# ASSESSING THE GLASS FORMING ABILITY OF OXIDES MELTS

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**Abstract**

$GRGFA_{ox}$ is a non dimensional model to compute the oxide Global Relative Glass Forming Ability [1] . This criterion takes into account the isobaric thermal capacity ($C_p$) and the ratio of the cell volume (V) with the ionic distance ($d_{ExOy}$). In this contribution, authors suggest a relative model to assessing the Glass Forming Ability of any oxides melt ($GRGFA_m$) incorporating P as the coefficient representing the quantitative probability of vitrification. The value of this corrective coefficient (P for probability) is linked with FO,IO and MO: the molar amounts sums of forming oxides (FO), intermediate and modifying oxides (IO and MO), respectively. The algebraic sum $\sum_{i=1}^{n} C_i \times GRGFA_i$ in the classical mixtures law is also added because being the melt intrinsic GFA ($IGFA_m$) value ($C_i$ and $GRGFA_i$ are the amount (%) and Global Relative Glass Forming Ability of the $i^{-th}$ oxide [1], while n is the total number of significant glass components). The computing permit to determine a $GFA_m$ frontier value sorting glasses from ceramics.

**Keywords:** Ability, Melts, Oxides, Vitrification

**Résumé**

GRGFAox est un modèle non dimensionnel pour calculer l'Aptitude Relative Globale à la Vitrification des oxydes [1]. Ce critère tient compte de la capacité thermique isobare (Cp) et du rapport du volume de la maille (V) à la distance interatomique ($d_{ExOy}$). Dans cette contribution, les auteurs suggèrent un modèle relatif pour l'évaluation de l'aptitude à la vitrification des mélanges d'oxydes ($GRGFA_m$) en incorporant la notion de probabilité quantitative de vitrification. La valeur de ce coefficient correcteur (P pour probabilité) est liée aux quantités molaires totales des oxydes formateurs (FO), intermédiaires et modificateurs (IO et MO). La somme algébrique $\sum_{i=1}^{n} C_i \times GRGFA_i$ de la loi classique des mélanges est alors considérée car étant la valeur intrinsèque de cette aptitude ($IGFA_m$) ; ($C_i$ et $GRGFA_i$ sont les teneurs (%) et les valeurs de l'Aptitude Relative Globale à la Vitrification de l'oxyde $i^{-th}$ oxyde [1], tandis que n est le nombre de composants du mélange. Les calculs ont permis de déterminer une valeur ''frontière'' faisant le tri entre les verres et les céramiques.

**Key words:** Aptitude, Mélanges, Vitrification, Oxydes.

## 1. INTRODUCTION

The glass forming ability (GFA) quantifies the behaviour of materials to solidify in an amorphous state. The oxide Global Relative Glass Forming Ability (GRGFA) is a validated analytic model to compute it [1]:

$$GRGFA_{ox.} = [(\frac{Ed}{I.T_m})x(\frac{1}{C_p})]x[(\frac{v}{(r_c+1{,}26)^2})x(\frac{V}{(r_c+1{,}26)})] \quad (1)$$

This criterion takes into account the isobaric thermal capacity ($C_p$) [2] and the ratio of the cell volume (V) with the ionic distance ($d_{ExOy}$) that were both omitted in all prior GFA models. The accuracy of this global and relative approach is comforted by its depending parameters panoply: values of the dissociation energy ($E_d$), the coordination number (I), the melting temperature ($T_m$), the cation and anion radii ($r_c$ and $r_a$ = 1.26. $10^{-10}$ m), the cation valence (v), the cell volume ($V_{ExOy}$) of the considered oxide combined to values of $C_p$ and $V/d_{ExOy}$. This criterion is more accurate because being expressed as the simultaneous influence of both thermodynamical ($E_d$, $T_m$, $C_p$) and cristallochemical (I, $v_c$, V, $V_{ExOy}$, $d_{ExOy}$) oxides characteristics.

Actually, various oxides melts with a wide range of properties are industrially produced. Since the 2nd half of the 20th century, the

abundance of large glass property databases [3-54] has facilitated systematic glass property modelling, property measurement/evaluation and glass fabrication. $SiO_2$ based glasses, in particular, are mass produced (the most used and popular) because of the mastering of their different formulations and processing techniques.

