Study of a Mixed Alkaline–Earth Effect on Some Properties of Glasses of the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ System

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In the present work, we studied a “Mixed Alkaline–Earth Effect”, i.e. the non-linear behaviour showed by the glass transition temperature as well as by the compressive strength of glasses of the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system, when a part of the CaO contained in them was substituted by a BaO/SrO mixture, in variable molar proportions. An important factor for the occurrence of this phenomenon was the difference in atomic weight, ionic radii and field strength of the Ba^{2+} and Sr^{2+} ions in comparison with those corresponding to the Ca^{2+} ion. Another factor considered was the likely occurrence of a microphase separation caused by the addition of BaO and/or SrO , together with the presence of F^- and Mg^{2+} in the glasses. Other glass properties studied as a function of the CaO substitution level were density, glass molar volume, oxygen molar volume, packing fraction, and chemical resistance in neutral, basic and acidic aqueous media. In general, the structural reinforcement of the glass network caused by the partial substitution of CaO by a BaO/SrO mixture was accompanied by an improvement in the alkaline resistance of the materials, which were found to be suitable for applications in corrosive environments, especially in basic media.

Keywords: Mixed alkaline–earth effect; $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system; glass properties.

Estudio de un efecto alcalinotérreo mixto sobre algunas propiedades de vidrios del sistema $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$

En el presente trabajo, se estudia el comportamiento no lineal mostrado por la temperatura de transición vítrea y por la resistencia a la compresión de vidrios del sistema $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$, cuando una parte del CaO contenido en los mismos es sustituido por una mezcla de BaO/SrO , en relación molar variable. Factores importantes para que se de este comportamiento son la diferencia entre pesos atómicos, radios iónicos e intensidad de campo de los iones Ba^{2+} y Sr^{2+} y los del propio ión Ca^{2+} . Otro factor considerado ha sido la probable existencia de una separación de microfases originada por la adición de BaO y/o SrO , junto con la presencia de flúor y magnesio en los vidrios. Otras propiedades estudiadas, en función del CaO sustituido, han sido la densidad, el volumen molar del vidrio, el volumen molar del oxígeno, la fracción de empaquetamiento, y la resistencia química en medios acuosos neutros, básicos y ácidos. En general, el refuerzo estructural del retículo vítreo causado por la sustitución parcial del CaO por una mezcla de BaO/SrO viene acompañada por una mejora en la resistencia alcalina, lo que hace que estos materiales sean adecuados para aplicaciones en ambientes corrosivos y especialmente en medios básicos.

Palabras clave: Efecto alcalinotérreo mixto; sistema $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$; propiedades de los vidrios.

1. INTRODUCTION

When the composition of a glass is altered by the gradual substitution of an alkaline ion (such as Na^+) by another alkaline ion (such as K^+), usually the glass properties which depend on the mobility of the modifier ions show a non-linear behaviour, acquiring either a maximum or a minimum value at a certain level of substitution. This is commonly associated with the occurrence of processes of viscous flow, ion exchange, electric conductivity, dielectric loss, chemical attack, and mechanical or thermal relaxation, and it is more pronounced at larger differences in the radii of the exchanged alkaline ions. Other glass properties such as density and thermal expansion coefficient are affected to a lesser extent. This phenomenon is known as “Mixed Alkaline Effect” (1), and its occurrence has been attributed to structural, thermodynamic and electrodynamic factors, as well as to changes in the

transport mechanism of ions within the glass network, among other causes (1-3). A similar phenomenon can be observed when an alkaline cation is substituted by a non-alkaline cation having the same valence, which is known as “Mixed Ion Effect” (3). It is also known (4-5) that the addition of alkaline-earth modifier cations such as Mg^{+2} , Ca^{+2} , Ba^{+2} or Sr^{+2} can affect considerably the “Mixed Alkaline Effect” occurring in a glass, and although the literature (6-7) gives some examples of anomalies (non-linear behaviour) observed on the properties of some glasses as a result of the gradual substitution of an alkaline-earth modifier by another oxide of the same nature, only very recently the existence of a “Mixed Alkaline–Earth Effect” has been recognized (8).

In the present work, we studied a “Mixed Alkaline–Earth Effect” affecting some properties of glasses of the CaO-MgO-

Al_2O_3 - SiO_2 system, which was caused by a partial substitution of CaO by BaO/SrO mixtures. The glass properties considered in this study were density, glass molar volume, oxygen molar volume, packing fraction, glass transition temperature, compressive strength and chemical resistance in neutral, basic and acidic aqueous media. The studied glasses were intended to be used later on for the production of glass-ceramics containing diopside-type pyroxenes [$\text{CaMgSi}_2\text{O}_6$] and monocelsian [$\text{BaAl}_2\text{Si}_2\text{O}_8$] as main crystalline phases, aiming to take advantage of the good mechanical properties of both phases, as well as of the good chemical resistance of the former and of the low thermal expansion coefficient of the latter (9,10), for possible structural applications. The results obtained for the studied glass-ceramic materials will be reported separately. It is worth mentioning that only one work has been found in the literature involving a study similar to a certain extent to ours. Barbieri et al. (11) studied the microstructure and thermal properties of glass-ceramics obtained from glasses belonging to the RO-MgO- Al_2O_3 - SiO_2 quaternary system, where R= Ca, Sr, Ba or Zn. Although in those glasses CaO was gradually substituted by SrO, BaO or ZnO, the mentioned authors did not observe the occurrence of a "Mixed Alkaline-Earth Effect" like the one reported in the present work. This is likely due to differences in the compositions of the glasses studied in both cases. We intended to produce glasses suitable for the formation of diopside as main crystalline phase, instead of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), during a posterior thermal treatment. It has been reported (12) that glass-ceramics based on the former phase are mechanically stronger than those based on the latter. The results reported in the present work could be particularly useful for those researchers interested in the production of glasses and glass-ceramics from recycled raw materials such as TV glass tubes, which contain BaO and SrO in their chemical composition (13). Materials similar to those reported here could also be obtained from siliceous industrial byproducts (14) combined with natural mineral resources containing Ba and/or Sr, which is being currently investigated in our laboratory.

