors students [3] and many research workers.

It deserve to be mentioned that after about 50 years the name quasicrystal is reused, this time for a new class of ordered inter metallic structures for which The Nobel Prize in Chemistry 2011 is awarded to Dan Shechtman [5]. It is of interest that the behaviors of these new quasicristals are more like those found in glasses than in normal crystals [6].

The scientific basis for glass study has been updated and completed. Were published new books: Glass Technology [7]; Introduction to the Physical Chemistry of the Vitreous State [8], and also many own research works.

2. The chemistry of glass formation

The chemical processes taking place at high temperatures by glass melt formation are always most interesting. From the numerous ideas existing in the specialized literature has been selected and used those inspired from the chemistry of organic polymers and named, many times, polymer theory of glass [7, 9, 10]. Schema in Figure 2 suggest that a SiO_2 granule, in contact with alkali oxides, lost tetrahedrons from surface, where the Si-O bonds toward interior are weak enough, forming different silicate molecules. The result is a so-called polymer distribution. It is a chemical equilibrium, which may be written as:

$$SiO_4Na_4 + Si_xO_{3x+1}Na_{2x+2} \leftrightarrow$$
$$\leftrightarrow Si_{x+1}O_{3x+4}Na_{2x+4} + Na_2O \quad (1)$$

Using the formulas and some experimental data published by Masson [9], was deduced the possibility to obtain the equilibrium constant for the equation (1) on the basis of the ionization potential P_i of cations, in eV [7, 8]:

$$\text{Log } K_{1x} = 0.64.P_i - 10.2 \quad (2)$$

In this way, it became possible to calculate the polymer distribution for sodium silicate glasses too. Pretnar, [10] proposed, for more acid silicates the relationship:

$$n_x = n_{SiO2}(1 - r)^2.\, r^{x-1} \quad (3)$$

where n_x is the number of the species with x tetrahedrons, n_{SiO2} the number of the SiO_2 moles in the studied composition and r is the constant rate between the concentrations of species with x+1 and x silicium atoms in molecule. In the Figure 3 is given the calculated numeric (mol %) and mass ($n_x.M_x$) polymer distribution for a sodium meta silicate melt, having on the abscissa the number x corresponding to the different molecule species.

Knowing the formulae of the binary alkali silicates (1) it was possible to calculate the dimensions of different anions. The values ob-

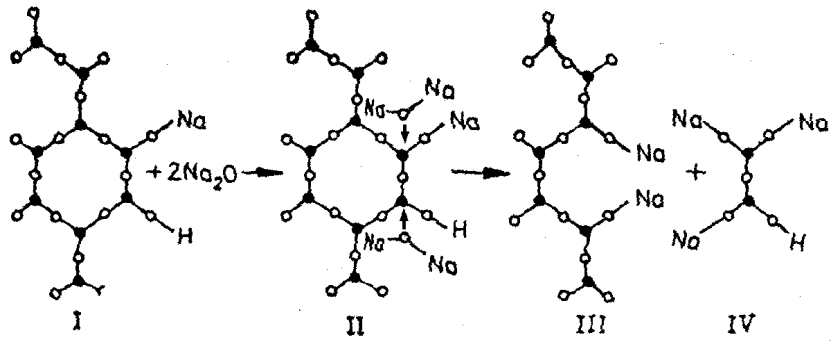

Fig. 2 - Schematic representation of the chemical interaction between a SiO_2 granule and Na_2O (for simplicity were represented only three of the four bonds of Si)/ *Reprezentarea schematică a interacțiunilor chimice între o granulă de SiO_2 şi Na_2O (pentru simplificare au fost reprezentate numai trei din cele patru legături ale Si).*

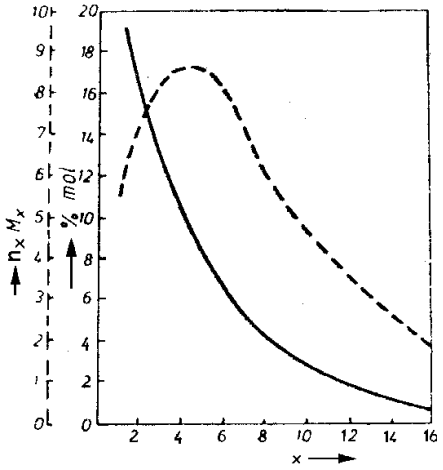

Fig. 3 - Polymer distribution in a melt of $Na_2O{\cdot}SiO_2$ composition/*Distribuția polimerilor într-o topitură de compoziția $Na_2O{\cdot}SiO_2$.*

