Correlation between Conductivity and Free Volume in Rubidium and Cesium Silicate Glasses

Marcio Luis Ferreira Nascimento
Vitreous Materials Laboratory, Department of Materials Engineering,
Federal University of São Carlos 13595-905, São Carlos-SP, Brazil

It is shown that conductivity and molar volume in binary rubidium and cesium silicate glasses, both measured at room temperature, obey a common cubic scaling relation due to increase in alkali content. The drastic drop in conductivity up to 15 orders of magnitude for so many ion-conducting binary alkali silicate glasses (in wide composition range) is mainly caused by the structure and the ion content. In particular, it is suggested that the glass network expansion, which is related to the available *free volume*, is a parameter that could explain the increase in ionic conductivity for these binary systems.

Keywords: Glass; Ionic conduction; Anderson-Stuart model; Free volume; Alkali silicate

I. INTRODUCTION

The interest in glasses with high ionic conductivity is growing rapidly because of their potential applications as solid electrolytes in new electrochemical devices such as solid state batteries, fuel cells, chemical sensors and 'smart windows'. Varieties of amorphous ionic conductors with conductivities comparable to those in liquid electrolytes have been structurally investigated [1], with the aim of understanding the diffusion mechanism, which occurs in an otherwise relatively frozen environment. However, despite considerable experimental and theoretical efforts, the mechanism is not yet fully understood [1], even in simple systems. Thus, several transport models have been proposed, and they vary from thermodynamics with principles from liquid electrolytes, such as the weak electrolyte model [2], to models based on solid state concepts such as the jump diffusion model [3], the strong electrolyte (Anderson-Stuart) model [4], and the dynamic structure model [5].

Obviously the detailed microscopic structure may be different for different kinds of fast ion conducting glasses, as in the present case study. In an ion-conducting glass the ions move via the voids. The void volume is characterized in terms of the free volume. The present paper reports on the ionic conductivities and activation enthalpies of glasses in Rb_2O-SiO_2 and Cs_2O-SiO_2 systems, with the purpose of correlating conductiviy with the free volume by means of experimental molar volume. Such molar volumes were calculated from *measured* density data in an attempt to evaluate proposals concerning the role of an open structure for ionic conductivity. Thus we test a general relation between the ionic conductivity enhancement and the expansion of the network forming unities, which shows that the alkali-induced volume expansion of the glass network could explain ionic conductivity, and that is related to the shear modulus.

II. BRIEF THEORY

Ionic conductivity σ in glass is a thermally activated process of mobile ions that overcome a potential barrier E_A, according to the Arrhenius equation:

$$\log_{10}\sigma = \log_{10}\sigma_0 - (\log_{10}e)E_A/k_BT, \quad (1)$$

where σ_0 is a pre-exponential factor. In the following sections it will be shown that σ_0 does not depend on concentration or ion species.

To understand the conduction mechanism it is essential to find structural properties that are common for all amorphous ionic conductors. In view of the most cited models, the Anderson-Stuart (A-S) [4] is considered to be the most directly related to physically meaning parameters, such as ionic radii, relative dielectric permittivity and the elastic modulus, as described below. For the rubidium and cesium silicate systems only recently has been published an analysis of conductivity considering wide composition range [6].

Anderson and Stuart [4] have provided a picture of the conduction energetics in an ion-conducting glass. In this model the activation enthalpy for conductivity E_A was considered as the energy required to overcome *electrostatic* forces (E_b), plus the energy E_s required to open up "doorways" in the structure large enough for the ions (in this case Rb^+ or Cs^+) to pass through (the *strain energy*). Thus, E_b represents the necessary energy to remove a cation from a non-bridging oxygen site, and E_s describes the expansion of the structure as the ion moves from one site to another, where cations sites require only the presence of non-bridging oxygens (Eq. (2)):

$$E_A = E_b + E_s = \frac{\beta z z_0 e^2}{\varepsilon(r+r_O)} + 4\pi G\lambda(r-r_D)^2 . \quad (2)$$

In effect, z and z_0 are the valences of the mobile ion and of the fixed counterion – in this case alkali and oxygen, respectively; r and r_O are the corresponding Pauling ionic radii for Rb^+ or Cs^+ and O^{2-}, λ is a jump distance, e is the electronic charge, and r_D is the effective radius of the (unopened) doorway.