2. EXPERIMENTAL WORK

2.1 Glass compositions

Sixteen glass compositions were considered, all of which corresponded to the general formula $\text{XZ-6CaF}_2\text{-5Al}_2\text{O}_3\text{-12MgO-(23-X)CaO-54SiO}_2$, where $X = 0, 3, 6$ and $9 \text{ mol}\%$; Z corresponds to BaO/SrO mixtures having molar ratios of 1/0, 0/1, 1/1, 2/1 or 1/2. These compositions were designed in such a way as to produce, during a posterior crystallization thermal treatment, diopside-type pyroxenes [$\text{CaMgSi}_2\text{O}_6$] and monocelsian [$\text{BaAl}_2\text{Si}_2\text{O}_8$] as main crystalline phases, plus a small amount of a residual glass. Since the latter was expected to act as a bonding phase for diopside and monocelsian in the glass-ceramics, it was expected to contain SiO_2 , Al_2O_3 , CaO and BaO/SrO, with $\text{SiO}_2/\text{Al}_2\text{O}_3 > 1$, according to the Loewenstein's rule or "aluminium avoidance principle", in order to ensure that Al^{3+} acquires a predominantly tetrahedral coordination. A ratio $\text{Al}_2\text{O}_3/\text{CaO} < 1$ was also desired in order to obtain good chemical resistance and mechanical strength in the residual glass (15,16). On the other hand, CaF_2 was employed as a flux and as a nucleating agent (17) in order to promote the bulk crystallization of diopside, since this phase is known to have

TABLE I. CHEMICAL COMPOSITION OF THE STUDIED GLASSES (MOL%). ALL GLASSES CONTAINED 54% SiO_2 , 12% MgO , 5% Al_2O_3 AND 6% CaF_2 .

BaO/SrO molar ratio	Sample	CaO molar substitution (X)	CaO	BaO	SrO
---	Ref.	0	23	---	---
1/0	1	3	20	3	---
	2	6	17	6	---
	3	9	14	9	---
0/1	4	3	20	---	3
	5	6	17	---	6
	6	9	14	---	9
1/1	7	3	20	1.5	1.5
	8	6	17	3	3
	9	9	14	4.5	4.5
2/1	10	3	20	2	1
	11	6	17	4	2
	12	9	14	6	3
1/2	13	3	20	1	2
	14	6	17	2	4
	15	9	14	3	6

a strong tendency to crystallize at the glass surface (12). SrO was employed as a stabilizing agent for monocelsian, since it is known (18) that hexagonal celsian, or hexacelsian, tends to be the predominant phase formed at high temperatures. Then, when this phase is cooled down to 300°C it suffers a fast structural transformation into an orthorhombic form, with an associated volume change of $\sim 3\text{-}4\%$. This gives rise to the formation of microcracks which affect negatively the mechanical properties of the material, particularly when it is subjected to thermal cycles under aggressive environments.

Throughout this work, the composition corresponding to the glass without BaO/SrO additions ($X = 0$) is referred to either as reference composition or as reference glass. This composition was formulated with an excess of $9 \text{ mol}\%$ CaO with respect to the amount required for the formation of diopside with all the MgO contained in the batch mixture. The other fifteen glass compositions studied resulted from the gradual substitution of the mentioned CaO excess by a BaO/SrO mixture, according to the formula given above. All glass compositions studied are given in detail in Table I.

2.2 Glass preparation

The raw materials employed were silica sand (purity of $99.98 \text{ wt}\%$, average particle size of $110\mu\text{m}$, MERASI, Mexico), alumina (HPA-0.5, purity of $99.99 \text{ wt}\%$, average particle size of $0.75\mu\text{m}$, Sasol, EUA), dolomite ($\text{CaMg}(\text{CO}_3)_2$, with $\sim 3 \text{ wt}\%$ of CaCO_3 as main impurity, average particle size of $35\mu\text{m}$, Química del Rey, Mexico), calcite (CaCO_3 , purity of $99.6 \text{ wt}\%$, average particle size of $45\mu\text{m}$, Materiales La Gloria, Mexico), fluorite (CaF_2), with $10.3 \text{ wt}\%$ SiO_2 , $2.2 \text{ wt}\%$ Al_2O_3 and $19.8 \text{ wt}\%$ CaCO_3 as main impurities, average particle size of $30\mu\text{m}$, Materiales La Gloria, Mexico), BaCO_3 (purity of $99.43 \text{ wt}\%$, average particle size of $3\mu\text{m}$, Solvay, Mexico) and SrCO_3 (purity of $97.86 \text{ wt}\%$, average particle size of $4\mu\text{m}$, Solvay, Mexico). The chemical analysis of the raw materials was carried out by atomic absorption, plasma emission and x-ray fluorescence techniques. Their mineralogical composition was determined by x-ray diffraction and their particle size was

measured by the laser scattering method.

Previously to the glass melting, suitable weight proportions of the raw materials were mixed and homogenized for 1h in a ball mill. After that, the prepared batch mixtures were molten at 1450°C for 1h in a Pt crucible using a high temperature electric furnace (BF51433 PC-1Lindberg/blue M). Then, the molten glass was poured on a stainless steel plate or inside a graphite mold in order to obtain samples for mechanical testing. Both the stainless steel plate and the graphite mold were pre-heated at 600°C. After casting, the glasses were annealed using a Thermolyne F62700 high temperature electric furnace, which was set at a temperature of 600°C, using subsequently a cooling rate of 5°C/min during the first hour and of 1°C/min during the next nine hours. A SEM/EDS analysis allowed us to verify that, in general, the obtained glasses had a chemical composition within ~5% with respect to their nominal composition, except for the case of F, which could not be analyzed with a suitable accuracy by using this technique. However, Green et al. (19) pointed out that the loss of F due to the volatilization of silicon tetrafluoride (SiF_4) during glass melting can be inhibited by the addition of suitable amounts of aluminum and basic modifier oxides, in such a way that at $\text{Al}/\text{F} > 1$ the loss of F can be neglected. Thus, since all compositions studied in the present work had an initial Al/F ratio of ~ 0.8, it was assumed that only a small loss of F occurred before a value > 1 was achieved for this ratio. All glass samples were optically clear and the absence of crystallization in them was verified by x-ray diffraction by using a Philips 3040 x-ray diffractometer, with nickel-filtered $\text{Cu-K}\alpha$ radiation, operated at 40 kV and 30 mA, in the 2θ range of 10-80°.

2.3 Determination of density, glass molar volume, oxygen molar volume and packing fraction

The glass densities were determined by the Archimedes' principle by using a helium pycnometer (Multi-Pycnometer Quantachrome model MVP-D150E). Three density measurements were carried out per each glass composition; the obtained average values are reported in the present work. These measurements were carried out at room temperature using glass powder samples weighting 3g, with a particle size < 150 μm . Then, the measured glass densities were employed to calculate the molar volume (V_M), the oxygen molar volume (V_O) and the packing fraction (C) of the glasses. These parameters were calculated in order to obtain structural information for the studied glasses as a function of the level of CaO substitution. V_M was calculated by using the expression (1,20):

$$V_M = \frac{\sum x_i M_i}{\rho} \quad (1)$$

where x_i and M_i are the atomic fractions and the atomic weights of Si, Al, Ca, Mg, Ba, Sr, O and F, respectively, and ρ is the measured glass density. For the calculation of V_O , the following formula was used (1):

