

Thermal and structural studies of $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{SrO}-\text{TiO}_2-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses by DTA, IR and EPR spectroscopy

H. Bih¹, H. Sinouh², H. Es-soufi², L. Bih^{2,*}, M. Haddad³, L. Bejjit³, B. Manoun^{4,5}, P. Lazor⁶

¹ Faculté polydisciplinaire de Taza, Université Sidi Mohamed ben Abdellah, Fes, Morocco.

² Equipe de Physico-Chimie de la Matière Condensée, PCMC, Faculté des Sciences de Meknes. Université Moulay Ismail, Morocco.

³ Laboratoire de Spectrométrie, des Matériaux et Archéomatériaux (LASMAR), Faculté des Sciences de Meknes, Université My Ismail, Morocco.

⁴ Univ Hassan 1er, Laboratoire des Sciences des Matériaux, des Milieux et de la Modélisation (LS3M), 25000, Morocco.

⁵ Materials Science and Nano-engineering Department, University Mohammed VI Polytechnic, Ben Guerir, Morocco.

⁶ Department of Earth Sciences, Uppsala University, SE-752 36, Uppsala, Sweden.

Received 16 July 2017; Revised 10 August 2017; Accepted 12 August 2017.

Abstract : Glasses in molar fraction in the system $33.33[\text{xNa}_2\text{O}-(1-\text{x})\text{Li}_2\text{O}]-2.5\text{SrO}-2.5\text{TiO}_2-45\text{B}_2\text{O}_3-16.67\text{P}_2\text{O}_5$ ($0.0 \leq x \leq 1.0$) were prepared by standard melt quenching procedures, their physical properties were characterized by thermal analysis and density measurements. Their local structures were comprehensively characterized by Infrared spectroscopy (IR) and electron paramagnetic resonance (EPR). The variation of the glass transition temperature as a function of the glass compositions is non-linear. The infrared spectroscopy of the glasses has identified the presence of different structural grouping units in the glassy-matrix. It is found that the stretching and bending vibration modes of borate groups are more sensitive to the substitution of alkali elements. EPR experiments have shown the presence of Ti^{3+} centers in the glasses. The variation of the g-factor as a function of the $\text{Na}/(\text{Na}+\text{Li})$ ratio presents a minimum around ($x=0.5$). The composition non-linearity behavior of T_g , vibration bending mode, and g-factor are signature of the mixed alkali effect in the glasses.

Keywords: Borophosphate Glasses; Thermal Analysis; IR; EPR; Mixed Alkali Effect (MAE).

1. Introduction

The advantages of glasses over their crystalline counterparts include physical isotropy, absence of grain boundaries and a possibility to continuously vary the compositions. Among them phosphate glasses are of particular interest due to the fact that they usually melt at low temperatures, have high thermal expansion coefficients and good optical transmittance in UV-region. Among phosphate families, metaphosphate is the less complicated glass structure. It contains tetrahedra with two bridging oxygens that form chains and rings. The chains and rings are attached by ionic bonds between various metal cations and the non-bridging oxygens. The phosphate glasses have a considerable potential for the application in optical data transmission, solid-state batteries, low-melting sealing, sensing and laser technology [1-4]. However, phosphate glasses typically have a relatively poor chemical durability, which often limits their usefulness. Several studies have shown that the chemical durability of phosphate glasses can be improved by addition of various oxides [5]. The improved water durability of phosphate glasses containing B_2O_3 has also been proved [3]. Addition of B_2O_3 , pure boron trioxide (B_2O_3) is a very good glass former, covalently bonded, with interesting physicochemical properties [6], to a phosphate glass improves the chemical durability as well as thermal and

mechanical stability of the pure phosphate glass [7]. The borate glasses are of exceptional importance due to their interesting linear and nonlinear optical properties [7]. Combination of phosphate and borate gives a new family of borophosphate glasses which have numbers of applications in different areas owing to their flat gain broadband amplification. Due to their bioresorbable properties, these glasses have received increasing attention in biomedical applications [8]. In addition, alkali-earthed-borophosphate glass matrices are of interest for many applications such as hosts for rare-earth dopants for fiber amplifiers [1]. Also, alkali-borophosphate glasses exhibit large electro-optical Kerr-like effect and so large third-order nonlinearity [9,10].

