Structural and Electrical Properties of Iron Phosphate Glasses

A. Mogus-Milankovic[1] A. Santic[1] and Delbert E. Day[2]
[1]*Rudjer Boskovic Institute, Department of Physics, 10000 Zagreb, Croatia*
[2]*University of Missouri-Rolla, Center for Materials Research, Rolla, MO 65409, USA*

The relationship between structure and electrical properties for iron phosphate glasses containing different content of alkali and alkaline earth oxides has been studied. The structural changes of these glasses have been investigated by Raman spectroscopy. The Raman spectra show that the iron play an important role in formation of P-O-Fe bonds that strengthens the cross bonding of shorter phosphate chains. The electrical conductivity of these glasses has been measured by thermally stimulated current and impedance spectroscopy. The investigation of cesium iron phosphate glasses has shown that the slowly moving cesium ions are more tightly bound to the non-bridging oxygen ions and make no measurable contribution to the dc conductivity in glasses containing up to 28 mol% Cs_2O. The dc conductivity in these cesium-containing glasses is totally electronic, controlled by hopping between iron ions. The electrical conductivity in the mixed alkali, sodium and potassium, iron phosphate glasses is also nearly independent of the different sodium and potassium content. This independence indicates that the mobility of sodium and potassium is almost invariant in the single and mixed alkali iron phosphate glasses. The electrical changes that are appeared in the alumino-phosphate glasses show that the addition of Fe_2O_3 content have an effect on the dc conductivity. With increasing Fe_2O_3 content electrical conductivity depends upon distance between iron ions suggesting electronic conduction. The impedance analysis for these glasses shows that the changes in the electrical conduction mechanisms coincide with the changes in the structure.

1. Introduction

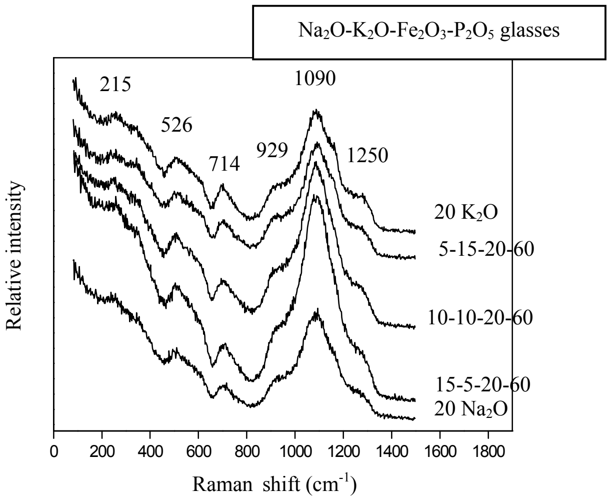
The structure and properties of phosphate glasses have attracted considerable interest [1] in recent years because of their unique structural and electrical properties. In binary iron phosphate glasses, with increasing Fe_2O_3 content, the number of Fe-O-P bonds increased, while the number of bridging oxygen P-O-P bonds decreased [2] so that the phosphate network changed from the chain-like metaphosphate structure through the dimeric pyrophosphate to the isolated orthophosphate structure [3]. Phosphate glasses containing transition metal ions such as iron are electronically conducting semiconductors. Conduction is achieved by electrons hopping from low, iron (II), to high valence, iron (III), sites and depends upon the average distance between iron ions and the relative fraction of iron(II)and iron(III) ions [4]. The charge transfer is usually termed a "small polaron hopping" [5]. In the present study the contribution of the alkali ions in both single and mixed alkali iron phosphate glasses to the total electrical conductivity and the effect of glass structure on the electrical conductivity in these glasses was examined by impedance spectroscopy. Also, the aim of the present work was to investigate how the addition of Al_2O_3 and Fe_2O_3 to the starting sodium phosphate glass affected the electrical conductivity.

2. Experimental

The glasses were melted in an alumina crucible in air at ~ 1300 K for approximately 1 h using a mixture of reagent grade oxides or carbonates and ammonium dihydrogen phosphate. All the composition in Table 1 formed glass and are the batch composition in mol%. The changes in the phosphate network for glasses investigated were measured using Raman spectroscopy. The electrical impedance was measured with an Impedance Analyzer I-100 while the thermally stimulated current (TSC) was measured with a Keithley 617 Electrometer. Gold electrodes, 7 mm in diameter, were evaporated onto both sides of a 1 mm thick piece of annealed glass.