$$V_O = \frac{\sum x_i M_i}{\rho \sum x_i O_i} \quad (2)$$

where O_i represents the number of oxygen atoms forming part of each glass component. The term $\sum x_i O_i$ is equal to the atomic fraction of oxygen in the glass. All cations were assumed to be present as oxides, while F⁻ was assumed to be present as ion in the glass. Lastly, the packing fraction, C , was calculated according to the following expression (19,20):

$$C = \frac{V_{\text{ion total}}}{V_M} \quad (3)$$

$$V_{\text{ion total}} = \sum (N_v V_i f) \quad (4)$$

$$V_i = \frac{4}{3} \pi r_i^3 \quad (5)$$

where N_v is the Avogadro's number, r_i is the ionic radius ($\text{\AA}$) of a cation or an anion having a given coordination number in the glass, and f is a conversion factor from $\text{\AA}^3$ into cm^3 . The ionic radii used for the calculation of V_M , V_O and C , were chosen from those reported by Shannon (21), taking into account the probable coordination number of each ion in the glass network, which was determined from an analysis of the related literature (1, 15-16, 22-29). In this way, a coordination number of 4 was assumed for Si^{4+} and Al^{3+} , while a coordination number of 6 was assumed for Ca^{2+} , Mg^{2+} , Ba^{2+} and Sr^{2+} . Lastly, coordination numbers of 3 and 6 were assumed for F⁻ and O^{2-} , respectively.

2.4 Determination of the glass transition temperature

The glass transition temperature (T_g) of the studied glasses was determined by Differential Thermal Analysis (DTA), which was carried out up to a maximum temperature of 1400°C, employing a PERKIN ELMER DTA 7 apparatus, using platinum crucibles and a heating rate of 5°C/min, under an atmosphere of still ambient air.

2.5 Determination of ultimate compressive strength

The ultimate compressive strength (hereafter simply referred to as compressive strength), i.e. the maximum stress that the studied glasses could withstand before they failed in compression, was determined by dividing the maximum load applied in compression by the original cross-sectional area of the testing samples. In these tests, we employed cylindrical samples with a height of 10mm and a diameter of 10mm, i.e. having a diameter/height ratio equal to one. These samples were obtained by casting the molten glass into pre-heated graphite molds. Three tests were carried out per each glass composition, the obtained average values are reported in the present work. For these tests, a CONTROLS press fitted with a 250 KN cell was used, employing a load application rate of 3 MPa/s.

2.6 Determination of chemical resistance

The chemical resistance of the studied glasses submerged in neutral, basic or acidic aqueous media, was determined according to the Russian GOST 10134-62 standard, under the

TABLE II. CONDITIONS EMPLOYED IN THE CHEMICAL RESISTANCE TESTS, ACCORDING TO THE RUSSIAN GOST 10134-62 STANDARD

Experimental Conditions	Aqueous Solution	
	H ₂ O	NaOH, HCl
Sample weight (g)	2	3
Solution concentration (N)	-	1
Time of test (h)	1	3
Particle size	< 150 μm	
Solution temperature ($^{\circ}\text{C}$)	96	
Time of drying (h)	24	
Drying temperature ($^{\circ}\text{C}$)	80	

conditions detailed in Table II. Again, three tests were carried out per each glass composition, and the obtained average values are reported in the present work. In all cases, pre-weighted powdered glass samples were kept submerged in the testing aqueous solutions inside sealed PET containers, without stirring, for time intervals and at temperatures established by the mentioned standard, inside a constant-temperature water bath. As soon as the tests were finished, the solid residues were separated from the liquid solution by filtration, and subsequently dried and weighted. This was made in order to determine the corresponding weight losses. Finally, some of the neutral, basic and acidic aqueous solutions that were used in the tests were analyzed by ICP and atomic absorption techniques in order to determine the kind of chemical attack received by the tested glass samples. These solutions corresponded to some of the tests for which the largest weight losses were observed. For each kind of aqueous solution employed, the solution that was in contact with the reference glass ($X = 0$) was analyzed, together with three other solutions that were in contact with glasses having CaO substitution levels of $X = 3, 6$ and 9 , in all cases with randomly chosen BaO/SrO molar ratios.

The Russian GOST 10134-62 standard is similar to the DIN 12116-1976, DIN 52322-1976, ISO 695-1975 and UNE 43705-76 standards, all of which are mentioned in Ref. (1). This standard procedure was employed due to its simplicity, since it can be used for the determination of the chemical stability of glass either in neutral, acidic or basic media, while the other standardized procedures are usually applied only for a specific attacking medium. When the Russian GOST 10134-62 standard is employed, the results are expressed as percentage of weight loss, while they are expressed as weight loss, or half weight loss, per surface area unit, when one of the other standardized procedures are used.

3. RESULTS AND DISCUSSION

3.1 Density, glass molar volume, oxygen molar volume and packing fraction

Figures 1-4 show the effect of the partial substitution of CaO by a BaO/SrO mixture on the density (ρ), molar volume (V_M), oxygen molar volume (V_O) and packing fraction (C) of the studied glasses. It is worth mentioning that the glass densities were measured with a standard error of 0.025%, and since the corresponding error bars were very small, it was decided not to represent them in Figure 1. Similarly, since the error involved in the calculation of V_M , V_O and C basically

Fig. 1- Effect of the partial substitution of CaO by a BaO/SrO mixture on the density of the studied glasses.

Fig. 2- Effect of the partial substitution of CaO by a BaO/SrO mixture on the glass molar volume (V_M). Fig. 3-Effect of the partial substitution of CaO by a BaO/SrO mixture on the oxygen molar volume (V_O). Fig. 4- Effect of the partial substitution of CaO by a BaO/SrO mixture on the glass packing fraction (C).

TABLE III. ATOMIC WEIGHT, IONIC RADII AND FIELD STRENGTH OF Ca^{2+} , Sr^{2+} AND Ba^{2+} .

Ion	Atomic weight	Ionic radii (Coordination 6) [Å], Shannon (20)	Field strength, Fernández- Navarro (1)
Ca^{2+}	40.08	1.00	0.33
Sr^{2+}	87.62	1.18	0.27
Ba^{2+}	137.33	1.35	0.24

depended on the error in the density measurements, the error bars were also omitted in Figures 2-4.