The parameters of interest in the A-S model are the elastic modulus (G), the 'Madelung' constant, or the 'lattice' parameter (β), which depends on how far apart the ions are, and the relative dielectric permittivity (ε), which indicates the degree of charge neutralization between the ion and its immediate neighbours. The inclusion of the λ parameter is due to

McElfresh & Howitt [7], that have reexamined the E_s term, and have suggested such modified form that overcomes certain limitations of the original A-S theory.

Briefly speaking, the McElfresch & Howitt picture is more appropriated to relate σ due to the configuration proposal of a cylindrical hole in the strain energy term E_s [7]. It was proved that the activation enthalpies for diffusion of inert gases in vitreous silica depends on $(r - r_D)^2$ [7], and the proportional factor should be λ and not r_D, as proposed by the A-S model. Finally, following A-S theory the β parameter was considered as $\beta = \frac{a-r}{b}$, where r is a value given in Å, as also a and b, that are fitting parameters as described below.

A.   Relation between Conductivity and Free Volume

Extensive studies have recently been made for obtaining a 'universal' equation (or "master curve") from the glass structure standpoint. Swenson and Börjesson [8] proposed a common cubic scaling relation of σ with the expansion volumes of the network forming units in salt-doped and -undoped glasses. This fact suggested that the glass network expansion, which is related to the available free volume, is a key parameter determining the increase of the high ionic conductivity in some types of fast ion conducting glasses.

The ion conduction should be determined by the ionic motion within an infinite pathway cluster (see Adams and Swenson [9]). For various silver ion conducting glasses [10-11], it was found that the cubic root of the volume fraction F of infinite pathways for a fixed valence mismatch threshold is closely related to both the absolute conductivity and the activation enthalpy of the conduction process:

$$\log_{10}\sigma T \approx \sqrt[3]{F} = \log_{10}\sigma_0' - (\log_{10} e)\, E_A/k_B T, \qquad (3)$$

where σ_0' is the pre-exponential factor (in K/Ω·cm), that seems to be near constant and equal to 50 $\Omega^{-1}\text{cm}^{-1}$, as recently showed [6] for the systems in this work. The cubic root of F may be understood as proportional to a mean free path length for the mobile ion [10], and could be related to the free volume as explained below.

According to Eqs. (1) and (3), more recently Nascimento *et al.* verified such *master curve* in binary silicate [12], borate [13], germanate [14] and tellurite [15] glasses. From these studies, the influence of alkali content and temperature was minor on the pre-exponential terms, considering both expressions $\mathbf{log_{10}\sigma}$ or $\mathbf{log_{10}\sigma T}$.

III.   RESULTS AND DISCUSSION

Figures 1a-b present results on conductivity that follows Eq. (1) in almost all rubidium and cesium conductivities measured up to know, respectively [16-30]. As will be detailed below, Eq. (1) may be more usefull when one considers $\sigma = \sigma(E_A, T)$, leading, in fact, to a more *general* rule, as presented recently [6].
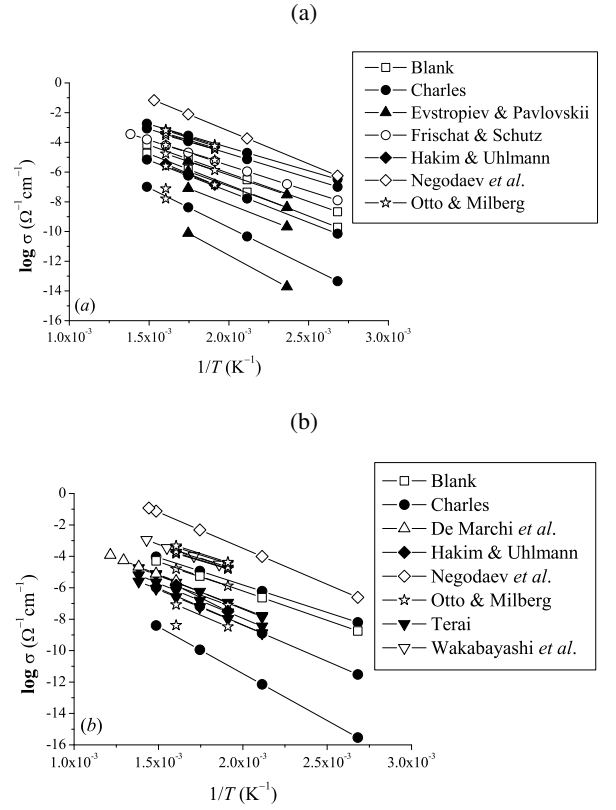

FIG. 1: Arrhenius plots of ionic conductivities in 22 and 21 binary rubidium (a) and cesium (b) silicate glasses, respectively [16-30].