3. Results and discussion

3.1. Raman spectra



The Raman spectra measured for the single- and mixed-alkali iron phosphate glasses are shown in Fig.1. In mixed and single alkali iron phosphate glasses the pyrophosphate, $(P_2O_7)^{4-}$, units dominate the structure along with a low concentration of metaphosphate $(PO_3)^{1-}$ groups, and isolated $(PO_4)^{3-}$ tetrahedra. The identical Raman spectra for all these glasses clearly indicate that the structure of these iron phosphate glasses does not depend in any detectable way upon the type (Na or K) or concentration of alkali ion present in the glass. Similarly, the Raman spectra for the cesium iron phosphate glasses consist predominantly of pyrophosphate $(P_2O_7)^{4-}$ units with a small amount of chains of $(PO_3)^-$ groups. The structural changes in the sodium phosphate glasses show that the addition of Al_2O_3 content has a different effect on the phosphate network than the addition of Fe_2O_3, Figs. 2(a) and 2(b). With increasing Fe_2O_3 content up to 20 mol% the structure changes from the chain-like metaphosphate to the pyrophosphate structure. The iron ions play an important role in forming P-O-Fe bonds that strengthen the cross-bonding of shorter pyrophosphate chains. On the other hand, with increasing Al_2O_3 content up to 20 mol%, the sodium metaphosphate is replaced by aluminum metaphosphate where $Al(OP)_6$ units cross-link phosphate chains.

3.2. Electrical conductivity

Fig. 3 shows the dc conductivity for cesium iron phosphate glasses calculated from TSC measurements. The dc conductivity is thermally activated and the activation energy, E_{dc}, can be determined from the slope of log σ_{dc}(TSC) vs. 1/T curves as shown in Fig. 3. The dc conductivity exhibits an Arrhenius temperature dependence, $\sigma_{dc} = \sigma_o \exp(-E_{dc}/k_BT)$, where σ_{dc} is the conductivity, σ_o is the pre-exponent, E_{dc} is the activation energy for the dc conductivity, k_B is the Boltzman constant and T is temperature (K). The activation energy for dc conductivity and the measured dc conductivity, σ_{dc}(TSC) at 300 K for the cesium iron phosphate glasses remained constant within experimental error, Fig 4(a). Similarly, neither the activation energy, E_{dc}, nor the measured dc conductivity, σ_{dc}, at 300 K for the mixed alkali (Na and K) iron phosphate glasses shows any evidence of a maximum or minimum, Fig. 4(b), which is typical of the mixed alkali effect seen in mixed alkali silicate or phosphate glasses.

The dc conductivity for the sodium phosphate glasses containing Al_2O_3 and/or Fe_2O_3 was calculated from the frequency dependence of the conductivity at different temperatures. The plateau in the conductivity at frequencies below ~ 100 Hz corresponds to the dc conductivity for each glass at the temperature used. At low frequency, the dc conductivity, $\sigma_{dc}(\omega)$, increases with increasing temperature and shows a weak frequency dependence [6]. The decrease in the dc conductivity and the activation energy, Table 1, for the N_2O-Al_2O_3-P_2O_5 glasses is attributed to the decrease in the Na_2O content from 35 to 20 mol%. The activation energy of 80.1 to 72.4 $kJmol^{-1}$ in the N_2O-Al_2O_3-P_2O_5 glasses is similar to the activation energy of ionic conductors [7]. On the other hand, an increase in dc conductivity and a decrease in activation energy for glass containing 15 and 20 mol% Fe_2O_3 suggests some changes in conduction mechanisms. It has been previously reported [4,5] that in iron phosphate glasses the dc conductivity is electronic and depends strongly upon the distance R between the Fe ions. Assuming that the conductivity is due to electron hopping from Fe(II) to Fe(III) then with decreasing R from R = 6.17 Å for the 35-5-60 glass to R = 3,79 Å for 20-20-60 glass in Na_2O- Fe_2O_3-P_2O_5 series it is reasonable to expect an increase in dc conductivity. At the same time, the activation energy of 53.1 $kJmol^{-1}$ for the 20-20-60 glass suggests that the dc conductivity is controlled by electron hopping and depends upon the distance R between the Fe ions. Such changes in conduction mechanisms is often related to changes in the structure of a glass. Although the relative Na, Al and P content affects the conductivity, Fe seems to play an important structural role in the phosphate network iron containing glasses. The Raman spectra for these glasses show that the substitution of Fe_2O_3 for Al_2O_3 changes the structure from metaphosphate dominated by the P-O-P chains to pyrophosphate where $(P_2O_7)^{4-}$ groups are connected by oxygen polyhedra that contain the iron in both oxidation states, as Fe(II) and Fe(III) [2,3,7]. It seems that the iron ions shorten the P-O-P chains and thus, increase the non-bridging $P\text{-}O^-$ oxygen bonds that form strong P-O-Fe bonds and cross-link shorter phosphate chains. This effect of Fe_2O_3 content on properties of the glasses is consistent with the structural role of iron ions that strengthen the glass network.