As can be seen in Figures 1-3, ρ , V_M and V_O increased with increasing substitution level of CaO by a BaO/SrO mixture. In all cases, the largest and the smallest effects corresponded to the addition of pure BaO and pure SrO, respectively. The density determined for our reference glass (2.74 g/cm^3) is similar to the value of 2.75 g/cm^3 reported by Leonelli et al. (30) for glasses of the $\text{MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2$ system. Salman and Gharib (7) also observed an increment in density, with a simultaneous increment in the index of refraction and a simultaneous decrease in the thermal conductivity and viscosity, when CaO was gradually substituted by BaO in a glass with a composition in weight of 20%Na₂O, 15%CaO and 65% SiO₂. Barbieri et al. (31) pointed out that the gradual substitution of BaO by CuO, Fe₂O₃ or MnO in glasses of the BaO-MgO-Al₂O₃-SiO₂ quaternary system, caused changes in the glass density which were proportional to the mass of the entering cation, in relation with the masses of the ions already present in the material. According to this, in the present work when Ca^{2+} was partially substituted by Ba^{2+} and/or Sr^{2+} , both of which have atomic weights higher than that of Ca^{2+} , see Table III, the glass density increased, with the largest increment corresponding to the addition of pure Ba^{2+} , which is the heaviest cation among all three.

The behavior of V_M and V_O indicates that an expansion of the glass network took place due to the partial substitution of CaO by a BaO/SrO mixture. This was confirmed by the behavior of the packing fraction (C), Figure 4, which decreased with increasing CaO substitution level. This was more pronounced for the addition of pure BaO, and less pronounced for the addition of pure SrO.

According to Eq. (3), when the values of $V_{\text{ion total}}$ and V_M approach each other, C approaches a value of 1, and the so-called free volume (total interstitial space) approaches a value of zero (20). However, when V_M increases due to an expansion of the glass network, C decreases, with a consequent increment in the free volume. Thus, the fact that in the present work the value of C decreased when CaO was partially substituted by a BaO/SrO mixture, indicates that such substitution caused an increment in the free volume of the glass. The latter phenomenon was related to differences in the field strength and polarizing power of the exchanged cations. Both parameters decrease in the order $\text{Ca} > \text{Sr} > \text{Ba}$, see Table III. Thus, when Ca^{2+} was substituted by a cation having smaller field strength and polarizing power, such as Ba^{2+} or Sr^{2+} , V_M and V_O increased probably due to a weaker attraction between the latter cations and the non-bridging oxygens (NBO's). In other words, the expansion and the concomitant decrease in compactness suffered by the glass structure were both caused by an increased distance between the modifying cations and the NBO's. The fact that the largest increase in V_M and V_O corresponded to the addition of pure Ba^{2+} , which is the cation

having the smallest field strength of all three, agrees with the findings of Barbieri et al. (31), who observed that V_O decreased when Ba^{2+} was substituted by other cations having higher field strength ($\text{Fe}^{3+} = 0.75$, $\text{Cu}^{2+} = 0.52$ and $\text{Mn}^{2+} = 0.42$, all of them in coordination 6).

3.2 Glass transition temperature and compressive strength

In the present work, for all the studied glasses, a non-linear behavior was observed in both glass transition temperature (T_g), Figure 5, and compressive strength, Figure 6, when CaO was partially substituted by a BaO/SrO mixture. The error involved in the determination of T_g was estimated to be $\pm 5^\circ\text{C}$, while the compressive strength was measured with a standard error of $\sim 5\%$. In both cases, the error bars were omitted in the corresponding graphs, since in general they were very small.

Figure 5 shows that T_g decreased with increasing substitution level of CaO by a BaO/SrO mixture, for all BaO/SrO molar ratios employed. The largest and the smallest total diminutions in T_g corresponded to the addition of pure BaO and pure SrO, respectively. In all cases, the smallest decrements in T_g took place at CaO substitution levels in the range of $X = 0 - 3$.

Fig. 5- Effect of the partial substitution of CaO by a BaO/SrO mixture on the glass transition temperature (T_g).

The results published by Fernández-Navarro (1), Greene et al. (19) and Hu and Tsai (32), can help us to explain the diminution in T_g observed in the glasses studied in the present work as a function of the CaO substitution level.

Hu and Tsai (32) studied the effect of the addition of BaO, in the range of 0-12 mol%, on the crystallization of glasses with cordierite composition ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$). These authors observed a decrease in T_g , especially at BaO levels above ~ 4 mol%, which was attributed to the formation of NBO's due to the network modifying role of Ba^{2+} , with a concomitant decrease in the glass viscosity. However, they also mentioned a likely occurrence of a separation of microphases in their glasses due to the large difference existing between the ionic radii of Mg^{2+} and Ba^{2+} . The occurrence of this phenomenon could also explain the decrease in T_g observed by them at BaO levels above 4 mol%. In fact, it is known (1) that phase separation facilitates the crystallization of glass, which is related with a decrease in T_g .

Greene et al. (19) studied the effect of the gradual substitution of BaO by K_2O on the glass molar volume, fractional glass compactness, microhardness, glass transition temperature and thermal expansion coefficient of glasses of the

MgF₂-K₂O-BaO-MgO-Al₂O₃-B₂O₃-SiO₂ system. In these glasses, MgO was also partially substituted by MgF₂. The mentioned authors observed, for boron free glasses, that T_g decreases with increasing substitution of BaO by K₂O, for molar fluorine substitution levels of 2-2.5. They indicated that the effects of alkali/alkaline earth modifier cation substitutions on the glass structure and properties can be analyzed either from the point of view of the replacement of NBO-Ba-NBO bridges by NBO-K terminations, where NBO = Non-Bridging Oxygen, or from the point of view of changes in cation field strength. They gave values of 110 and 105 nm² for the cation field strength of Ba²⁺ and 2K⁺, respectively, and since both values are very close to each other, the diminution in T_g observed at the mentioned fluorine substitution levels was attributed to the replacement of NBO-Ba-NBO bridges by NBO-K terminations, with a consequent decrease in the level of association of the glass network and in the rigidity of the latter. Further fluorine substitutions resulted in less significant T_g decreases, except when all BaO was substituted by K₂O, when an abrupt decrease in T_g took place. This was attributed to a likely occurrence of a phase separation in the glass, caused by the joint action of Ba²⁺ and F⁻, which resulted in the formation of a fluorine and modifier (K, Ba and Mg) rich phase plus an aluminosilicate rich phase.

In the present work, since the exchanged cations were all divalent, the replacement of NBO-M^{II}-NBO bridges by NBO-M^I terminations did not occur (M^{II} and M^I are divalent and monovalent modifier cations, respectively), and thus, our glasses had always essentially the same crosslinking density. In addition to that, the total concentration of the exchanged divalent modifier cations (Ca²⁺ + Ba²⁺ + Sr²⁺) was kept constant at all times, with variations only in their relative proportions. This indicates, together with the fact that the concentration of the other glass constituents was not varied, that the number of NBO's can be safely assumed to be constant in our glasses. Thus, the decrease in T_g observed by us with increasing CaO substitution levels cannot be attributed to a diminution in the level of association of the glass network or to the creation of an increased number of NBO's. On the other hand, the trends observed in the values of V_{M'}, V_O and C indicate that a change in the field strength of the cations is an important factor determining the behavior of T_g. The diminution observed in the latter parameter could be explained based on the weaker attraction existing between the Sr²⁺ or Ba²⁺ ions and the NBO's, due to the fact that both modifier cations have smaller field strength and polarizing power when compared to the Ca²⁺ ions (Table III). Another contributory factor to the diminution in T_g observed in our glasses could be the likely occurrence of a separation of microphases, which could be promoted by the simultaneous presence of Ba²⁺, F⁻ and other ions, as will be explained in detail later on.