Several glasses exhibit a linear-like behavior of their physical properties with varying chemical composition. An exception exists for glasses containing two different alkali oxides where large deviation from linearity occurs having maxima or minima. This is called the mixed alkali effect (MAE) and is one of the longest studied subjects in glass science [5,11,12]. From the literature, one could find several explanations and theoretical models put forward to understand this peculiar but common phenomenon. The deviation from linearity, when the concentration ratio between the two alkali ions is changed, keeping the total alkali content constant, is observed in those properties which are related to ionic

* Corresponding author: E-mail: bihlahcen@yahoo.fr (Lahcen BIH)

transport, such as ionic conductivity, ionic diffusion, dielectric relaxation, and mechanical loss and internal friction [13-15]. In addition, macroscopic properties such as molar volume and density, refractive index, thermal-expansion coefficient and elastic moduli usually change linearly or only slowly with composition. Properties related to structural relaxation, such as viscosity and glass transition temperature, usually exhibit some deviations from linear behavior.

The purpose of this paper is to provide detailed information about the influence of substituting Li_2O by Na_2O on structure and some physical properties in the $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{SrO}-\text{TiO}_2-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses. By keeping the Sr-Ti-B-P ratio constant and the total concentration of alkali cation as 20 mol%, we show that it is possible to investigate the (MAE) in the $33.33[\text{xNa}_2\text{O}-(1-\text{x})\text{Li}_2\text{O}]-2.5\text{SrO}-2.5\text{TiO}_2-45\text{B}_2\text{O}_3-16.67\text{P}_2\text{O}_5$ glasses.

2. Experimental

The $33.33[\text{xNa}_2\text{O}-(1-\text{x})\text{Li}_2\text{O}]-2.5\text{SrO}-2.5\text{TiO}_2-45\text{B}_2\text{O}_3-16.67\text{P}_2\text{O}_5$ glasses ($0 \leq x \leq 1$) were prepared from appropriate mixtures of reagent-grade Li_2CO_3 , Na_2CO_3 , TiO_2 , H_3BO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$. In order to prevent the excess boiling and consequent spillage, water and ammonia in $\text{NH}_4\text{H}_2\text{PO}_4$ were removed initially by preheating the mixture at 300°C for about 12h. The resulting mixture was then melted for a while at 1000°C . Finally, they were quenched to room temperature in air. All prepared glasses have been first characterized by means of X-ray diffraction (XRD), using a Seifert XRD 3000 instrument, in order to verify the vitreous character (or crystalline) of the elaborated samples. Differential Thermal Analysis (DTA) was performed using a Seiko DTA apparatus under nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$. The density of the samples was determined using Archimedes method with diethyl orthophthalate as the displacing medium. X-band ESR spectra of powdered glass samples at ambient temperature were recorded on a Varian E-109 EPR spectrometer. The modulation amplitude and power level were adjusted to avoid saturation of the peak resonance. The powdered glass samples were mixed with KBr powder and pressed as pellets. These pellets are used for the recording of IR spectra using JASCO FTIR-5300 in the wave number range $450 - 4000\text{ cm}^{-1}$ at room temperature.

3. Results and discussion

3.1. Glass formation

By the procedure described above, homogeneous glasses were prepared. The composition dependencies of physical properties of the glasses have been determined along the $33.33[\text{xNa}_2\text{O}-(1-\text{x})\text{Li}_2\text{O}]-2.5\text{SrO}-2.5\text{TiO}_2-45\text{B}_2\text{O}_3-16.67\text{P}_2\text{O}_5$ series.

The studied glasses offer a fixed total alkali content (33.33%) and a constant Sr:Ti:B:P ratio. The structure nature of the samples was checked by X-ray diffraction and their XRD patterns confirm the glassy nature of

these samples (Fig.1). They showed broad peak around $20-30^\circ$ (2θ values) and the absence of crystalline peaks in all the investigated compositions. The glasses are stable and non-hygroscopic at ambient temperature. The color of the glasses changed from clear to brown with increasing Na/Ti ratio. Color is associated with the ability to promote an electron from one energy level to another. Exactly the right amount of energy to do this is obtained by absorbing the light of a particular wavelength. Indeed, the d orbitals of titanium ions are not all identical in energy; it is possible to promote electrons from one d level to another d level. This corresponds to a small energy difference, thus light is absorbed in the visible region. Since the empty d -shell Ti^{4+} metal ion is not contributing to color of the glasses, one could state that the color of the glasses is due to the presence of some amounts of Ti^{3+} ions in the glassy-matrix [16].