Thus, differences observed in the activation enthalpies, shown in Figs. 1a-b, are likely to be associated with differences in the chemistry and/or structure of the glass samples. Figs. 2a-b confirm this fact showing molar volumes V_m from experimental densities [21-45] of rubidium and cesium systems, respectively. These figures show a markedly increase of V_m with alkali content. Then, the structure expands with increasing alkali, but it is important to note that conductivity also increases. Authors that measured both conductivity and density are indicated by full symbols in Figs. 1-2. In consequence, simple questions arise: *a*) how the alkali ions move in these systems? *b*) How do the alkali ions move if the volume expansion could be related to ionic conductivity? Following there are proposed some evidences to answer these questions, the first one related to the A-S theory, and the last to a recent finding relating σ and the free volume.

A.   Application of the Anderson-Stuart model

In this work was considered the modified expression using λ as a fitting parameter to all data, following McElfresh & Howitt's proposal [7], different that was presented previously [6], where the original A-S theory was applied. The shear modulus G from Nemilov [24] and Shelby and Day [46] showed a decrease with increasing rubidium content.
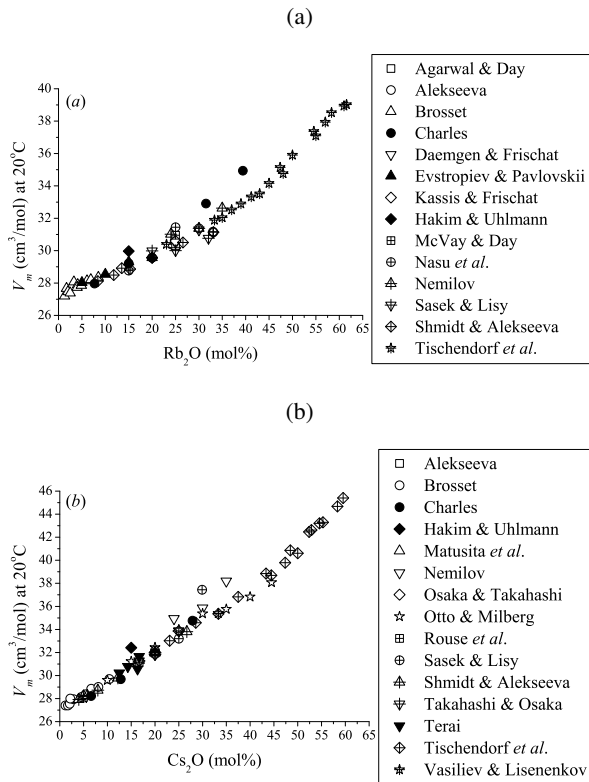
FIG. 2: Molar volumes from measured densities at room temperature of 63 and 66 binary rubidium (a) and cesium (b) silicate glasses, respectively [21-45]. Full symbols correspond to the same glasses presented in Fig. 1.

FIG. 3: a) Non-linear fit (full line) on activation enthalpies E_A from various authors of Rb_2O-SiO_2 (a) and Cs_2O-SiO_2 (b) systems considering McElfresh & Howitt proposal (Eq. (2)). E_b is the binding energy (dashed line), and E_s is the strain energy (dotted line).

Data from Nemilov [24], Takahashi and Osaka [28] and Terai [29,30] presented the same decreasing behavior with increasing cesium content, according to previous work [6]. In fact, following this recent paper, it was verified that G presented a linear fit of form $G = G_0 - \frac{dG}{dn}n$, where n is the alkali oxide mol percentage (mol%) and G_0 is a constant.

The relative dielectric permittivity ε from Amrhein [47] and Charles [21] showed a small and monotonic increase with increasing rubidium content; but Charles' [21] and Matusita *et al.*'s [26] data did not follow the linear increasing as measured by Amrhein [47] and Hakim & Uhlmann [48] in cesium composition, as presented in Ref. [6]. All linear fits follow the form $\varepsilon = \varepsilon_0 + \frac{d\varepsilon}{dn}n$, where ε_0 is another constant.