The observation that the smallest decrements in T_g took place at CaO substitution levels of X = 0-3, could be related to a "stuffing effect" of Ba taking place in the glass network. The occurrence of this effect has been proposed by Hu and Tsai (32). These authors reported that BaO contents up to ~4 mol% suppressed the crystallization of α-cordierite in their glasses. It was suggested that since the Ba²⁺ ion is very big, see Table III, it has a limited mobility in the glass network, blocking the movement of the Mg²⁺ ions, and therefore inhibiting the formation of α-cordierite. The introduction of Ba into the glass also raises its viscosity, and since the kinetics of growth of α-cordierite strongly depends on this property,

an increment in it slows down appreciably the formation of the mentioned phase due to a decreased diffusivity of Mg²⁺. Thus, the slight increment in T_g observed by them at BaO additions in the range of 0 ~ 4 mol% was associated with a corresponding increment in the glass viscosity. The results of Hu and Tsai (32) indicate that at low concentrations BaO acts as a stabilizer for the glass network. This makes the glass more difficult to crystallize due to increased network stiffness, with a consequent increase in the glass viscosity and transition temperature. In fact, according to Fernandez-Navarro (1), BaO is considered to be a glass network stabilizer. This author also mentions that the glass viscosity increases with the addition of BaO due to the big size of the Ba²⁺ ions.

In the present work, it is very likely that at low CaO substitution levels a "stuffing effect" of Ba²⁺, similar to that proposed by Hu and Tsai (32), affected the properties of the studied glasses, with an analogous effect being caused by Sr²⁺. This would explain the small decrement observed in T_g for glasses with CaO substitution levels of X = 0-3, independently of the BaO/SrO molar ratio in the added mixture. At higher CaO substitution levels the change in the cation field strength as well as the likely occurrence of a microphase separation become the predominant factors. As a result, a larger decrease in T_g is observed for X > 3.

According to Figure 6, the compressive strength of the studied glasses increased for the CaO substitution levels of X = 0-6, reaching a maximum value at X = 6, whose magnitude increased with increasing BaO proportion in the added BaO/SrO mixture, see Figure 7. Then, the compressive strength decreased for X > 6, achieving at X = 9 values which were similar to or slightly higher than those obtained for the reference composition (X = 0).

Fig. 6- Effect of the partial substitution of CaO by a BaO/SrO mixture on the compressive strength of the studied glasses.

Saddeek (33) mentions that an increased stiffness results in an increment in the compressive strength of glass, thus, the "stuffing effect" of Ba²⁺ and Sr²⁺ could also explain the increment observed in this property at BaO/SrO mixture additions in the range of X = 0-6. Later on, the compressive strength decreased likely due to the occurrence of a microphase separation in the glasses.

The compressive strength of the studied glasses increased from an initial value of ~60 MPa at X = 0, up to a maximum value at X = 6, which was of ~190 MPa for the BaO/SrO molar ratios of 1/0 and 2/1, and of ~135 MPa for the BaO/

Fig. 7- Variation in the compressive strength of the studied glasses at constant CaO substitution levels.

SrO molar ratio of 1/1. For the case of the BaO/SrO molar ratios of 1/2 and 0/1, the maximum compressive strength achieved was ~115 MPa, at the same CaO substitution level. Later on, as already mentioned, at $X = 9$ the compressive strength decreased to values which were similar to or slightly higher than that corresponding to the reference glass. As can be appreciated, the maximum increment observed in the compressive strength was substantial in all cases. This was ~320% for both BaO/SrO molar ratios of 1/0 and 2/1, and ~225% for the BaO/SrO molar ratio of 1/1, while the corresponding increment was ~190% for both BaO/SrO molar ratios of 1/2 and 0/1. Thus, it is clear that the effect on the compression strength was more pronounced as the proportion of BaO increased in the added BaO/SrO mixture. This "mixed alkaline-earth effect" constitutes a phenomenon not reported previously by other researchers.

Finally, since both the glass transition temperature (T_g) and the compressive strength of the studied glasses seem to have been strongly affected by the likely occurrence of a separation of microphases in our glasses, and since the presence of F^- could have an important contribution to the latter, it is worth discussing some relevant structural and physicochemical aspects of F^- .

It is well-known (1) that F^- can substitute O^{2-} in the glass network because both anions have similar ionic radii. However, the difference in their charges originates broken links which interrupt the continuity of the glass network:

As a result, the glass viscosity decreases. The modifier cations accommodate themselves near the structural discontinuities, and the aperture of the Si-O links produces a local structural relaxation as well as a diminution in the surface tension. In this way, two zones having different compositions are formed with increasing fluoride addition, one of which is rich in silica, while the other one is rich in modifier cations and F^- ions. Then, these zones separate forming two immiscible liquid phases, one of which may evolve later on into a crystalline phase. At F^- levels above ~4% the glass can become opaque due to the formation of alkaline or alkaline earth fluoride microcrystals. This is commonly preceded by a process of phase separation. The main factor determining the glass opacification is the fluoride concentration in the glass; however, the cation present in the latter also affects the

phase separation and crystallization processes. In general, the occurrence of both phenomena becomes more favorable with increasing cation field strength. In fact, even in the absence of F^- ions in the glass, the phase separation tendency increases with decreasing ionic radius and with increasing cation field strength, which occurs in the order $\text{Ba} < \text{Sr} < \text{Ca} < \text{Mg}$ (1). A tendency of the separated phase to become more enriched in the modifier cation also exists in the same order. All of this has been well documented for the case of binary MO-SiO_2 systems, where $\text{M} = \text{Ba}, \text{Sr}, \text{Ca}$ or Mg .