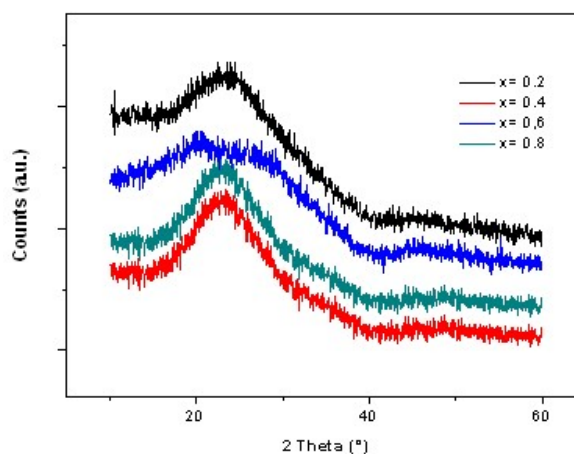


Fig.1. XRD patterns of the $33.33[\text{xNa}_2\text{O}-(1-\text{x})\text{Li}_2\text{O}]-2.5\text{SrO}-2.5\text{TiO}_2-45\text{B}_2\text{O}_3-16.67\text{P}_2\text{O}_5$ glasses

3.2. Density and molar volume

The density measurements (D) of glasses are determined by the Archimedes method using diethyl orthophthalate at 25°C as the suspension medium. Molar volume (V_m) of each glass is derived from the density and molar weight values ($V_m=M/D$) where M is the molecular weight of the glass expressed as the mole fractions of the oxides multiplied by their molecular weights. The density and molar volume of the studied glasses are gathered in Table 1 and their variations as a function of composition are shown in Fig.2. It was observed that the density decreases with increasing Na_2O content at the expense of Li_2O . The composition dependence of the density shows a slight positive deviation from linearity when sodium replaces lithium. Even though this deviation is small it could indicate the presence of mixed alkali effect (MAE) in the glasses. Mixed alkali effect is observed in other mixed alkali glasses [17,18]. The decrease of density with Na/Li ratio is not due to the substitution of the heavier cation sodium for lithium even though density is a macroscopic property: introducing heavier molecule into the structure of glass instead of lighter one could increase

the density. The decrease of the density is accompanied with an increase of the molar volume (Fig.2). The analysis of Fig.2 shows that the molar volume presents a slight negative non-linear deviation showing MAE. According to the literature [19,20], in alkali borate glasses the increase in Li₂O content up to 30 mol% results in an increase in density, although the relative molecular mass of Li₂O is much lower than that for B₂O₃. The increase in density in such cases is attributed to the conversion of BO₃ units into BO₄ ones. The density of the latter is markedly higher than that of the former. Above 30 mol% added modifier content, the formation of non-bridging oxygen on BO₃ unit occurs. In alkali phosphate glasses, the added alkali oxide causes the formation of non-bridging oxygen ions (NBOs) in the phosphate matrix [21-24]. The structure is generally described using Qⁿ terminology, where n represents the number of bridging oxygens per tetrahedron. For each value of O/P ratio, defined by a glass composition, the structure contains a fixed ratio (Q³/Q²/Q¹/Q⁰) of structural units. In the studied glasses the contents of SrO, TiO₂, B₂O₃, P₂O₅ are fixed, while Li₂O is replaced by Na₂O. Thus the oxygen/boron and oxygen/phosphorous ratios do not change when replacing one alkali oxide by another. Therefore, there would be neither significant change in the relative number of borate units nor the significant change in the population of the phosphate units in the network of the glasses. However, the conversion between borate units (from BO₃ to BO₄ and vice-versa) or between phosphate groups is not excluded. Thus, the decrease in density may be due to: (i) an expansion in the glass matrix when replacing the smaller Li⁺ ions by the larger Na⁺ ones; (ii) the possibly BO₃/BO₄ unit conversions. The molar volume increases as a result of the creation of non-bridging oxygens (NBO) which increase spaces and free volume in the network.

Table 1

Some physical properties of the 33.33[xNa₂O-(1-x)Li₂O]-2.5SrO-2.5TiO₂-45B₂O₃-16.67P₂O₅ (0 ≤ x ≤ 1) glasses.

x	Density/ g/cm ³	V _m / cm ³ /mol	T _g /°C	T _c /°C	g-factor
0	3.22	21.7	411	470	1.9360
0.2	3.15	22.9	393	460/550	1.9358
0.4	3.05	24.4	388	536	1.9353
0.5	2.98	25.3	382	539	1.9351
0.6	2.92	26.1	385	446/551	1.9352
0.8	2.81	27.9	389	452	1.9357
1	2.69	29.9	410	472	1.9364

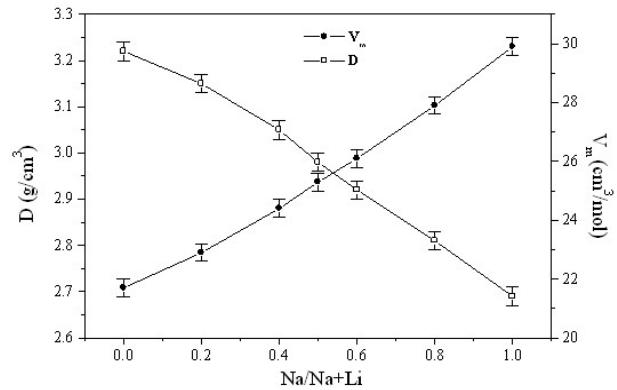


Fig.2. Density (D) and molar volume (Vm) as a function of Na/(Na+Li) for the 33.33[xNa₂O-(1-x)Li₂O]-2.5SrO-2.5TiO₂-45B₂O₃-16.67P₂O₅ glasses.