Table 1 summarizes the obtained G and ε values from linear fittings. More details about G and ε fittings could be found elsewhere [6]. It is recognized that the G and ε assumptions may provide inadequate descriptions with alkali content, but it seems to represent only an approximation. In such assessment is considered the "frozen in" of the glass structure, and consequently its physical properties, as G and ε, assumed only as compositional-dependent.

The variation of activation enthalpy E_A with alkali content over such different glasses are shown in Figs. 3a-b, and these data correspond to the same experimental data in Figs. 1a-b. A careful analysis was carried out in all data to find some pos-
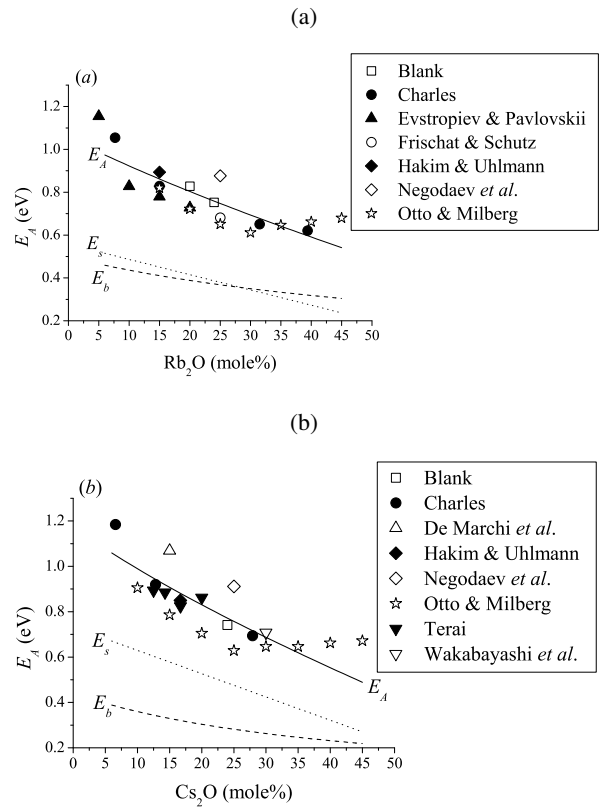
sible discrepancies on the scattering. For example, the activation enthalpies E_A in both systems which have been measured by Negodaev *et al.* [25] differ considerably from others, but were also considered from a statistical point of view.

Besides some scatter, effects of glass composition on E_A could be parametrized by the A-S theory. This model could even be applied in alkali silicate glasses to predict, for example, the dependence of E_A with alkali content (Figs. 3a-b). The A-S model calculations of E_A gives a better agreement at medium range alkali content and the departure is notable at lower and higher alkali content. In fact, the scattering values in E_A should correspond to chemical and/or thermal history, more than by measurement procedure. Indeed, Figs. 3a-b are dealing with with different structures considering a fixed alkali composition, as shown below.

With regard to the fitting procedure – following McElfresh & Howitt's suggestion – the radii values were considered fixed (r_{Rb}= 1.48 Å and r_{Cs}= 1.69 Å for rubidium and cesium ions, respectively, with r_O = 1.4 Å, see Figs. 3a-b, full line). The fitting parameters (for both systems) were the doorway radius and the jumping distance, that resulted in r_D = 1.1 Å and r_D = 1.3 Å, and with λ = 2 Å and λ = 3 Å, respectively. Shear modulus G and the relative dielectric permittivity ε were used for all data as presented in Tab. 1. The β parameters used

TABLE I: Linear fittings from experimental G and ε data of rubidium and cesium silicate systems [6].

System	G_0(GPa)	dG/dn(GPa/mol %)	ε_0 (1)	$d\varepsilon/dn$ (2)	References
Rb	24.6 ± 1.7	0.315 ± 0.060	5.30 ± 0.19	0.075 ± 0.010	[24, 26-30, 46]
Cs	20.46 ± 0.69	0.287 ± 0.027	4.83 ± 0.33	0.109 ± 0.017	[21, 26, 29-30, 47-48]

resulted in 0.26 and 0.23 (a = 2.14; b = 2.5 in the rubidium case, and a = 2.41; b = 3.18 in the cesium case) respectively.

