

## Universal Curve of Ionic Conductivities in Binary Alkali Tellurite Glasses

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The main objective of this work is to present an analysis and brief discussion of experimental ionic conductivity  $\sigma$  data in the binary alkali tellurite system, including on 47 glasses that extend the ionic conductivity range by more than 14 orders of magnitude in a wide compositional range. A 'universal' behavior is obtained, using  $\log \sigma$  or  $\log \sigma T$  vs.  $E_A/k_B T$ , where  $E_A$  is the activation enthalpy for conduction,  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature. This finding further indicates the importance of a scaling factor  $F$  recently proposed, that is correlated to the free volume of glass composition. For a given value of  $E_A/k_B T$ , the difference between large and small values of  $\sigma$  is only one order of magnitude in 87% of these glass systems. The influence of alkali content and temperature was minor on the pre-exponential terms, considering both expressions  $\log_{10} \sigma$  and  $\log_{10} \sigma T$ . Indeed, the pre-exponential term  $\sigma_0$  varies around an average value of  $50 \Omega^{-1} \text{cm}^{-1}$  considering different compositions in this system. The fact that  $\sigma$  lies on these single 'universal' curves for so many ion-conducting binary tellurite glasses means that  $\sigma$  is governed mainly by  $E_A$ . The composition dependence of the activation enthalpy is explained in the context of the Anderson-Stuart theory.

Keywords: Glass; Electrical properties; Ionic conduction

### I. INTRODUCTION

The room temperature ionic conductivity in solid materials is technologically interesting for various solid state electrochemical devices such as batteries, sensors and 'smart windows'. It is well known that the ionic conductivity increases rapidly when a network glass former (for instance  $\text{TeO}_2$ ) is modified by the addition of a metal alkali. So far only a limited number of publications have been concerned with the study of the ionic conduction in tellurite glasses. The importance of studying such phenomenon in this system is due to many industrial and technological applications, as excellent optical properties (good transmission in the visible and infrared regions). Also, tellurite glasses have been widely studied due to their chemical stability, high homogeneity, high electrical conductivity and resistance to devitrification.

Since the initial studies of the fast ionic conductivity in glasses, there has been a large interest in explaining the diffusion mechanism. Despite considerable experimental and theoretical attempts, there is currently no consensus regarding the involved diffusion mechanism [1]. Several models have been proposed, and they vary from thermodynamics models based on 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 model [4], and the dynamic structure model [5].

Ionic conductivity  $\sigma$  in glass is a thermally activated process of mobile ions surmounting a potential barrier  $E_A$ , according to the equation

$$\log \sigma = \log \sigma_0 - (\log e) E_A/k_B T, \quad (1)$$

where  $\sigma_0$  is a pre-exponential factor,  $k_B$  is the Boltzmann con-

stant and  $T$  is the temperature. Arrhenius plots according to Eq. (1) are presented in Fig. 1 for 47 alkali tellurite glasses and demonstrate the noticeable scattering values of  $E_A$  against composition. As will be detailed below, Eq. (1) may be more useful when one considers  $\sigma = \sigma(E_A, T)$ , leading, in fact, to a more general rule.

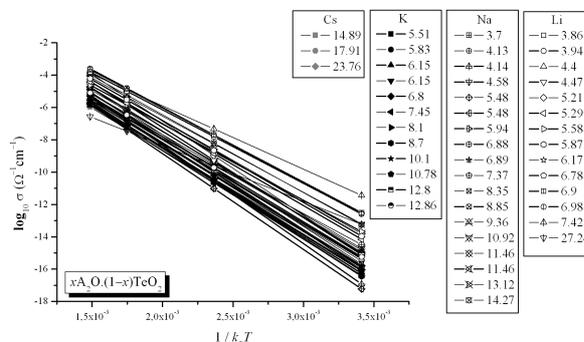


FIG. 1: Arrhenius plots of ionic conductivities in 47 binary alkali tellurite glasses [16], of form  $x\text{A}_2\text{O} \cdot (1-x)\text{TeO}_2$  ( $A = \text{Li, Na, K, Cs}$ ,  $x$  in wt.%, indicated). The temperatures measured are 20, 150, 300 and 400°C.

Extensive studies have recently been made for obtaining a 'universal' equation from the glass structure standpoint. For example, Nascimento *et al.* [6] presented 23 and 30 binary rubidium and cesium silicate glasses, respectively, that follow a 'universal' conductivity rule. Swenson and Börjesson [7] proposed a common cubic scaling relation between  $\sigma$  and the expansion volumes of the networking 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.