3.3. Glass transition temperature (T_g)

Glass transition temperatures T_g were determined by DTA. Fig.3 shows the plot of T_g as a function of the Na₂O/(Na₂O + Li₂O). As can be deduced from this figure, T_g decreases with increasing the ratio Na/(Na+Li) and reaches a minimum for the value Na/(Na+Li) = 0.5. We have observed that the glass transition temperature is lower for mixed glasses than for the original compositions (x = 0 and x = 1). This kind of T_g variation was also reported for other vitreous systems, e.g. Li₂O-Na₂O-Al₂O₃-P₂O₅ [25], Li₂O-(Na,K,Rb)₂O-B₂O₃ [26], Li₂O-Na₂O-MO₃-P₂O₅ (M=Mo, W) [27,28]. This non linearity variation of T_g reveals the presence of the well-known mixed alkali-effect (MAE) in the glasses under study.

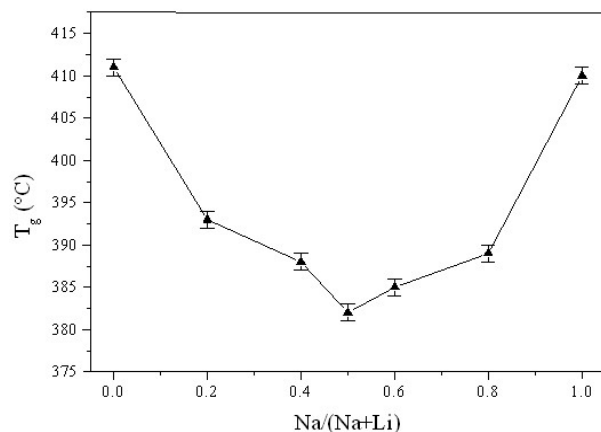


Fig.3. Variation of the glass transition temperature T_g as a function of Na/(Na+Li) ratio.

The mixed-alkali effect is a phenomenon observed in many oxide glasses in which several ionic transport-related properties change as a function of composition in a highly non-additive fashion when one alkali oxide is replaced by another. In addition to ionic conductivity, the glass transition temperature, T_g, which is not directly dependent upon ionic transport, shows a pronounced departure from linearity at intermediate mixed alkali ion compositions [29]. The conductivity and T_g are expected to behave in a similar manner since both properties are associated with the dynamics of the glass system. The MAE observed in the glass transition

temperature could be associated to the 'structural disorder' imposed by the presence of two kinds of cations and/or the formation of an excess of non-bridging oxygen atoms.

3.4. Infrared spectroscopy

The IR absorption spectra give significant information about molecular vibrations as well as rotation associated with a covalent bond. The IR spectra occur due to the change in the dipole moment of the molecule. It involves the twisting, bending, rotating and vibrational motions in a molecule. According to the chemical composition of the glasses, the network of these materials should contain a combination of phosphate and borate structural units. The basic units of pure phosphate glasses are PO_4 tetrahedra linked through covalent bridging oxygen atom, whereas the basic units of vitreous borate are BO_3 units. The introduction of alkali oxides, such as Li_2O or Na_2O , to phosphate and borate modifies their glass matrix. For instance, in the phosphate matrix it has a depolymerization effect in the sense that the addition of a modifying oxide to P_2O_5 results in the creation of non-bridging oxygens (NBO) at the expense of bridging oxygen atoms (BO). Phosphate glasses can be made with a range of structures, from a cross-linked network tetrahedral (vitreous P_2O_5) to polymer-like metaphosphate chains of tetrahedra to 'invert' glasses based on the O/P ratio [3,21]. However, in borate glasses the addition of a modifier A_2O oxide ($\text{A}=\text{Li}, \text{Na}$) has the opposite effect since it increases the degree of polymerization up to 30 mol% of alkali oxide content. The boron coordination changes from trigonal to tetrahedral and part of the basic borate groups changes from BO_3 to BO_4 structural units. When content of the modifier oxide exceeds 30 mol%, the borate network is depolymerized and non-bridging oxygen atoms are formed in the glass-matrix [30]. In borophosphate glasses, the mixed structural units based on phosphorous and boron atoms are formed within the glassy-framework [31].