The adjustment for activation enthalpies E_A in Figs. 3a-b were performed using a Levenberg-Marquardt non-linear fitting. It is surprising that a simple theory could adjust data from several authors with different glass preparation processes in a wide range of compositions. Significantly, E_b decreases with increasing alkali oxide in both results of Figs. 3a-b. One reason concerns with the relative dielectric permittivity ε, that increases with increasing alkali oxide. Figs. 3a-b also show that E_s is equal to or higher than E_b considering McElfresh and Howitth proposal [7]. In particular, E_s is higher considering cesium silicates probably due to high Cs^+ ionic radius, and makes sense from a structural point of view. It is important to note that the A-S model is limited to only *one* site energy distribution and with fixed r_D to all composition range. However, the model reasonably agrees with with experimental data, describing E_A decreasing tendency with alkali oxide composition. The main difference between this and the previous results [6] concerning E_A is related to the λ parameter.

B. Experimental Correlation between Conductivity and Free Volume

The *modified* Arrhenius plots of σ for the 22 rubidium and 21 cesium silicate glasses, from x = 4 to 45 mol% in both systems), ranging from 7.9×10^{-2} $\Omega^{-1}cm^{-1}$ to 1.9×10^{-14} $\Omega^{-1}cm^{-1}$ in rubidium and 2.3×10^{-1} $\Omega^{-1}cm^{-1}$ to 2.9×10^{-16} $\Omega^{-1}cm^{-1}$ in cesium systems, all between 20^oC to 450^oC were previously presented [6]. In such work, the range of activation enthalpy E_A lies between 0.61 and 1.15 eV (rubidium) and 0.62 and 1.18 eV (cesium) in all glasses studied, as indicated in Figs. 3a-b. These data were compared with the 'universal' equation using $\sigma_0 = 50$ $\Omega^{-1}cm^{-1}$ in Eq. (1). Following previous works by Nascimento *et al* [12-15], such "universal" equation was also found, with few data exceptions [23, 25].

In fact, in view of many different binary alkali silicate glasses according to Ref. [6] it is remarkable that there is so strong correlation between σ with E_A/k_BT. It is interesting to note that the increase in ionic conductivity with alkali content is almost entirely due to the fact that the activation enthalpy E_A required for a cation jump decreases, as presented in Figs. 3a-b. Thus, the term σ_0 in Eq. (1) is largely unaffected upon alkali content.

As evidenced by the intercept of σ at infinite temperatures ($1/T$ = 0) from Eq. (1), and presented by Ngai & Moynihan considering many systems [49], σ_0 reaches approximately

$\approx$ $\sigma_0 = 50$ $\Omega^{-1}cm^{-1}$ indenpendently of the circumstance if the material is an ionic crystal or a molten ionic glass former. Using the electrical-field Maxwell relaxation time τ defined by the relation:

$$\sigma = \frac{\varepsilon_{free}\varepsilon_\infty}{\tau},\qquad(4)$$

where ε_{free} is the dielectric permittivity of free space, ε_∞ is the high-frequency dielectric constant typically having a order of magnitude of 10, and σ is the DC electrical conductivity, one finds that the limiting high temperature conductivity σ_0 corresponds to a relaxation time of about 10^{-13} s, and a corresponding frequency $\nu = 1/(2\pi\tau) \approx 2 \times 10^{12}$Hz The latter value is close to the vibrational frequency of mobile ions in glasses. Thus, from theory it is possible to expect a pre-exponential fixed σ_0 value.

Another "universal" curve, following Eq.(3) and considering some binary alkali silicate glasses, resulted in the same 'universal' behaviour [6, 12-15], as cited above. The pre-exponential value was σ_0 = 50 000 K/Ω·cm. The conclusions for this case also follow the above described considering Eq. (1), which means that pre-exponential factor is independent of temperature, or at least weaker-dependent. The fact that σ lies on this single 'universal' curve for many ion-conducting glasses means that σ is governed mainly by E_A.

In order to investigate the possibility of another general relation between ionic conductivity and the volume occupied by the network skeleton, the author calculated the expansion $(V_m - V)/V$ of glass network, where V and V_m are the calculated volume network of SiO_2 forming units and the experimental molar volumes, respectively. As shown in Figs. 2a-b, the dopant Rb_2O (or Cs_2O) added increases the experimental molar volume before occupied by SiO_2. The volume of pure silica was assumed as 27.23 cm^3/mol. The difference $V_m - V$ increases slightly and could be considered as *proportional* to the free volume, following similar procedure done by Swenson & Börjesson [8]. This is a rather rough approximation: the increase in molar volumes of Rb_2O or Cs_2O units is the main factor involved in the increasing in conductivity and also in free volume. Thus, the free volume defined here is a macroscopic quantity. The necessary condition for ion transport may rather be the presence of microscopic pathways available for alkali ions. A given material may be called 'conductive' if it is equipped with ample ionic pathways, irrespective of the amount of the free volume. Better approximation of free volume could be provided using positron annihilation spectroscopy, as recently published [50].