According to Adams and Swenson [8], the ion conduction should be determined by the ionic motion within an infinite pathway cluster. For various silver ion conducting glasses [9-10], 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,

$$\log \sigma T \propto \sqrt[3]{F} = \log \sigma_0' - (\log e) E_A / k_B T, \quad (2)$$

where  $\sigma_0'$  is the pre-exponential factor (in  $\text{K}/\Omega\cdot\text{cm}$ ). The cubic root of  $F$  may be thought of as proportional to the mean free path of the mobile ion [7].

## II. RESULTS AND DISCUSSION

According to Bahgt and Abou-Zeid [11], the  $\text{TeO}_2$  glass has a unique structure as a consequence of the structural unit and its connecting style differs from conventional glass formers as  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{GeO}_2$  and  $\text{P}_2\text{O}_5$ .  $\text{TeO}_2$  glass is composed mostly of  $\text{TeO}_4$  trigonal bipyramids. Generally, it was shown that the primary structural unit of tellurite glasses having high  $\text{TeO}_2$  content is  $\text{TeO}_6$  polyhedron. Together with distorted  $\text{TeO}_4$  trigonal bipyramids and fractions of  $\text{TeO}_3$  trigonal pyramids the proportions of the structural units increase with increasing monovalent cation content [11]. So, when the alkali oxides are introduced in the tellurite network there exist different structural units at different alkali oxide contents [12].

In recent papers the present authors have shown the existence of a ‘universal’ behavior in binary silicate [13], borate [14], and germanate [15] glasses, considering both Eqs. (1) and (2). This paper aims to present new results considering binary alkali tellurite glasses.

Figure 2 shows *modified* Arrhenius plots of  $\sigma$  for 47 binary alkali tellurite glasses, of the form  $x\text{A}_2\text{O}\cdot(1-x)\text{TeO}_2$  ( $\text{A} = \text{Li, Na, K, Cs}$ ,  $x$  in wt. %, indicated [16]), ranging from  $3.6 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$  to less than  $6 \times 10^{-18} \Omega^{-1}\text{cm}^{-1}$  between  $20^\circ\text{C}$  to  $400^\circ\text{C}$ . The range of activation enthalpy  $E_A$  lies between 0.6 and 1.2 eV in all of the studied glasses. These data were compared with ‘universal’ equation for  $\sigma_0 = 50 \Omega^{-1}\text{cm}^{-1}$  in Eq. (1). Following previous work by Nascimento *et al.*, the ‘universal’ equation appears in Fig. 2 as a dashed line. Only a few glasses do not obey the ‘universal’ curve, as 3.86, 4.4, 4.47, 5.21 and 27.24  $\text{Li}_2\text{O}$  plus 4.14  $\text{Na}_2\text{O}$  composition (in wt%). It is important to note that similar compositions, as 3.94 and 5.29  $\text{Li}_2\text{O}$  are between the dotted lines, and this different behavior should be investigated.

The replacement of a mobile ion with one of another type affects the ionic conductivity in various ways, such as causing modifications in the glass structure. Therefore, the results shown in Fig. 2 are remarkable in the sense that so many different binary alkali tellurite glasses present linear plots of  $\log \sigma$  vs.  $E_A/k_B T$  very close to each other and to the ‘universal

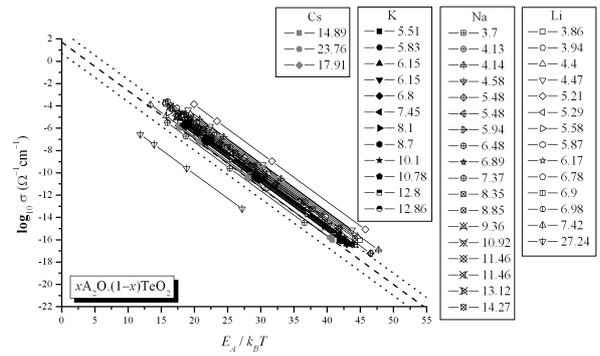


FIG. 2: Modified Arrhenius plots of ionic conductivities in 47 binary alkali tellurite glasses [16], of form  $x\text{A}_2\text{O}\cdot(1-x)\text{TeO}_2$  ( $\text{A} = \text{Li, Na, K, Cs}$ ,  $x$  in wt. %, indicated). These data are the same presented in Fig. 1. The dashed line is the ‘universal curve’, Eq. (1), with  $\sigma_0 = 50 \Omega^{-1}\text{cm}^{-1}$ , and the dotted lines correspond to one order of magnitude higher or lower than Eq. (1).