IR spectra for the $33.33[\text{xNa}_2\text{O}-(1-\text{x})\text{Li}_2\text{O}]-2.5\text{SrO}-2.5\text{TiO}_2-45\text{B}_2\text{O}_3-16.67\text{P}_2\text{O}_5$ glasses are shown in Fig.4. One can observe that the substitution of lithium by sodium do not induce major changes in the IR spectral features. One can anticipate this result since the contents of both the oxide formers B_2O_3 and P_2O_5 are maintained constants and the ratio $\text{O}/(\text{P}+\text{B})$ is unchanged. IR bands are significantly broader leading to significantly greater spectral overlap of borate and phosphate units. However, some assignments can be made, the bands at high wavenumbers $1200-1300\text{ cm}^{-1}$ are ascribed both to asymmetric stretching $\nu_{\text{as}}(\text{PO}_2^-)/\nu_{\text{as}}\text{P}=\text{O}$ of non-bridging oxygen in phosphate chains. The band located in the range $1345-1480\text{ cm}^{-1}$ is attributed to the asymmetric stretching modes of borate triangles BO_3 and BO_2O^- units [32]. The broad band in the range $1000-1250\text{ cm}^{-1}$ is ascribed to the symmetrical

stretching vibration of different phosphate units [16]. The broad band at about $900-970\text{ cm}^{-1}$ belongs to the asymmetric vibrations of $\text{P}-\text{O}-\text{F}$ ($\text{F}=\text{P}, \text{B}$) linkages. The band near $760-780$ is ascribed to $\text{BO}_3\text{-O-BO}_4$ bond bending vibration [32]. It is noted that borate vibrational modes are difficult to discern, although the content of boron is larger than that of phosphorous in the glasses, due to the weaker IR absorption coefficients. Weak band around $725-680\text{ cm}^{-1}$ is assigned to symmetric stretching vibrations $\nu_s\text{P-O-P}$ and or titanate $[\text{TiO}_4]$ and $[\text{TiO}_6]$ units. It is also indicative of the B-O-B bond bending modes. The broad bands in $600-400\text{ cm}^{-1}$ wavenumbers range belongs to bending vibrations of basic structural units of borophosphate glasses. The Li-O and Na-O are observed also in this latter range. Thus, the spectra of all the investigated mixed alkali glasses are fully consistent with the structure of borate and phosphate units. The IR band assignments related to phosphate and borates groups are gathered in Table 2. A deep analysis of the spectra shows that the intensity and the wavenumber position of the bands ascribed to BO_3 and BO_4 structural units ($1250-1500\text{ cm}^{-1}$ and $755-950\text{ cm}^{-1}$, respectively) are dependent on the composition. For instance, the stretching bands of BO_3 ($1250-1500\text{ cm}^{-1}$) show no significant peak position shifts but their intensity change with the composition. The intensity of the band at 1240 cm^{-1} assigned to asymmetric stretching of B-O in orthoborate groups and/or $\nu_{\text{as}}(\text{PO}_2^-)$ varies when Na replaces Li and it becomes very weak for the compositions above ($\text{x}=0.5$).

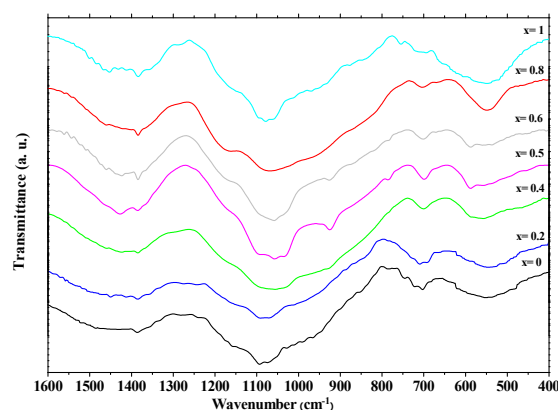


Fig.4. IR spectra of the $33.33[\text{xNa}_2\text{O}-(1-\text{x})\text{Li}_2\text{O}]-2.5\text{SrO}-2.5\text{TiO}_2-45\text{B}_2\text{O}_3-16.67\text{P}_2\text{O}_5$ ($0 \leq \text{x} \leq 1$) glasses.

In addition to the observed intensity changes, some bands show peak position shifts with the Na/Li ratio. It is worth to note that the bands around 950 cm^{-1} and 755 cm^{-1} show shift peak positions when the composition varies. It seems that B-O stretching modes and B-O-B bending vibrations are the most sensible to the substitution of lithium by sodium. The composition dependence of the peak position of the $\text{BO}_3\text{-O-BO}_4$ bond bending mode (around 755 cm^{-1}) varies non-linearly with the $\text{Na}/(\text{Li}+\text{Na})$ ratio as shown in Fig.5, indicating the mixed alkali effect (MAE) in the glasses. The

composition dependence of the peak position of the band ascribed to B-O in BO_4 units (near 950 cm^{-1}) shows also a non-linear variation and its plot is given in Fig.5. This non-linearity suggests also that this vibration mode shows MAE in the glasses under study. The Most change of the position of modes appears for the composition $x=0.5$. The MAE is also reported in borosilicate glasses [32] in which stretching and bending modes of borate units showed non-linearity with the composition.