The $\mathbf{log}_{10}\sigma T$ values of the glass systems plotted in Fig. 4a-b cover a wide composition range, between 4 to 45 mol%.
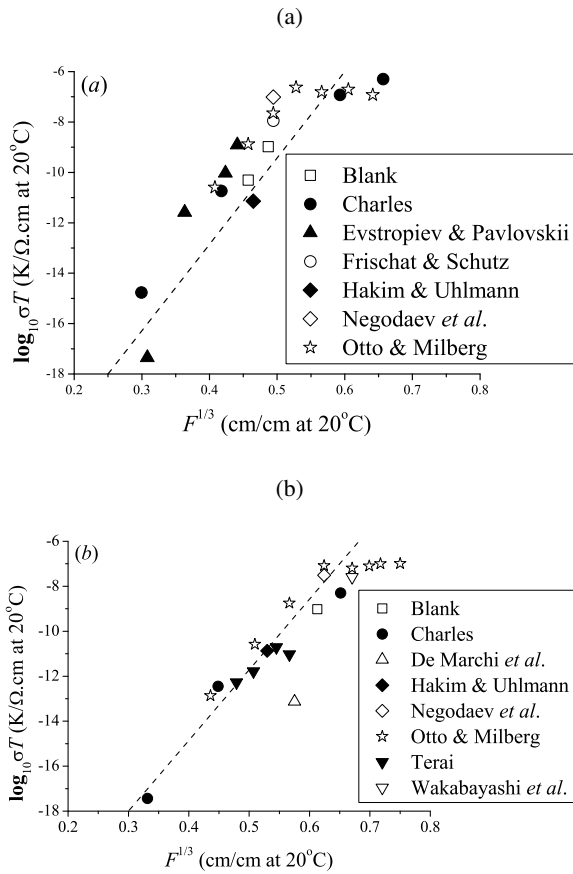
(a)

(b)

FIG. 4: Measured ionic conductivity σ at 20^oC versus the cubic root of expansion of glass network F calculated from density measurements at same temperature for rubidium (a) and cesium (b) silicate glasses, respectively.

(a)

(b)

FIG. 5: Correlation between the experimental activation enthalpy for ionic conductivity E_A and the volume fraction F estimated from density measurements considering a fixed temperature of 20^oC for rubidium (a) and cesium (b) silicate glasses, respectively.

An outstanding common relation between the conductivity (at room temperature) and the cubic root of free volume $F = (V_m - V)/V$ calculated from molar volumes at same temperature is evident; *i.e.*, for a given expansion all the different systems respond with the same increase on σ, regardless of chemical (such as relative water content) or microstructural details (such as phase separation). Note that data in Figs. 4a-b represent σT values that vary by more than 11 orders of magnitude in both systems. The relation found is not *exactly* linear, what could suggest that the conductivity is a bit dependent on the number of mobile ions than on the free volume itself (*e.g.*, there is a stronger interaction between cations at high ion content, near the $50A_2O \cdot 50SiO_2$ mol% composition, A=Rb,Cs).