The next step in modeling this phenomenon (GFA) is to move from the level of single oxide to the level of oxides melts, i.e.: finding a formula for calculating the oxides melts GFA. Based on the above cited $GRGFA_{ox.}$ model, the new model will be global, non-dimensional. It will quantitatively take into account (the simultaneous and opposite influence of oxides: the positive effect of forming oxides (FO) and the negative one of both modifying and intermediates oxides (MO and IO).

## 2. ON METHODS OF STATISTICAL ANALYSIS IN OXIDES GLASSES

In 2009, Fluegel published his brilliant tutorial on statistical regression modelling of glass properties [23]. He cited all contributors and listed the methods of statistical analysis in glass science (and technology) that are: a) single linear regression using linear functions, b) single linear regression using polynomial functions, c) multiple linear regression using linear functions, d) multiple linear regression using polynomial functions, e) multiple nonlinear regression using advanced functions and finally f) neural network regression. Author fully described these methods and assessed ''…the creation of large glass property databases has facilitated systematic glass property modelling and property measurement evaluation....''. The relationship ''Property = f (chemical composition)'' has been the object of an infinite number of theoretical studies and allowed the development of software packages [2-22] highlighting this interdependence, such as ILIS Batch Maker, OGIS of Glass Global Consulting GmbH, GLASSEXPERTE of Schmeller Expertise and Tech-data, Czech EcoGlass KMEN, PIRIKA software for Properties and Reverse Design of Glass , GLASSMASTER of the Fraunhofer-Gesellschaft Research Organisation, ; SciGlass V. 6.5 Database and Information System, and INTERGLAD V. 6 International Glass Database System.

Furthermore, predictions are possible in some packages (Interglad, Pirika software) including predictive linear regression features.

Simple statistical analysis is the most basic tool of data organisation and interpretation [1, 23], they are relatively simple, do not require a high level in computing and programming methods, but are sufficiently accurate and reliable. Winkelmann and Schott [3] have opted for the additivity principle (multiple regression using linear functions) in their model allowing the prediction of glass properties as function of the chemical composition assessing that the relation between the glass composition and a specific property is linearly related for all component concentrations.

As precised by Fluegel [23], the additivity principle allows for very precise and accurate predictions within limited concentration ranges, (3, 14, 26-28) that cannot be reached by structural, (29-33) thermodynamic, (34-51) or molecular dynamic (52-54) modelling approaches. The additivity principle is expressed in the multiple linear regression using linear functions as follows: $Ch = \beta_0 + \sum_{i=1}^{n} \beta_i . C_i$ where Ch is the studied characteristic/property, $\beta_0$ is the model uncertainty, n: the total number of significant glass components excluding the main component (usually silica), i values: the individual numbers of the significant glass components, $\beta_i$ : coefficient value of $^{i\text{-th}}$ component, and $C_i$ : the concentrations values of the $i^{-th}$ glass component (model factors or independent variables). This equation is used (for temperature nondependent glass property modelling and where component interactions are not considered) in multicomponent systems within narrow concentration ranges. Its simplest formulation (mixtures law) is : $\mathrm{Ch} = \sum_{\mathrm{i=1}}^{\mathrm{n}} \beta_{\mathrm{i}} . \mathrm{C_i}$ .

## 3. ASSESSING THE GLASS FORMING ABILITY OF OXIDES MELTS

The aim of this study is to find a mathematical expression (using the additivity principle in the multiple linear regression functions) of the Glass Forming Ability for any oxides melt ($GFA_m$). The starting data are melt chemical composition (oxides concentrations: C; weight %) and the specific values of the Global Relative Glass Forming Ability ($GRGFA_{ox}$) of all oxides [1]. This criterion is based on thermodynamical and cristallochemical considerations. It takes into account updated values [24] of the isobaric thermal capacity ($C_p$) and the ratio of the cell volume (V) with the ionic distance ($d_{ExOy}$) along with values of the dissociation energy ($E_d$), the coordination number (I), the melting

temperature ($T_m$), the cation and anion radii ($r_c$ and $r_a$), the cation valence ($v_c$), the cell volume ($V_{ExOy}$) of the considered oxide combined to values of $C_p$ and $V/d_{ExOy}$ (see Table 1 in [1].