Table 2

IR band assignments of borate and phosphate groups in the range $400\text{--}1600\text{ cm}^{-1}$

Position of band (cm^{-1})	Band assignment
470	$\delta(\text{O-B-O})$ bending mode
550	$\delta(\text{O-P-O})$ bending mode
720	$\nu_s(\text{P-O-P})$, B-O-B bending vibration
755	$\text{BO}_3\text{-O-BO}_4$ bond bending vibration
950	$\nu_{as}(\text{P-O-P})$, $\nu_{as}(\text{B-O-B})$, $\nu_{as}(\text{B-O})$ in BO_4 unit
1000-1230	Different phosphate groups
1240	B-O asymmetric stretching in orthoborate.
1345-1480	A symmetric stretching of BO_3 and BO_2O^- units

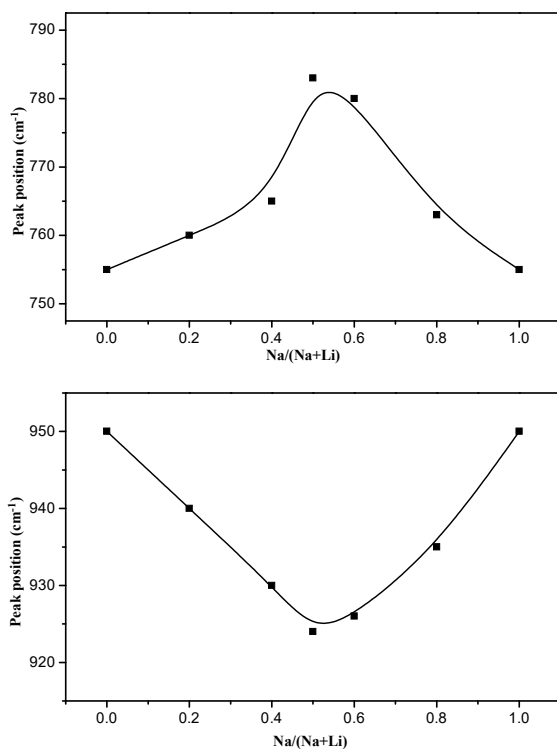


Fig.5. Compositional dependence of IR peak positions in the regions $750\text{--}780\text{ cm}^{-1}$ and $925\text{--}950\text{ cm}^{-1}$ of the glasses.

3.5. EPR spectroscopy

The EPR spectra of the glasses were carried out in order to identify the nature of the paramagnetic entities existing in the framework of the glasses. The obtained spectra of the glasses belonging to the series $33.33[x\text{Na}_2\text{O}-(1-x)\text{Li}_2\text{O}]-2.5\text{SrO}-2.5\text{TiO}_2-45\text{B}_2\text{O}_3-6.67\text{P}_2\text{O}_5$ are shown in Fig.6. All the EPR spectra showed the same shape. The shape of the EPR line is simply due to the fact that the glass has isotropic properties. These EPR spectra exhibit resonance signals similar to those reported for Ti^{3+} ions in other glassy systems [17,18]. The spectra of all the glasses are dominated by a peak located near $g \sim 1.90$. According to the literature [17,18], this signal was assigned to Ti^{3+} ion in a distorted octahedral environment. It has an electric spin $S=1/2$, a nuclear spin $I=1/2$ and electron configuration $3d^1$. Therefore, one can state that the glasses under study contained Ti^{3+} species and the coloration of these samples could be due to the presence of these paramagnetic ions. The g values are determined from Fig.6 where EPR spectra between 0 and 5500 gauss are recorded around 2048 points. Thus, the sensitivity in magnetic field is around 2.6 gauss and 0.0016 error for the g values. The evaluated g values for the mixed alkali glasses are gathered in Table 1. Even though, the g -values for the glasses are similar, one can deduce that it changes with the composition since they are determined with the accurate of 0.0016.