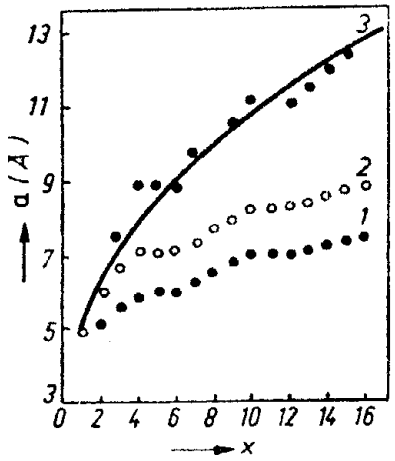

Fig. 4 - The rigid sphere diameters [11]/ *Diametrele sferelor rigide.*

tained according to three different hypotheses [13] are presented in the Figure 4. Some of them are compared, in the Table 1, with the published by other authors values, obtained in different other ways. Those corresponding to the curve 3 seem to match beter, suggesting that are closer to the reality.

Table 1

Comparison between anion diameter obtained in different ways
Comparare între diametrele anionilor obținute pe diferite căi

The anion, (without the negative charges) *Anionul (fără încărcăturile negative)*	Diameter in Å after: *Diamentru în Å după:* Fray [11]	Kumar [12]	Baltă and Radu [13]
Si_4O_{12}	5.4	-	4.5
Si_8O_{20}	7.5	9.6	9.8
$Si_{12}O_{28}$	9.2	10.9	11.4
$Si_{16}O_{36}$	11.0	11.3	12.7

The acquired information confirmed the presence of a variety of chemical components in melted and solid glass with dimensions, generally, of the order of nanometers. In time, the term nano-aggregates were preferred for them. Considering the chemical composition of the nano-aggregates it became possible the glass proprieties calculation on the basis of the calculated glass structure [14-16].

Three interesting structural schemas suggesting such nano-heterogeneities are presented in [17]. The own one, intended to illustrate the nano-aggregates distribution calculated for metasilicate glass was elaborated in 1972 [18]. The other two were published by Greawes [19] and Goodman [20] in 1985.

Some of the other works elaborated in our department and dedicated to glass structure, published in the last years, are listed in references [21 – 26] including two new books [27, 28].

3. Attempts to determine experimentally the nano-aggregates distribution in glass

Preoccupations in this direction were always present in the specialized literature and

also in our laboratory but with little successes.

The most interesting were the chromatographic methods if glass was soluble enough in a convenient solvent. This condition is rarely fulfilled by the usual industrial glasses. The positive aspect is the fact that practically all the chromatograms obtained with different methods show the traces of a number of different nano-aggregates, confirming, in principle, the concept. The identification of the nature of the nano-aggregates is very difficult or even impossible. As a rule, the recorded traces belong to smallest nano-aggregates the bigger ones being not separate or insoluble. In the Figure 5 [15] each maximum seems to indicate a molecule species and the general aspect is comparable with a numeric distribution. Unfortunately, excepting the first maximum which correspond to monomer, the identification of other nano-aggregate species was not possible in that time.

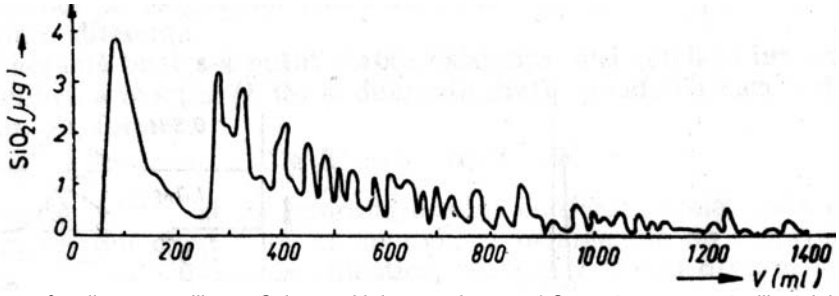

Fig. 5 - Chromatogram of sodium metasilicate. Column with ions exchangers/ *Cromatograma metasilicatului de sodiu. Coloană cu schimbători de ioni.*

In the case of phosphate glasses, being soluble, the obtained information is more complete and interesting (8, 29, 30], in agreement with that accumulated in the field of silicate glasses.