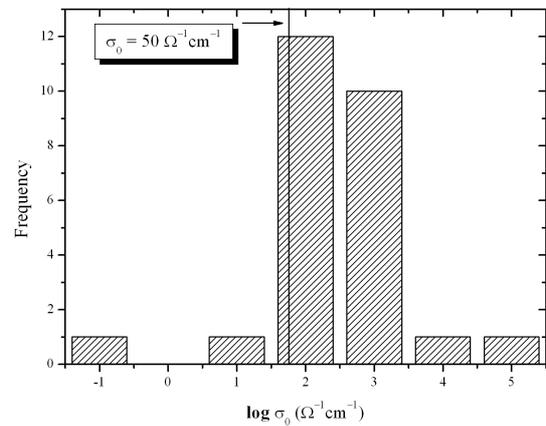


FIG. 3: Frequency distribution of  $\sigma_0$  values from Eq. (1) corresponding to the experimental ionic conductivities of 26 binary alkali tellurite glasses. The vertical line corresponds to  $\sigma_0 = 50 \Omega^{-1}\text{cm}^{-1}$ .

curve’’. There is then a strong correlation between  $\sigma$  and  $E_A$  values in a wide range of temperatures. 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 ref. [4].

In addition, one can conclude that the pre-exponential factor  $\sigma_0$  varies only weakly with glass composition. The frequency of  $\sigma_0$  distribution is shown in Fig. 3. It is possible to note that the medium value is near  $50 \Omega^{-1}\text{cm}^{-1}$ , the intercepting value at y-axis of Fig. 2. Thus, the  $\sigma_0$ -value in Eq. (1) is practically unaffected by alkali content. Other results, considering binary alkali silicate [13], borate [14], and germanate [15] glasses, also display this behavior.

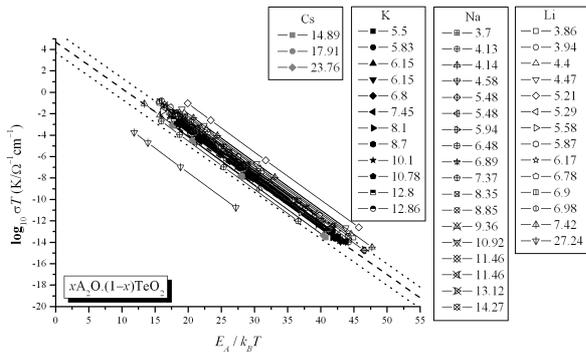


FIG. 4: Modified Arrhenius plots of ionic conductivities in 47 binary alkali tellurite glasses [16], of form  $x\text{A}_2\text{O} \cdot (1-x)\text{TeO}_2$  ( $\text{A} = \text{Li}, \text{Na}, \text{K}, \text{Cs}$   $x$  in wt.%, indicated). These data are the same presented in Fig. 2. The dashed line is the ‘universal curve’, Eq. (2), with  $\sigma_0 = 50\,000$   $\text{K}/\Omega\text{-cm}$ , and the dotted lines correspond to one order of magnitude higher or lower than Eq. (2).

It is important to note that the  $\sigma$ -values for several binary alkali tellurite glasses lie close to a “universal” curve. Although the  $\sigma$ -values for each glass at very low and very high temperatures differ by more than 14 orders of magnitude, for a given value of  $E_A/k_B T$ , the difference between large to small values of  $\sigma$  is only one order of magnitude in 87% of the glass systems considered in Fig. 2. Therefore, if one measures  $\sigma$  at a fixed temperature, it is possible to estimate  $E_A$  from Eq. (1) considering  $\sigma_0 = 50/\Omega\text{-cm}$ , and obtain a rough sketch of  $\sigma$  at different temperatures. This means that, if  $E_A$  is obtained by some experimental or theoretical technique, the ionic conductivity can be readily calculated.

Another “universal” curve, following Eq. (2), was obtained, and is presented in Fig. 4. The pre-exponential value was  $\sigma_0 = 50\,000$   $\text{K}/\Omega\text{-cm}$ , considering the same conductivity data of Figs. 1-2. The conclusions for this case are similar.