The common behavior of the conductivity increase with expansion of the network structure observed for the various binary rubidium and cesium glasses suggests that the excess volume introduced by the dopant is an important parameter that influences the conductivity properties, as expressed by Eq. (3). Thus, at first sight it appears that the details of the microscopic structure have direct impact on the ionic conductivity in this sys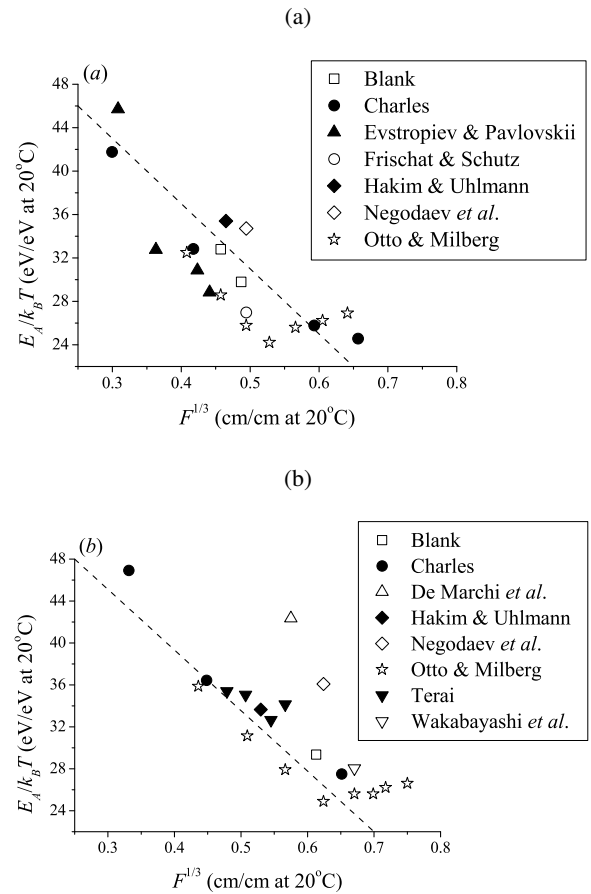tem. For example, it should be noted that the microscopic interactions (mainly mechanical and dielectrical, as predicted by the Anderson-Stuart theory) lead to variations of the degree of expansion. For this reason, in order to explain the conducting properties and the increase of the ionic conductivity with alkali content the A-S theory was focused. The present finding on the common scaling between the conductivity enhancement and the expansion suggests that the expansion of the glass skeleton and therefore the strain energy part E_s have influence on the conduction properties in this system.

Finally, Figs. 5a-b shows that an increase in volume fraction reduces the activation enthalpy for an ionic jump (considering a fixed temperature $T = 20^oC$), which demonstrates that E_A/k_BT varies roughly with the cube root of the volume fraction F. Thus, this approach, besides not linear (as the previous figure), emphasizes the importance of "free volume" to the ion mobility, and is roughly related to the strain energy term, E_s, that showed a proeminent role in the E_A calculation using the A-S theory.

IV.   CONCLUSIONS

A simple relation between the increase in ionic conductivity and the expansion of the glass network skeleton was presented for very different binary rubidium and cesium silicate glasses. The results show that an open structure with excess free volume can easily improve σ. Thus, the approach presented here could be considered valid, relating ionic conductivity with the "expansion of the glass network" (or the "free volume") partially originated from the conduction pathways. By other way, the McElfresh and Howitt proposal on A-S model showed more influence on E_s (the strain energy term), and consequently on the free volume available.