In aluminosilicate glasses, the substitution of O^{2-} by F^- ions causes a replacement of some of the $\equiv \text{Al} - \text{O} - \text{Si} \equiv$ crosslinks by $\equiv \text{Al} - \text{F}$ terminations in the glass network, with a consequent decrease in the crosslinking density (19). However, for the case of aluminosilicate glasses containing Ba, Ca or Mg, Kiczinski et al. (29) observed that the number of F-modifier cation links increases with an increment in the cation field strength. This indicates that cations with higher field strength are able to compete more effectively with Al^{3+} in order to form links with the F^- ions. Mg is an extreme case in the sense that this cation is preferred over the Al^{3+} cations by the F^- ions. However, independently of the type of modifier cation, the formation of a small amount of Si-F links always takes place, which explains the diminution in viscosity observed whenever F^- is added to glass. In Mg-containing aluminosilicate glasses, it was also observed that the number of Al-F links increases with increasing $\text{Al}^{3+}/\text{Mg}^{2+}$ ratio. When $\text{Al}^{3+}/\text{Mg}^{2+} < 1$, only a few Al-F links are formed. Thus, in the present work it can be assumed that F^- can be found associated basically with Mg^{2+} , with a coordination number of 3. However, a small amount of Al-F links could also form. The formation of Mg-F links, together with the presence of cations such as Ba, Sr and Ca in our glasses, could favor the occurrence of a phase separation as well as a posterior crystallization process in them. This is supported by the work of Tulyaganov et al. (12) and by that of Lucas et al. (34). Tulyaganov et al. (12) pointed out that the catalytic effect of fluorides during the crystallization of pyroxene-based glass systems is due to an intensification of phase separation in liquid phase, which results in an enrichment of the segregated zones with the pyroxene component. For this reason, the formation of diopside-type solid solutions, rich in divalent metal oxides, occurs during the first stages of crystallization of fluoride-containing compositions. Lucas et al. (34) also mentioned that the alkaline earth oxides present in the glass composition act as mineralizers which favor the crystallization of pyroxene. It must be emphasized that no direct evidence of the occurrence of phase separation was observed in the present work, neither by XRD nor by SEM analyses, which could be due to the following reasons: a) the separated phase was amorphous, b) probably this phase was constituted by droplets of nanometric size, and c) probably this phase was present in very small levels in the glass.

3.3 Chemical resistance

According to Table IV, the glasses whose CaO content was partially substituted by a BaO/SrO mixture, after being subjected to the chemical resistance tests showed weight loss ranges of: 1) 2.65-2.85% in water, 2) 1.15-4.55% in the basic solution, and 3) 10.75-11.85% in the acidic solution. The corresponding weight losses of the reference glass were 2.83% in water, as well as 5.44% and 12.78% in NaOH and HCl aqueous solutions, respectively. Therefore, although the

TABLE IV. WEIGHT LOSS (%) IN GLASSES SUBJECTED TO THE CHEMICAL RESISTANCE TESTS. NUMBERS IN PARENTHESES INDICATE THE STANDARD DEVIATION OF THE MEASUREMENTS

Aqueous solution	CaO substitution level (X)	BaO/SrO molar ratio					
		Reference glass	1/0	2/1	1/1	1/2	0/1
H ₂ O	0	2.83 (0.03)					
	3		2.76 (0.01)	2.67 (0.01)	2.77 (0.02)	2.78 (0.03)	2.81 (0.03)
	6		2.70 (0.02)	2.77 (0.02)	2.72 (0.01)	2.75 (0.01)	2.82 (0.03)
	9		2.72 (0.02)	2.73 (0.04)	2.78 (0.01)	2.76 (0.02)	2.82 (0.03)
NaOH	0	5.44 (0.04)					
	3		3.63 (0.02)	3.98 (0.04)	4.24 (0.05)	4.43 (0.03)	4.53 (0.04)
	6		2.80 (0.02)	2.00 (0.03)	3.14 (0.03)	2.46 (0.03)	3.88 (0.02)
	9		1.19 (0.03)	1.51 (0.03)	2.16 (0.03)	1.80 (0.03)	2.01 (0.02)
HCl	0	12.78 (0.04)					
	3		11.39 (0.03)	11.48 (0.01)	11.06 (0.03)	11.84 (0.03)	11.66 (0.02)
	6		10.93 (0.03)	10.78 (0.02)	10.96 (0.02)	11.19 (0.03)	11.46 (0.02)
	9		10.82 (0.04)	10.96 (0.02)	11.12 (0.05)	11.22 (0.03)	11.30 (0.03)

partial substitution of CaO by a BaO/SrO mixture did not produce a substantial change in the chemical resistance of the glasses with respect to the neutral solution, an appreciable improvement was observed in this property when those glasses were immersed in the basic and acidic aqueous media, which was more pronounced for the case of the basic solution. As can be noticed, the reference glass had the largest weight losses for the three aqueous solutions employed. This was followed by the glasses with additions of pure SrO, while those with additions of pure BaO showed the best chemical resistance. On the other hand, an increase in the CaO substitution level in the $X = 3 - 9$ range tended to increase the chemical resistance of the glasses. In this way, the glasses with a CaO substitution level of $X = 9$ had the best chemical resistance, for all BaO/SrO molar ratios employed. This was more evident in the case of the basic and the acidic aqueous solutions. This result was expected, since a high Ca concentration in alkali-free glasses is commonly associated with poorer chemical resistance properties.

Table V shows the results obtained for the selected solutions that were chemically analyzed after the chemical resistance tests. As can be seen, for the case of the tests that were carried

out in water, comparable amounts of Si^{4+} and Mg^{2+} were leached from all glasses. However, while an appreciable amount of Ca^{2+} was leached from the reference glass, this did not happen in the glasses with partial substitution of CaO by a mixture of BaO/SrO, which showed instead a small release of Ba^{2+} and Sr^{2+} . On the other hand, in the case of the tests that were carried out in a NaOH aqueous solution, only Si^{4+} and Al^{3+} were leached from the reference glass, while in the CaO-substituted glasses the release of both ions was also observed, although in a much smaller proportion, together with the release of a small amount of Ba^{2+} and Sr^{2+} . In the latter glasses, the release of Si^{4+} and Al^{3+} tended to decrease with an increasing proportion of BaO in the added BaO/SrO mixture. Lastly, in the case of the tests that were carried out in a HCl aqueous solution, the leaching of all the analyzed ions was observed, which decreased in the order Si^{4+} , Ca^{2+} , Al^{3+} and Mg^{2+} . Meanwhile, in the CaO-substituted glasses the release of the same ions, together with the release of Ba^{2+} and Sr^{2+} , was observed to occur in the order Si^{4+} , Ca^{2+} , Al^{3+} , Ba^{2+} , Mg^{2+} and Sr^{2+} . For this kind of aqueous solution, the partial substitution of CaO by a BaO/SrO mixture had the effect of decreasing particularly the release of Si^{4+} and Ca^{2+} , with a smaller effect

TABLE V. RESULTS OF THE CHEMICAL ANALYSES CARRIED OUT FOR THE SOLUTIONS SELECTED AFTER THE CHEMICAL RESISTANCE TESTS.