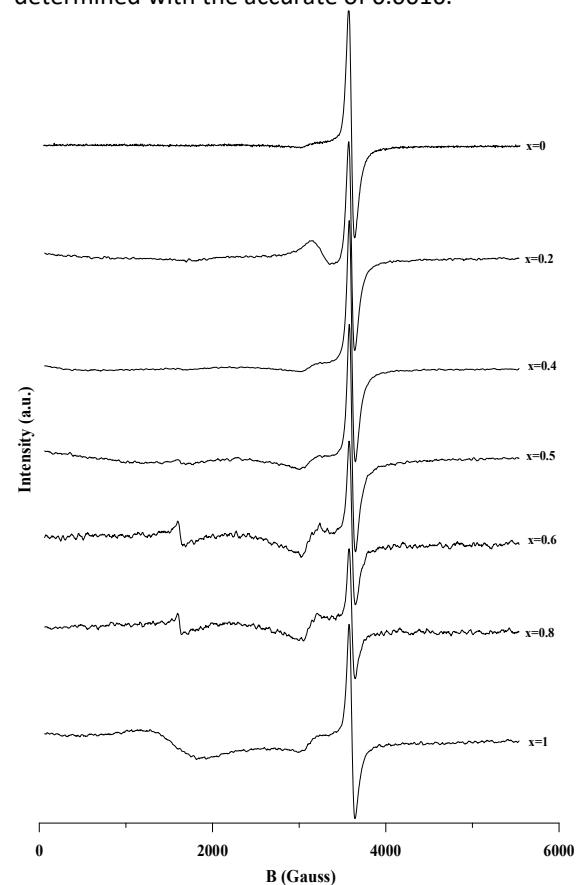


Fig.6. EPR spectra of the glasses $33.33[x\text{Na}_2\text{O}-(1-x)\text{Li}_2\text{O}]-2.5\text{SrO}-2.5\text{TiO}_2-45\text{B}_2\text{O}_3-16.67\text{P}_2\text{O}_5$ ($0 \leq x \leq 1$).

Fig.7 shows the variation of g factor as a function of the composition (x). It is quite interesting to note that g seems to go through a minimum around $x = 0.5$ showing mixed alkali effect (MAE) in the glasses. The non-linearity in the variation of g with composition was also observed in other glass systems [19,20,33,34]. The variation may be due to structural changes taking place within the composition. The alkali oxides Li_2O and Na_2O are modifiers and make weakly bonded O^{2-} around each Ti^{3+} ions. Li^+ and Na^+ ions should remain in the neighborhood of these ions. Replacement of Li_2O by Na_2O causes a smooth change in the micro-environmental fluctuations around Ti^{3+} ion which could be at the origin of the observed non-linear variation of g -factor versus the composition.

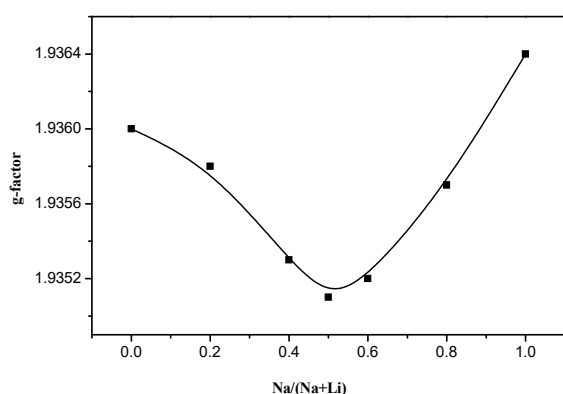


Fig.7. Variation of the parameter (g -factor) as a function of the $\text{Na}/(\text{Na}+\text{Li})$ ratio.

4. Conclusion

The results of this study have shown that the composition dependence of some physical properties such as density and molar volume are linear suggesting that the structure is almost unchanged by the substitution of Li_2O by Na_2O . The decrease of density with the ratio $\text{Na}/(\text{Na}+\text{Li})$ is due to an expansion in the glass matrix when replacing the smaller Li^+ ions by the larger Na^+ ones. The variation of the glass transition temperature T_g as a function of the composition shows a pronounced mixed alkali effect at the composition ($x=0.5$). This MAE is associated to the 'structural disorder' imposed by the presence of two kinds of cations. Infrared spectroscopy has shown that the substitution of lithium by sodium induces non-linear variation of peak positions of some stretching and bending vibrational modes of borates indicating the presence of MAE. EPR spectra exhibits resonance signals relatives to Ti^{3+} ions. The coloration of the glasses under study could be due to the presence of these paramagnetic ions. It is observed that the composition dependence of the parameter g shows a minimum around $x = 0.5$ suggesting mixed alkali effect (MAE) in the glasses. Finally, it is interesting to note that thermal analysis, infrared spectroscopy and EPR experiments showed the mixed alkali effect in the glasses.

Acknowledgements

The authors would like to thank the Swedish Research Council for the financial grant SRL(MENA) # 348- 2014-4287. BM is also grateful to the University Hassan 1st and the Office Chérifien des Phosphates in the Moroccan Kingdom (OCP group) and Mohammed VI Polytechnic University and its Materials Science and Nano-engineering Department, (MSN) for their support.