Among different other method tested for nano-aggregates detection in glasses it deserve to be mentioned the distribution of the five tetrahedron species in silicate glasses, discussed mainly in [31, 32]. This tendency to begin the study of glass structure at the level of tetrahedrons was stimulated, in the last years, by the apparition of a new and powerful method – MAS-RMN. The recorded spectra allow evaluating the concentration of different tetrahedron species existing in the analyzed solid glass. On the basis of the small displacements of the specific maxima, it is now possible to estimate the nature of the cations linked to the non-bridging oxygen atoms and, in certain measure, the nature of the nano-aggregate. However, it is difficult or even impossible to obtain concrete information about the nano-aggregates distribution. The inverse way seems to be possible and an attempt in this sense was made in [33].

The tetrahedron distributions were calculated for different compositions in the system K_2O-SiO_2 (which was chosen because of the lack of micro-phases separation), using the calculated nano-aggregates distributions [33]. The results are presented in Figure 6 together with the experimental data obtained by means of MAS-RMN. It can be remarked a quite good fit and the possibility to compare the calculated data with ones obtained experimentally. These results show that both approaching manners are valid and conduct to a similar image of the structure.

4. The experimental method SBD (spectral basicity distribution)

This experimental method for nano-aggregate distribution in glass determination is derived from the method for glass basicity determination using the charge transfer absorption of Cu^{2+} introduced in glass as probe ion [34 - 36]. In Figure 7 is shown a Cu^{2+} spectrum in a silicate glass the UV peack being used for basicity measurement [35]:according to formula

$$pB = 151 - 0.00259 \cdot \nu \quad (4)$$

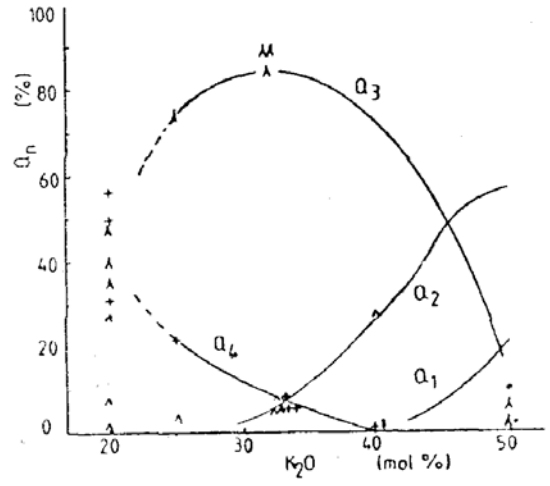

Fig. 6 - Distribution of the calculated tetrahedron species Q_n in the system K_2O-SiO_2, (curves), compared with the experimentally obtained MAS-RMN data, marked as: Q_1; Q_2, Λ; Q_3, Y; Q_4 +./*Distribuția speciilor de tetraedre Q_n calculate, în sistemul K_2O-SiO_2 (curbele), comparată cu datele experimentale obținute cu MAS-RMN marcate prin: Q_1; Q_2, Λ; Q_3, Y; Q_4 +.*

In this original formula (4) ν is in cm^{-1}. Expresing ν in nm one obtain formula (5), more convenient for actual recorded spectra and alowing to read the basicities of the nano-aggrega-

tes covered by the copper UV maximum (Fig. 8).

pB = 151 – 25900/ν (in nm) (5)