Aqueous solution	BaO/SrO molar ratio	CaO substitution level (X)	Ion concentration (ppm)					
			Al	Mg	Ca	Ba	Sr	Si
H ₂ O	Ref.	0	---	4	46	---	---	52
	1/1	3	---	4	16	5	4	49
	1/1	6	---	4	14	4	5	55
	2/1	9	---	4	13	6	3	53
NaOH	Ref.	0	175	---	---	---	---	443
	1/2	3	95	---	---	10	8	384
	1/0	6	56	---	---	14	---	271
	1/1	9	49	---	---	9	4	216
HCl	Ref.	0	716	678	2872	---	---	2841
	2/1	3	594	510	655	691	491	666
	1/1	6	543	485	310	764	536	697
	0/1	9	703	628	1663	---	871	964

Note: --- indicates a concentration below the detection limit of the technique employed. The estimated standard error was ~3% for all measurements.

on the lixiviation of Al^{3+} , which was more pronounced at high proportions of BaO in the added mixture.

The chemical analysis of the solutions after the chemical resistance tests can provide a basis for the theoretical interpretation of the type of attack received by the glasses, which could be either by ion exchange or by network dissolution. If the ion/Si^{+4} ratio is found to be equal in both the solution and the glass, then the chemical attack occurs by network dissolution, otherwise the chemical attack takes place by ion exchange (35). As can be seen in Table VI, in all cases we have $(\text{ion/Si}^{+4})_{\text{glass}} \neq (\text{ion/Si}^{+4})_{\text{solution}}$, which indicates that the glasses are attacked by the ion exchange (leaching) mechanism. Since this is a less severe kind of attack compared to that occurring by the network dissolution mechanism, our results suggest that the glasses studied in the present work are suitable for applications in corrosive environments, especially in contact with basic media. The kinetics of the attack by ion exchange is controlled by the interdiffusion of ions in the glass, and for this reason a compositional gradient profile obeying Fick's second law is expected to be established at the glass surface, with a concentration of the ions increasing in the attacking solution as a function of $(\text{time})^{1/2}$ (20). This could not be verified in the present work since a constant test time was employed for each kind of attacking solution employed.

Lastly, our results related to the chemical resistance and the compressive strength of the studied glasses confirm the statement made by Fernández-Navarro (1) in the sense that, in general, any structural reinforcement of the glass network implies an improvement in the alkaline resistance of the material.

b) In all cases, the glass transition temperature (T_g) decreased with increasing CaO substitution level. For $X = 0 - 3$, the decrease in T_g was limited by a "stuffing effect" caused in the glass network by the big size of the Ba^{2+} and Sr^{2+} ions. At $X > 3$, the relatively small field strength of these cations, combined with the likely occurrence of a microphase separation in the glasses, caused a larger decrease in T_g . These factors also explained the increment observed in the compressive strength of the glasses for $X = 0 - 6$, as well as the diminution of the latter for $X > 6$. This property achieved a maximum value at $X = 6$, whose magnitude was substantial in all cases, increasing with increased proportion of BaO in the added BaO/SrO mixtures.

c) The chemical attack suffered by the glasses that were submerged in neutral, basic and acidic aqueous solutions, was found to be caused by an ion exchange mechanism. This suggests that these materials are suitable for applications in corrosive environments, especially in basic media.

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TABLE VI. ION/Si^{+4} RATIOS CALCULATED FOR THE TESTED GLASSES AS WELL AS FOR THE ANALYZED AQUEOUS SOLUTIONS.

Aqueous solution	BaO/SrO molar ratio	CaO substitution level (X)	$(\text{ion/Si}^{+4})_{\text{glass}}$					$(\text{ion/Si}^{+4})_{\text{solution}}$				
			Al/Si	Mg/Si	Ca/Si	Ba/Si	Sr/Si	Al/Si	Mg/Si	Ca/Si	Ba/Si	Sr/Si
H_2O	Ref.	0	0.179	0.193	0.608	---	---	---	0.08	0.88	---	---
	1/1	3	0.179	0.193	0.529	0.136	0.087	---	0.08	0.33	0.10	0.08
	1/1	6	0.179	0.193	0.45	0.272	0.174	---	0.07	0.25	0.07	0.09
	2/1	9	0.179	0.193	0.37	0.545	0.174	---	0.08	0.25	0.11	0.06
NaOH	Ref.	0	0.179	0.193	0.608	---	---	0.40	---	---	---	---
	1/2	3	0.179	0.193	0.529	0.091	0.116	0.25	---	---	0.03	0.02
	1/0	6	0.179	0.193	0.45	0.545	---	0.21	---	---	0.05	---
	1/1	9	0.179	0.193	0.37	0.409	0.261	0.23	---	---	0.04	0.02
HCl	Ref.	0	0.179	0.193	0.608	---	---	0.25	0.24	1.01	---	---
	2/1	3	0.179	0.193	0.529	0.182	0.058	0.89	0.77	0.98	1.04	0.74
	1/1	6	0.179	0.193	0.45	0.272	0.174	0.78	0.70	0.44	1.10	0.77
	0/1	9	0.179	0.193	0.37	---	0.522	0.73	0.65	1.73	---	0.90

4. CONCLUSIONS

a) The glass density (ρ), glass molar volume (V_M) and oxygen molar volume (V_O) increased with increasing CaO substitution level by a BaO/SrO mixture. The increase in density was related to the higher atomic weights of Ba^{2+} and Sr^{2+} , when compared to that of Ca^{2+} . The increase in V_M and V_O was due to an expansion of the glass network caused by an increment in the free volume, with a consequent decrease in the packing fraction (C). This was related to the smaller field strengths of Ba^{2+} and Sr^{2+} , when compared to that of Ca^{2+} .

REFERENCES

1. J. M^a. Fernández Navarro, El Vidrio, Consejo Superior de Investigaciones Científicas, 2^a Edición, Madrid, España (1991).
2. P. Maass, "Towards a theory for the mixed alkali effect in glasses", J. Non-Cryst. Solids 255, 35-46 (1999)
3. K. J. Rao, S. Kumar, "Multialkali phosphate glasses: A new window to understand the mechanism of ion transport", Current Science 85 (7), 945-955 (2003)
4. M. Todorović, L. Radonjić, "Study of the mixed alkali effect in glasses and its relation to glass structure and alkali earth ion content", Ceram. Int. 15 (6), 383-388 (1989)