[1] C. A. Angell, Ann. Rev. Phys. Chem. **43**, 693 (1992).
[2] D. Ravaine and J. L. Souquet, Phys. Chem. Glasses **18**, 27 (1977).
[3] K. Funke, Prog. Solid State Chem. **22**, 111 (1993).
[4] O. L. Anderson, and D. A. Stuart, J. Am. Ceram. Soc. **37**, 573 (1954).
[5] A. Bunde, M. D. Ingram, and P. Maass, J. Non-Cryst. Solids **172/174**, 1222 (1994).
[6] M. L. F. Nascimento, E. do Nascimento, and S. Watanabe, Braz. J. Phys. **35**, 626 (2005).
[7] D. K. McElfresh and D. G. Howitt, J. Am. Ceram. Soc. **69**, C237 (1986).
[8] J. Swenson and L. Börjesson, Phys. Rev. Lett. **77**, 3569 (1996).
[9] S. Adams and J. Swenson, Phys. Chem. Chem. Phys. **4**, 3179 (2002).
[10] J. Swenson and S. Adams, Phys. Rev. B **64**, 024204 (2002).
[11] S. Adams and J. Swenson, Solid State Ion. **154/155**, 151 (2002).
[12] M. L. F. Nascimento and S. Watanabe, J. Mater. Sci. **40**, 5079 (2005).
[13] M. L. F. Nascimento and S. Watanabe, J. Mat. Sci. **40**, 4423 (2005).
[14] M. L. F. Nascimento, E. do Nascimento, and S. Watanabe, Mat. Chem. Phys. **96**, 55 (2006).
[15] M. L. F. Nascimento and S. Watanabe, Braz. J. Phys. **36**, 795 (2006).
[16] K. Blank, Glastech. Ber. **39**, 489 (1966).
[17] G. H. Frischat, and H. -E. Schutz, Glastech. Ber. **49**, 162 (1976).
[18] G. Marchi, P. Mazzoldi, and A. Miotello, Proc. XVth *Intern. Congr. on Glass*, Leningrad, 231 (1989).
[19] K. Matusita and S. Sakka, *Proc. Xth Intern. Congr. on Glass*, Kyoto, 44 (1974).
[20] H. Wakabayashi, R. Terai, and H. Watanabe, J. Ceram. Soc. Jpn. **94**, 677 (1986).
[21] R. J. Charles, J. Am. Ceram. Soc. **49**, 55 (1966).
[22] R. M. Hakim, and D. R. Uhlmann, Phys. Chem. Glasses **8**, 174 (1967).
[23] K. K. Evstropiev, and V. K. Pavlovskii, Neorg. Mater. **3**, 673 (1967).
[24] S. V. Nemilov, Zh. Fiz. Khim. **47**, 1479 (1973).
[25] G. D. Negodaev, I. A. Ivanovand, and K. K. Evstropiev, Neorg. Mater. **8**, 342 (1972).
[26] K. Matusita, S. Sakka, A. Osaka, N. Soga, and M. Kunugi, J. Non-Cryst. Solids **16**, 308 (1974).
[27] K. Otto, and M. E. Milberg, J. Am. Ceram. Soc. **51**, 326 (1968).
[28] K. Takahashi and A. Osaka, J. Ceram. Soc. Jpn. **91**, 116 (1983).
[29] R. Terai, J. Ceram. Soc. Jpn. **77**, 318 (1969).
[30] R. Terai, J. Non-Cryst. Solids **6**, 121 (1971).
[31] A. K. Agarwal and D. E. Day, J. Am. Ceram. Soc. **65**, 111 (1982).
[32] Z. D. Alekseeva, *Khimiya Redkikh Elementov*, Leningrad, 122 (1964).
[33] C. Brosset, *Trans. VIIIth Intern. Ceram. Congr.*, Copenhagen, 15 (1962).
[34] M. Daemgen and G. H. Frischat, Glastech. Ber. **56**, 281 (1983).
[35] N. Kassis and G. H. Frischat, J. Am. Ceram. Soc. **64**, C28 (1981).
[36] G. L. McVay and D. E. Day, J. Am. Ceram. Soc. **53**, 508 (1970).
[37] H. Nasu, O. Sugimoto, J. Matsuoka, and K. Kamiya, J. Non-Cryst. Solids, **182**, 321 (1995).
[38] L. Sasek and A. Lisy, Sb. Vys. Sk. Chem. Technol. Praze, Chem. Technol. Silik. **2**, 217 (1972).
[39] Yu. A. Shmidt and Z. D. Alekseeva, Zh. Prikl. Khim. **37**, 2299 (1964).
[40] B. Tischendorf, C. Ma, E. Hammersten, P. Venhuizen, M. Peters, M. Affatigato, and S. Feller, J. Non-Cryst. Solids, **239**, 197 (1998).
[41] Z. D. Alekseeva, Neorg. Mater. **10**, 902 (1974).
[42] A. Osaka and K. Takahashi, J. Ceram. Soc. Jpn, **90**, 703 (1982).
[43] K. Otto and M. E. Milberg, J. Am. Ceram. Soc. **50**, 513 (1967).
[44] G. B. Rouse, E. I. Kamitsos, and W. M. Risen, J. Non-Cryst. Solids, **45**, 257 (1981).
[45] A. I. Vasiliev and A. A. Lisenenkov, Fizika i Khimiya Stekla, **8**, 546 (1982).
[46] J. E. Shelby and D. E. Day, J. Am. Ceram. Soc. **53**, 182 (1970).
[47] E. M. Amrhein, Glastech. Ber. **36**, 425 (1963).
[48] R. M. Hakim and D. R. Uhlmann, Phys. Chem. Glasses **14**, 81 (1973).
[49] K. L. Ngai and C. T. Moynihan, Mat. Res. Soc. Bull. **23**, 51 (1998).
[50] M. D. Ingram, S. J. Pas, C. Cramer, Y. Gao, and A. J. Hill, Phys. Chem. Chem. Phys. **7**, 1620 (2005).