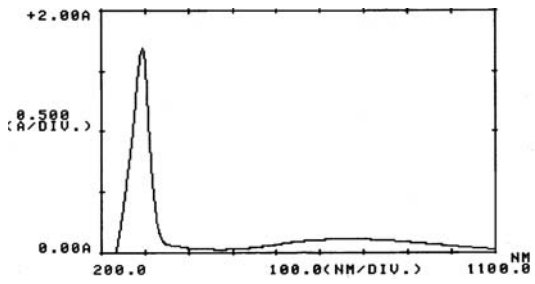

Fig. 7- Cu^{2+} spectrum in a silicate glass/ *Spectrul Cu^{2+} într-o sticlă silicatică.*

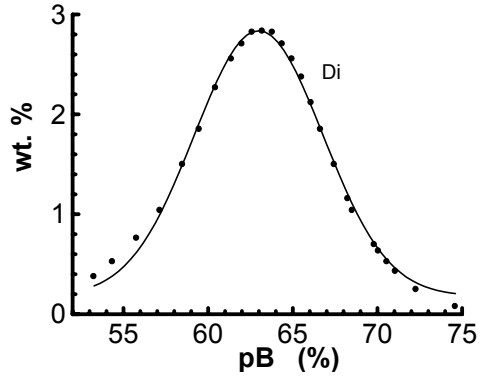

Fig. 8 - The pB values of nano-aggregates in a disilicate glass/ *Valorile pB ale nano-agregatelor într-o sticlă de disilicat.*

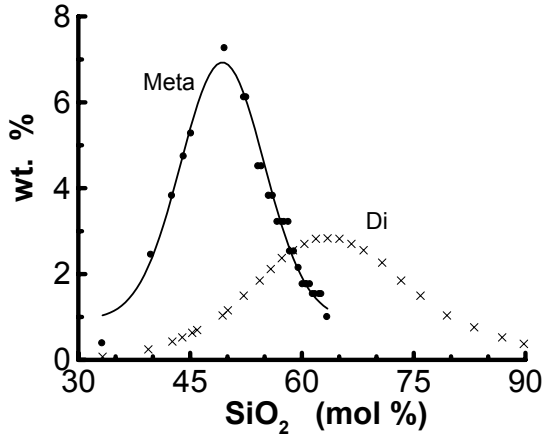

Fig. 9 - The nano-aggregate compositions in meta and disilicate glasses determined with SBD/*Compozițiile nano-agregatelor în sticle de meta şi disilicat, determinate cu SBD.*

The nano-aggregate distribution obtained in this manner can be represented with composition on the abscissa (Fig. 9) using a correlation like (6):

SiO_2 (% mol) = 266.89 – 0.6843·ν (nm) (6)

deduced for de binary SiO_2 – Na_2O system. The information content is the same as in calculated distributions. As expected, the maxima correspond to the nominal compositions of the studied glass. A certain dispersion of data for individual nano-aggregates may depend probable on the technological factors too. In the original work [34] the possibility to apply this experimental method to ternary or even to more complex glasses is showed, by solving some not very complicated calculation problems.

5. Conclusions

The impulse given by Professor Solacolu was received and followed, in the glass structure field too, by many of his students, with interesting and useful results.

Were communicated and published more than 80 research works and about 10 books, among them one translated in English and Chinese and available worldwide to specialists in glass science and technology.

The heterogeneity of glass structure was re-demonstrated and sustained with contribution to many calculation methods for deeply understanding the specific theoretical aspects.

The original experimental method Spectral Basicity Distribution seems to offer the unique and, for the moment, single possibility to obtain direct information about the nano-aggregates present in glass. This method may be adapted, with certain efforts, for use in the industrial condition in order to evidence the influences of technological peculiarities on the structure and properties of glass.

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In the Romanian Journal of Materials 2012, 42 (2), 179, the correct authors of the paper

EFECTUL CONCENTRAȚIEI ALCALIILOR ASUPRA PROPRIETĂȚILOR MECANICE ALE GEOPOLIMERILOR PE BAZA DE CAOLIN

EFFECT OF ALKALI CONCENTRATION ON MECHANICAL PROPERTIES OF KAOLIN GEOPOLYMERS

are: HEAH CHENG YONG, KAMARUDIN HUSSIN, MOHD MUSTAFA AL BAKRI ABDULLAH, MOHAMMED BNHUSSAIN, LUQMAN MUSA, KHAIRUL NIZAR ISMAIL, LIEW YUN MING