References

- [1] L. Petit, T. Cardinal, J. J. Videau, F. Smektala, T. Jouan, K. Richardson, and A. Schulte, *Mater. Sci. Eng. B* 117 (2005) 283-286.
- [2] V. Nazabal, E. Fargin, C. Labrugère, G. Le Flem, *J. Non-Cryst. Solids* 270 (2000) 223-233.
- [3] L. Koudelka, P. Mošner, M. Zeyer, C. Jäger, *J. Non-Cryst. Solids* 326&327 (2003) 72-76.
- [4] A.P. Ahoussou, J. Rogez, A. Kone, *J. Non-Cryst. Solids* 353 (2007) 271-275.
- [5] D. E. Day, *J. Non-Cryst. Solids* 21 (1976) 343-372.
- [6] H. Zhang, S. Koritala, K. Farooqui, R. Boekenhauer, D. Bain, S. Kambeyanda, S.A. Feller, *Phys. Chem. Glasses*, 32 (5) (1991) 185-187.
- [7] J. F. Duce, J. J. Videau, *Matter Lett.* 13 (1992) 271-274.
- [8] J. C. Knowles, *J. Mater Chem*, 13 (2003) 2395-2401.
- [9] T. Cardinal, E. Fargin, G. Le Flem, and S. Leboiteux, *J. Non-Cryst. Solids* 222 (1997) 228-234.
- [10] M. Dussauze, O. Bidault, E. Fargin, M. Maglione, and V. Rodriguez, *J. Appl. Phys.* 100 (2006) 034905-034912.
- [11] J. O. Isard, *J. Non-Cryst. Solids* 1 (1969) 235-261.
- [12] M. D. Ingram, *Phys. Chem. Glasses* 28 (1987) 215-234.
- [13] A. Bunde, M. D. Ingram, P. Maass, *J. Non-Cryst. Solids*, 172 (1994) 1222-1236.
- [14] J. Swenson, S. Adams, *Phys. Rev. Lett.* 90 (2003) 155507-155511.
- [15] M. Tomozawa, M. Yoshiyagawa, *Glastech. Ber.*, 56k (1983) 939-944.
- [16] H. Sinouh, L. Bih, M. Azrour, A. ElBouari, S. Benmokhtar, B. Manoun, B. Belhorma, T. Baudin, P. Berthet, R. Haumont, D. Solas, *J. Phys. Chem. Solids* 73 (2012) 961-968.
- [17] E. Mansour, *Physica B* 362 (2005) 88-94.
- [18] D. Kim, C. Hwang, D. Gwoo, T. Kim, N. Kim, B-Ki Ryu, *Electronic Mat. Lett.*, 7 (2011) 343-347.
- [19] H. Doweidar, *J. Mater. Sci.* 25 (1990) 253-258.
- [20] H. Budhwani, S. Feller, *Phys. Chem. Glasses* 36 (4) (1995) 183-190.
- [21] R. K. Brow, R. J. Kirkpatrick, G. L. Turner, *J. Am. Ceram. Soc.*, 76 (1993) 919-928.
- [22] B.M.G. Melo, M.P.F. Graça, P.R. Prezas, M.A. Valente, A.F. Almeida, F.N.A. Freire, L. Bih, *J. Non-Cryst. Solids* 434 (2016) 28-35.
- [23] P.K. Jha, O.P. Pandey, K. Singh, *J. Mol. Struct.* 1094 (2015) 174-182.
- [24] L. Bih, A. Nadiri, M. El Omari, A. Yacoubi, M. Haddad, *Phys. Chem. Glasses*, 43 (3), (2002) 153-157.
- [25] A. Faivre, D. Viviani, J. Phalippou, *Solid State Ionics* 176 (2005) 325-332.
- [26] Y. Gao, *Chem. Phys. Lett.* 417 (2006) 430-433.
- [27] L. Abbas, L. Bih, A. Nadiri, Y. El Amraoui, D. Mezzane, B. Elouadi, *J. Mol. Struct.* 876 (2008) 194-198.
- [28] L. Bih, L. Abbas, S. Mohdachi, A. Nadiri, *J. Mol. Struct.* 891 (2008) 173-177.

- [29] F. Behrends, H. Eckert, J. Phys. Chem. C, 115 (2011) 17175-17183.
- [30] P.J. Bray, J.G. O'Keefe, Phys. Chem. Glasses 4 (2) (1963) 37-46.
- [31] S.W. Martin, Eur. J. Solid State Chem., 1 (1991) 163-205.
- [32] V. Padmaja, P. Kistaiah, J. Phys. Chem. A, 113 (2009) 2397-2404.
- [33] R.P.Sreekanth Chakradhar, K.P. Ramesh1, J. L. Rao, J. Ramakrishna, J. Phys.: Condens. Matter 15 (2003) 1469-1486.
- [34] G. Giridhar, M. Rangacharyulu, R.V.S.S.N. Ravikumar1, P. Sambasiva Rao, IOP Conf. Series: Mat. Sci. Eng. 2 (2009) 012058-012063.