Table 1: Values of the quantitative probability of vitrification (corrective coefficient P)

| Total amount (molar %) | | $P = 1 + [\frac{FO\ (\ MO + IO)}{100}]$ |
|---|---|---|
| FO | (IO+MO=100-FO) | |
| 99.0 | 1.0 | 1.98 |
| 90.0 | 10.0 | 1.8 |
| 60.0 | 40.0 | 1.2 |
| 51.0 | 49.0 | 1.02 |
| 50.0 | 50.0 | 1.0 |
| 49.0 | *51.0* | *0.98* |
| 40.0 | *60.0* | *0.8* |
| 10.0 | *90.0* | *0.2* |
| 1.0 | *99.0* | *0.02* |

In accordance with the additivity principle [23], this model might be:

$$GFA_m = G_0 + \sum_{i=1}^{n}(C_i x GRGFA_i) \quad (2)$$

where $G_0$ is the model uncertainty, $C_i$ and $GRGFA_i$ are the amount (%) and Global Relative Glass Forming Ability of the $i^{-th}$ oxide [1], and n: the total number of significant glass components ($C_i$ values are mathematically called model factors or independent variables). From a strictly statistical point of view, $G_0$ values are strictly limited as: $G_0 \leq 0.25x\frac{\sum_{i=1}^{n} G_i}{n}$. This allows that all the ''n'' components contribute with 75% to the mean value of the studied property.

In the multiple linear regressions, $G_0$ is considered to be a corrective coefficient. It is compiled following several calculations and comparisons between the real and the theoretical values of the studied property. In our case, such compilation is impossible and thus, value(s) for $G_0$ are not calculable. To avoid this inconvenience and aiming to increasing the accuracy of the proposed model, let us express this adjustment as following:

$$GFA_m = P \times \sum_{i=1}^{n} C_i \times GRGFA_i) \quad (3)$$

where $GFA_m$ is the relative GFA of the studied (m) melt, P is the coefficient representing the quantitative probability of vitrification (the adjustment coefficient) value. The corrective coefficient (quantitative probability) is assessed by:

$$P = 1 + \frac{FO - (IO + MO)}{100} \quad (4)$$

where FO,IO and MO are the amounts (molar percent) sums of forming oxides (FO), intermediate and modifying oxides (IO and MO), respectively and (IO + MO) = 100- FO.

It is the quantitative effect of the total amount of forming oxides compared to the total amount of modifying and intermediate oxides. This corrective coefficient expresses the melt vitrification probability that increases (> 1.00) if the total content of forming oxides is greater than the total amount of other (intermediate and modifying) oxides (see values of adjustment coefficient P on Table 1).

Obviously:

a- if : 0 < P < 1 (the total amount of intermediate and modifying oxides is greater than the total amount of glass-forming oxides (IO + MO) > FO. Glass formation may be possible if, in the same time, all intermediate and modifying oxides (IO and MO) have low values of their specific GFA while the existing forming oxides (FO) have large values of their specific GFA (see Table 1 in [1]).

b- if : P = 1.00 (the total amount of FO is equal to the total amount of Mo and IO), the glass formation will be easier while choosing, in one hand, FO with high GRGFA values (> $0.238384$ ) and avoiding, in the other hand, MO and/or IO with low GRGFA values ( $\geq 0.131534$ );

c- if : 1 < P ≤ 2, i.e (FO > 50 and (IO + MO) < 50): the glass formation is already theoretically assured (due to the high GRGFA values of existing FO).

In consequence, the algebraic sum $\sum_{i=1}^{n} C_i \times GRGFA_i$ will be considered as the melt intrinsic GFA ($IGFA_m$) value. Thus, equation 3 becomes:

$$GFA_m = [P \times IGFA_m] = [1 + \frac{FO - (IO + MO)}{100}]x[\sum_{i=1}^{n}(C_i x GRGFA_i)] \quad (5)$$

The adopted model combines the consensual principle of additivity (2nd term of eq. 5) with the simultaneity one (1st term of eq. 5).

On Table 2 are reported chemical composition (molar %; [3, 12, 16, 17, 23, 32 – 34, 55]), adjustment coefficient, intrinsic GFA and melt GFA values for some virtual (italic characters), industrial glass (regular characters) and crystalline (bold characters) oxides compositions.