5. J.-O. Byun, B.-H. Kim, K.-S. Hong, H.-J. Jung, S.-W. Leed, A. A. Izyneve, "Properties and structure of $\text{RO-Na}_2\text{O-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ ($\text{R} = \text{Mg, Ca, Sr, Ba}$) glasses", *J. Non-Cryst. Solids* 190 (3), 288-295 (1995)
6. K.-D. Kim, "Influence of $\text{BaO}/(\text{SrO}+\text{BaO})$ on melt properties in $\text{R}_2\text{O-RO-SiO}_2$ glasses for plasma display panel substrates", *Glass Technol.* 41 (5), 161-164 (2000)
7. S. M. Salman, S. Gharib, "Some physical properties concerning the thermal conductivity data of BaO-containing silicate glasses in relation to structure", *Thermochim. Acta* 82 (2), 345-355 (1984)
8. B. Roling, M. D. Ingram, "Mixed alkaline-earth effects in ion conducting glasses", *J. Non-Cryst. Solids* 265 (1-2), 113-119 (2000)
9. T. Kobayashi, K. Okada, T. Kuroda, K. Sato, "Osteogenic cell cytotoxicity and biomechanical strength of the new ceramic diopside", *J. Biomed. Mater. Res.* 37(1), 100-107(1997).
10. N. P. Bansal, "Solid state synthesis and properties of monoclinic celsian", *J. Mater. Sci.* 33 (19), 4711-4715 (1998)
11. L. Barbieri, C. Leonelli, T. Manfredini, M. Paganelli, G. C. Pellacani, "Microstructure and thermal properties in the $\text{RO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ ($\text{R} = \text{Ca, Sr, Ba, Zn}$) glass-ceramic systems", *Bol. Soc. Esp. Ceram. V.*, 31 [5] 27-32 (1992)
12. D.U. Tulyaganov, S. Agathopoulos, J.M. Ventura, M.A. Karakassides, O. Fabrichnaya, J.M.F. Ferreira, "Synthesis of glass-ceramics in the CaO-MgO-SiO_2 system with B_2O_3 , P_2O_5 , Na_2O and CaF_2 additives", *J. Eur. Bol. Soc. Esp. Ceram. V.*, 26, 1463-1471 (2006)
13. A. R. Boccaccini, M. Bücke, P. A. Trusty and J. Ma. Rincón, "Sintering behaviour of compacts made from Television Tube (TV) Glasses", *Glass Technol.* 38, 128-133 (1997)
14. M. Aineto and A. Acosta, "Las escorias de la central térmica GICC ELCOGAS como materia prima para la síntesis de materiales vitrocerámicos. Parte 1: Comportamiento en fusión de las escorias GICC y obtención del vidrio original", *Bol. Soc. Esp. Ceram. V.*, 44 [6], 399-404 (2005)
15. L.A. Balewick, J.E. Shelby, "Properties of calcium, strontium, and barium galliosilicate glasses", *J. Am. Bol. Soc. Esp. Ceram. V.*, 73 [2] 213-216 (1990)
16. P. Ganster, M. Benoit, W. Kob, J.-M. Delaye, "Structural properties of a calcium aluminosilicate glass from molecular-dynamics simulations: A finite size effects study", *J. Chem. Phys.* 120 (21), 10172-10181 (2004)
17. J. M. Rincón, "Principles of nucleation and controlled crystallization of glasses", *Polym.-Plast. Technol. Eng.* 31 (3 -4), 309-357 (1992)
18. R. E. Newham, H. D. Megaw, "The crystal structure of celsian (barium feldspar)", *Acta Cryst.* 13, 303-312 (1960)
19. K. Greene, M.J. Pomeroy, S. Hampshire, R. Hill, "Effect of composition on the properties of glasses in the $\text{K}_2\text{O-BaO-MgO-SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-MgF}_2$ system", *J. Non-Cryst. Solids* 325, 193-205 (2003)
20. A.K. Varshneya, *Fundamentals of Inorganic Glasses*, Academic Press, San Diego, CA. USA (1994)
21. R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides", *Acta Cryst.* A32, 751-767 (1976)
22. H. Bach, D. Krausse (Eds.), *Analysis of the composition and structure of glass and glass-ceramics*, Springer-Verlag, Berlin, Germany (1999)
23. J.F. Stebbins, Z. Xu, "NMR evidence for excess non-bridging oxygen in an aluminosilicate glass", *Nature* 390, 60-62 (1997)
24. J.J. Videau, J. Etorneau, C. Garnier, P. Verdier, Y. Laurent, "Structural influence of nitrogen in alkaline earth aluminosilicate glasses: IR absorption spectroscopy", *Mater. Sci. Eng.* B15, 249-254 (1992)
25. L. Cormier, G. Calas, S. Creux, P.H. Gaskell, B. Bouchet-Fabre, A.C. Hannon, "Environment around strontium in silicate and aluminosilicate glasses", *Phys. Rev. B* 59, 13517-13520 (1999)
26. L. Cormier, D. Ghaleb, D.R. Neuville, J.-M. Delaye, G. Calas, "Chemical dependence of network topology of calcium aluminosilicate glasses: A computer simulation study", *J. Non-Cryst. Solids* 332, 255-270 (2003)
27. T. Taniguchi, M. Okuno, T. Matsumoto, "X-ray diffraction and EXAFS studies of silicate glasses containing Mg, Ca and Ba atoms", *J. Non-Cryst. Solids* 211, 56-63 (1997)
28. H. Schlenz, A. Kirfel, K. Schulmeister, N. Wartner, W. Mader, W. Raberg, K. Wandelt, C. Oligschleger, S. Bender, R. Franke, J. Hormes, W. Hoffbauer, V. Lansmann, M. Jansen, N. Zotov, C. Marian, H. Putz, J. Neuefeind, "Structure analyses of Ba-silicate glasses", *J. Non-Cryst. Solids* 297, 37-54 (2002)
29. T.J. Kiczinski, L.-S. Du, J. F. Stebbins, "F-19 NMR study of the ordering of high field strength cations at fluoride sites in silicate and aluminosilicate glasses", *J. Non-Cryst. Solids* 337, 142-149 (2004)
30. C. Leonelli, T. Manfredini, M. Paganelli, P. Pozzi, G. C. Pellacani, "Crystallization of some anorthite-diopside glass precursors", *J. Mat. Sci.* 26, 5041-5046 (1991)
31. L. Barbieri, S. Bruni, F. Cariatì, C. Leonelli, G.C. Pellacani, C. Siligardi, U. Russo, "Influence of some transition metal cations on the properties of BaO-containing glasses and glass-ceramics", *Mater. Res. Bull.* 34 (12-13), 1825-1836 (1999)
32. Y. Hu, H.-T. Tsai, "The effect of BaO on the crystallization behaviour of a cordierite-type glass", *Mater. Chem. Phys.* 52, 184-188 (1998)
33. Y. B. Saddeek, "Structural interpretations of aluminosilicate glasses", *Physica B* 363, 19-24 (2005)
34. F. Lucas, A. Belda, F. J. Torres and J. Alarcón, "Estudio y caracterización de vidriados vitrocerámicos basados en piroxeno", *Bol. Soc. Esp. Ceram. V.*, 43 [5], 849-854 (2004)
35. F.V. Tooley, Section 17 in *The handbook of glass manufacture*, Volume II, H.E. Hagy (Ed.), Books for Industry Inc. and The Glass Industry Magazine, N.Y., USA (1974)

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