The composition dependence of the activation enthalpy in a wide composition range can be understood in the framework of the Anderson-Stuart model [4]. The expansion of the glass skeleton and the introduction of the alkali ions in voids in the structure forming narrow pathways lead to two effects that lower the activation enthalpy and thus promote the ionic conductivity. In this model the total activation enthalpy  $E_A$  for ionic conduction is the sum of two parts, the binding energy,  $E_b$  (the average energy that a cation requires to leave its site), and the strain energy,  $E_s$  (the average kinetic energy that a cation needs to structurally distort the environment and to create a “doorway” through which it can diffuse to a new site). The A-S theory leads to the equation

$$E_A = \frac{\beta z z_0 e^2}{\epsilon(r+r_D)} + 4\pi G r_D (r-r_D)^2, \quad (3)$$

where  $z$  and  $z_0$  are the valence of the mobile ion and of the

fixed counterion (in this case the alkali and oxygen, respectively),  $r$  and  $r_D$  are the corresponding Pauling ionic radii for the alkali ion and  $\text{O}^{2-}$ ,  $e$  is the electronic charge, and  $r_D$  is the effective radius of the (un-opened) doorway. The parameters of interest in the A-S model are the elastic modulus ( $G$ ), the ‘Madelung’ constant ( $\beta \approx 0.3$ ), which depends on how far apart the ions are, and the relative dielectric permittivity ( $\epsilon$ ), which indicates the degree of charge neutralization between the ion and its nearest neighbours [4].

The cation-induced expansion of the network skeleton leads to a lowering of the strain energy part  $E_s$  of the activation energy and the formation of pathways, in which the cations may coordinate with oxygens of the network, leading to a lowering of  $E_b$ .

The ionic conductivity in the lithium tellurite glasses with varying  $\text{Li}_2\text{O}$  content have been recently investigated by Pan and Ghosh [12]. Thus, in this system the strain energy part is expected to play a dominant role in the total activation enthalpy  $E_A$ , as expected if one considers that structural changes could modify ionic conductivity, as expressed in Eq. 2 (due to the scaling factor  $F$ ). In other words, the cubic root of  $(V_m - V)/V$  is proportional to  $F$  and should increase slightly, following similar procedures by Swenson and Börjesson [7]. Following this approach, 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 approximations for free volume could be provided using positron annihilation spectroscopy, as recently published [17].

### III. CONCLUSIONS

In summary, there are *strong connections* between the microscopic structure and the ionic conductivity. At first sight,  $E_A$  and  $k_B T$  are independent, and  $E_A$  varies strongly with composition (the effect of glass composition is clearly demonstrated in Fig. 1). But almost all of these compositions fall into identifiable patterns where conductivity is related to structure, as expressed by *modified* Arrhenius plots.

These relations have an important feature. Regardless of the type of ionic conductor, or the oxide glassformer, if one plots  $\log \sigma$  or  $\log \sigma T$  against  $E_A/k_B T$ , all systems will follow the same rule, with a few exceptions. In other words, as it has been recently proposed, both  $E_A$  and  $k_B T$  are related to the cubic root of the scaling factor  $F$ . Furthermore, the frequency distribution of the pre-exponential term  $\sigma_0$  (or  $\sigma_0'$ ) varies weakly with glass composition (and also temperature), and could be considered as an other evidence of the ‘universal’ finding.

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- [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**, 11 (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] J. Swenson and L. Börjesson, *Phys. Rev. Lett.* **77**, 3569 (1996).
- [8] S. Adams and J. Swenson, *Phys. Chem. Chem. Phys.* **4**, 3179 (2002).
- [9] J. Swenson and S. Adams, *Phys. Rev. B* **64**, 024204 (2001).
- [10] S. Adams and J. Swenson, *Solid State Ion.* **154/155**, 151 (2002).
- [11] A. A. Bahgat and Y. M. Abou-Zeid, *Phys. Chem. Glasses* **42**, 361 (2001).
- [12] A. Pan and A. Ghosh, *Phys. Rev. B* **60**, 3224 (1999).
- [13] M. L. F. Nascimento and S. Watanabe, *J. Mater. Sci.* **40**, 5079 (2005).
- [14] M. L. F. Nascimento and S. Watanabe, *J. Mater. Sci.* **40**, 4423 (2005).
- [15] M. L. F. Nascimento, E. do Nascimento, and S. Watanabe, *Mat. Chem. Phys.* **96**, 55 (2006).
- [16] Sciglass<sup>®</sup> database. <http://www.esm-software.com/sciglass>
- [17] M. D. Ingram, S. J. Pas, C. Cramer, Y. Gao, and A. J. Hill, *Phys. Chem. Chem. Phys.* **7**, 1620 (2005).