Table 2. Chemical composition (molar %), corrective coefficient (P), intrinsic GFA (IGFA) and melt GFA ($GFA_m$) values for some virtual (italic characters), industrial glass (regular characters) and crystalline (bold characters) oxides compositions.

| Designation ($GRGFA_{ox}$) | $B_2O_3$ (1.841) | $P_2O_5$ (0.891) | $SiO_2$ (1.135) | $Al_2O_3$ (0.131) | ZnO (0.039) | $PbO_2$ (0.091) | $Fe_xO_y$ (0.011) | MgO (0.007) | CaO (0.01) | BaO (0.009) | $Na_2O$ (0.0053) | $K_2O$ (0.0056) | P | IGFA | $GFA_m$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Virtual $99As_2O_5+1TiO_2$* | | | | | | | | | | | | | *1.98* | *2.28* | *4.514* |
| *Virtual $51SnO_2+49Cs_2O$* | | | | | | | | | | | | | *1.02* | *0.123* | *0.125* |
| Heavy flint glass | 0.0 | | 29.3 | | 0.0 | 67.5 | 0.2 | | | 0.0 | 0.0 | 3.0 | *0.586* | *0.338* | *0.198* |
| Light Flint glass | 1.5 | | 54.3 | | 0.0 | 33.0 | 0.2 | | 0.0 | | 3.0 | 8.0 | *1.116* | *0.646* | *0.721* |
| Crown Ba glass | 12.0 | | 49.0 | 0.0 | 9.0 | | 0.0 | | | 29.0 | 0.5 | 0.5 | *1.22* | *0.828* | *1.01* |
| $Na_2SiO_3$ glass | 0.0 | | 66.5 | | 0.0 | | 0.05 | | 0.95 | | 32.5 | 0.0 | *1.33* | *0.738* | *0.982* |
| $Na_2Ca\ Si_2O_5$ glass | | 0.0 | 71.5 | | | | 0.0 | | 13.5 | 0.0 | 15.0 | | *1.43* | *0.813* | *1.162* |
| Boron Crown glass | 10.0 | | 68.0 | 0 | 2.0 | | | 0.0 | 0.0 | | 10.0 | 10.0 | *1.56* | *1.061* | *1.655* |
| Zn Crown glass | 17.0 | | 65.0 | 0.5 | 2.0 | | | | | 1.0 | 5.0 | 9.5 | *1,65* | *0.409* | *0.675* |
| Pyrex glass | 11.8 | | 80.5 | 2.0 | 0.6 | 0.0 | 4.3 | | 0.2 | | 0.4 | 0.2 | *1.886* | *1.134* | *2.15* |
| $B_2O_5SiO_2$ glass | 13.0 | | 80.0 | 3.0 | 0 | | 0.0 | | 0.0 | | 4.0 | 0 | *1.92* | *1.151* | *2.21* |
| Dielectric glass | 0.0 | 72.0 | 8.0 | 10.0 | 10.0 | | | | | 0.0 | 0.0 | | *1.8* | *0.745* | *1.341* |
| **Common red brick** | | 0.0 | 20.0 | 10.0 | 0.0 | | 3.0 | | 50.0 | | 10.0 | 7.0 | **0.4** | **0.045** | **0.018** |
| **Clinker** | | 0.3 | 21.35 | 6.0 | MnO = 0.25 (0.01) | | 5.0 | 1.00 | 65.0 | | 0.25 | 0.85 | **0.433** | **0.253** | **0.109** |
| ***Virtual $49SnO_2+51Cs_2O$*** | | | | | | | | | | | | | ***0.98*** | ***0.118*** | ***0.115*** |
| ***Virtual $1SnO_2+99Cs_2O$*** | | | | | | | | | | | | | ***0.02*** | ***0.051*** | ***0.001*** |

## 4. RESULTS AND DISCUSSION

Analysing data on Table 3, one can predict that the VIRTUAL GLASS with the highest GFA should be melted with two (02) components: 99% of the best glassforming oxide ($GRGFA_{As2O5}$ = 0.006286) mixed with 1% of the intermediate/modifying oxide with the highest GRGFA ($GRGFA_{TiO2}$ = 0.000180 but not $Al_2O_3$ that is considered as a conditionally modifying oxide). Thus, its melt GFA will be:

$$GFA_{(99As_2O_5+1TiO_2)} = 1.98x2.28 = 4.514 \quad 5.1)$$

In this case, the single forming oxide ($As_2O_5$) contributes with 99.97 % (0.00479) of the melt GFA (0.048). Thus, it may be replaced by a total amount of 99% of ‘‘n’’ other forming oxides with high values of oxide GFA.

Moreover, among glassy melts containing < 50% of modifying/intermediate oxides, the GLASSY VIRTUAL mixture containing (51%$SnO_2$ + 49%$Cs_2O$) will have the lowest $GFA_m$ value (as $SnO_2$ and $Cs_2O$ are, respectively, the forming oxide with the lowest GRGFA value and the most unsuitable modifying oxide for glass formation) according to:

$$GFA_{(51SnO_2+49Cs_2O)} = 1.02x0.123 = 0.125 (5.2)$$

The VIRTUAL CRISTALLINE formulation with the highest GFA is a ceramic material with the following composition and $GFA_m$:

$$GFA_{49SnO_2+51Cs_2O} = 0.98x0.118 = 0.115 \quad 5.3)$$

According to these reasonings, the $GFA_m$ value of the VIRTUAL CRISTALLINE material with the lowest GFA is melted with 1%$SnO_2$ and 99%$Cs_2O$:

$$GFA_{(1SnO_2+99Cs_2O)} = 0.02x0.051 = 0.001 \ (5.4)$$

The obtained results revealed a critical value for glass formation: for all oxides-based formulations, glass formation is probable if (and only if) $GFA_m$ > 0.198. This means that these values may be considered to be ‘‘positive’’. The analysis of the results also showed the existence of a boundary value of $GFA_m$ values between glasses and ceramics: 0.198 > boundary interval > 0.109. While taking into account more data (more glass and ceramic compositions), it is possible to refine, to contract the upper and lower limits of this range!

## 5. CONCLUSION

This theoretical contribution to the study of the oxides melts Glass Forming Ability is based on concepts of non-dimensional

mathematical analysis with the combination of the additivity and simultaneity principles [1, 2, 23].

The adopted non-dimensional model (eq.5) is validated using known (behaviour and chemical composition) oxides melt. It quantitatively describes the vitrification phenomenon. Simple theoretical considerations on oxides formulations helped to detect the $GFA_m$ limit value (it must be ≥0.198) that allows the glass formation. Ceramics may have a real ''positive'' GFA while increasing the amount of glassforming oxides and decreasing the total amount of intermediate/modifying oxides (this will increase both probability P and intrinsic ability IGFA of the material).

Moreover, this assessment model melts GFA can be considered as a prediction tool. Indeed, aiming to study the behaviour (crystallization or vitrification) of any oxides composition, it is necessary to have the following data: the amounts and the specific GFA values of each component (oxide) of the studied mixture. A simple comparison of the obtained value with the upper (0.125) and lower (0.115) a $GFA_m$ value permits to answer the question: will this composition will be a crystalline or an amorphous material?

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**REFERENCES**

1. Boubata N et al., *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B*, 2012, 53 (3), 115.
2. Boubata N et al., *Bull. Mater. Sci.,* Vol. 36, No. 3, 2013, 457–460.
3. Winkelmann A., Schott O. *Ann. Physik Chemie,* 1893, 49, 401, 1894: 51, 697, 1894, 51,730.
4. English S. *J. Soc. Glass Technol.*, 1924, 8, 205.
5. English S. *J. Soc. Glass Technol.*, 1925, 9, 83.
6. English S. *J. Soc. Glass Technol.,* 1926, 10, 52.
7. Gehlhoff G., Thomas M. *Z. Techn. Physik,* 1925, 6 , 544.; Z. Techn. Physik, 1926, 7, 105.
8. Kröger, C. *Glastechnische Berichte,* 1953, 26 (7), 202 –14
9. Lakatos T, Johansson L G. *Glass Technology*, 1972, 13 (3), 88.
10. Alves J. A et al., *Materials Research*, 2014, V. 17 (1), 213.
11. Bottinga Y et al., *Am. J. Sci.,* 1972, 272 (5), 438.
12. Vogel W. Glass chemistry, Berlin, (1994) Springer-Verlag.
13. Kucuk A., Clare. A. G & al. *Glass Technol.*, 1999, 40 (5), 149.
14. Choudhary M K, Potter R M. Heat Transfer in Glass-Forming Melts, Boca Raton: CRC. (2005).
15. Mazurin O V, Prokhorenko O A. Electrical conductivity of glass melts, in: Properties of Glass-Forming Melts. Boca Raton: CRC. (2005).
16. Fluegel A. *Glass Technol.: Eur. J. Glass Sci. Technol. A*, 2007, 48 (1), 13.
17. Fluegel A. *J. Am. Ceram. Soc.,* 2007, 90 (8), 2622.
18. Dreyfus C. *J. Non-Cryst. Solids,* 2003, 318, 1–2, 63.
19. Hanni J B, Pressly, E & al. *J. Mater. Sci.,* 2005, 20 (12), 3346.
20. Huff N T, Call A D. *J. Am. Ceram. Soc.*, 1973, 56 2, 55.
21. Fluegel A. *Glass Technol. : Europ. J. Glass Sci. Technol. A,* 2007, 48, 1 13.
22. Bingham P A, Hand R J & al. *J. Non-Cryst. Solids*, 2009, 355 (28-30) 1526
23. Fluegel A. *Glass Technol.: Eur. J. Glass Sci. Technol. A*, 2009, 50 (1), 25.
24. Lide D R. CRC Handbook of Chemistry and Physics, 90th ed., CRC Press, New York, 2009.
25. Bishop C, Neural Networks for Pattern Recognition, Oxford University Press, 1995.
26. Blume R, Drummond III C, *J. Am. Ceram. Soc.,* 2002, 5 (5), 1070.
27. Gehlhof G, Thomas M. Z, *Techn. Phys.,* 1925, 5 , 44; 1926, 7, 105
28. Gehlhof G, Thomas M. Z, Lehrbuch der techn. Physik, Barth-Verlag, Leipzig, 1924, p 376.
29. Appen A. A. Glass Chemistry, Leningrad, 1959.
30. Gan Fuxi, *Sci. Sinica,* 1963, 1, 1365.
31. Gan Fuxi , *Sci. Sinica,* 1974, 7, 533.
32. Demkina L. I. Physicochemical Principles of the Manufacture of Optical Glass, Ed. Khimia, Leningrad, 1976.

33. Priven A. I, *Glass Technol.,* 2004, 45 (6), 244.
34. Priven A. I, et al., *Glass Technol.,* 2003, 4, 156.
35. Botinga Y Weill P & all. Thermodynamic modelling of silicate melts in Thermodynamics of minerals and melts, Ed. R. C. Newton, Springer-Verlag, Heidelberg, 1981, p. 207–245.
36. Nemilov S. V. Thermodynamic and kinetic aspects of the vitreous state, CRC Press, Boca Raton, 1995.
37. Pelton A. D, Blander M. *Metallurg. Trans. B*, 1986, 17B (4), 805.
38. Pelton A. D, Wu P. *J. Non-Cryst. Solids*, 1999, 53 (1–3), 178.
39. Conradt R.Z. *Glastech. Ber. Glass Sci. Technol.,* 1994, 7 (11), 304.
40. Conradt R. Z. *Metall./Mater. Res. Adv. Tech.,* 2001, 9 (10), 1158.
41. Björkvall J, Sichen Du et al., *Glass Phys. Chem.,* 2001, 7 (2), 132.
42. Vedishcheva N. M, Shakhmatkin B A. *J. Non-Cryst. Solids*, 1994, 171 (1), 1.
43. Shakhmatkin B. A., Vedishcheva N. M & al. *J. Non-Cryst. Solids,* 1994, 177 (1), 249.
44. Vedishcheva N. M, Shakhmatkin B.A & al. *J. Non-Cryst. Solids*, 1996, 19, 239.
45. Shakhmatkin B. A., Vedishcheva N.M & al. *J. Non-Cryst. Solids*, 2001, 93-95, 220.
46. Shakhmatkin B. A. Vedishcheva N.M & al. *J. Non-Cryst. Solids*, 2001, 93-95, 312.
47. Besmann T. M & all, *Materials Research Society Symp. Proc.*, 1999, 55, 383.
48. Spear K. E, Besmann T. M, Beahm E. C. *MRS Bull.*, 1999, (4), 37.
49. Besmann, T. M. , Spear, K. E. *J. Am. Ceram. Soc.*, 2002, 5 (12), 2887.
50. Allendorf M. D, Spear K. E. *J. Electrochem. Soc.*, 2001, 1 (2), B59.
51. Minaev V. S, Petrova V. Z. & al. *Glass Phys. Chem*., 2004, 30 (3), 215.
52. Tischendorf B. C et al., *J. Non-Cryst. Solids*, 2003, 31, (2–3), 261.
53. Kresse G. *J. Non-Cryst. Solids*, 2002, 31, 52.
54. Cormack A. N, Du Jincheng. *J. Non-Cryst. Solids*, 2001, 29 3–295, 283.
55. Roula A, Boudeghdegh K, Boufafa N, Cerâmica 2009 (55) 206-208.