4. Conclusion

The electrical conductivity of alkali and mixed alkali iron phosphate glasses is dominated by electron hopping between Fe(II) to Fe(III) sites in the glass and the mobility of the alkali ions is so low that they make no detectable contribution to the overall electrical conductivity. The structural and electrical changes show that with increasing Fe_2O_3 content in sodium phosphate glasses there is a corresponding decrease in the number of P-O-P bonds as pyrophosphate $(P_2O_7)^{4-}$ units are formed. The decrease in activation energy with increasing Fe_2O_3 content lead to the conclusion that the electrical conductivity depends upon the distance between iron ions, which suggests electronic conduction. The changes in conduction mechanisms are attributed to the significant effect of iron ions on the phosphate structure.

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6. Figure Caption

Fig. 1. Raman spectra for the single- and mixed-alkali iron phosphate glasses.

Fig. 2. Raman spectra for N_2O-Al_2O_3-P_2O_5 (a) and Na_2O- Fe_2O_3-P_2O_5 (b) glasses where glasses are identified by their batch composition given in Table 1.

Fig. 3. The dependence of dc conductivity measured at 300 K upon the Cs_2O content (a) the mixed-alkali content (b). Inset: dc conductivity for cesium iron phosphate glasses calculated from TSC measurements.

Table 1. Composition in mol% and selected data for iron phosphate glasses

Batch compositions (mol%)						O/P	Fe(II)/Fe$_{tot}$*	D	R	σ_{dc}(TSC)**	E$_{dc}$
Na$_2$O	K$_2$O	Cs$_2$O	Al$_2$O$_3$	Fe$_2$O$_3$	P$_2$O$_5$			(gcm^{-3})	(Å)	(Ωm)$^{-1}$	(kJmol^{-1})
				35.3	64.7	3.32	0.20	nm	-	1.16x10^{-8}	51.7
		5.0		33.5	61.5	3.36	0.14	nm	-	3.60x10^{-9}	55.0
		17.4		29.1	53.5	3.48	0.15	nm	-	5.50x10^{-9}	53.3
		17.6		29.7	52.7	3.51	0.13	nm	-	6.10x10^{-9}	52.2
		24.0		26.8	49.2	3.56	0.15	nm	-	8.40x10^{-9}	54.9
		28.0		23.4	48.7	3.57	0.15	nm	-	6.10x10^{-9}	55.1
5.3				29.2	65.6	3.21	0.23	3.13	2.87	6.13x10^{-9}	55.9
10.2				27.6	62.2	3.25	0.27	3.15	2.88	2.04x10^{-8}	52.0
14.9				26.2	58.9	3.29	0.28	3.14	2.90	3.15x10^{-8}	48.2
20.0				20.0	60.0	3.17	0.24	2.87	3.55	1.62x10^{-9}	56.8
15.0	5.0			20.0	60.0	3.17	0.26	2.86	3.56	1.48x10^{-9}	56.1
10.0	10.0			20.0	60.0	3.17	0.25	2.85	3.58	1.68x10^{-9}	55.2
5.0	15.0			20.0	60.0	3.17	0.24	2.83	3.61	2.29x10^{-9}	53.2
20.0				20.0	60.0	3.17	0.26	2.80	3.63	2.95x10^{-9}	52.7
35.0			5.0		60.0	2.90	-	2.45	-	3.14x10^{-8}	80.1
30.0			10.0		60.0	3.00	-	2.49	-	3.14x10^{-8}	74.3
20.0			20.0		60.0	3.20	-	2.59	-	1.40x10^{-8}	72.4
20.0			15.0	5.0	60.0	3.20	nm	2.61	6.24	6.31x10^{-9}	69.5
20.0			10.0	10.0	60.0	3.20	nm	2.76	4.86	5.88x10^{-9}	66.6
20.0			5.0	15.0	60.0	3.20	nm	2.79	4.23	1.41x10^{-8}	55.9
35.0				5.0	60.0	2.90	nm	2.69	6.17	4.08x10^{-8}	74.3
30.0				10.0	60.0	3.00	nm	2.83	4.82	3.90x10^{-8}	73.3
20.0				20.0	60.0	3.20	nm	2.89	3.79	1.17x10^{-8}	53.1

*calculated area of Fe(II) and Fe(III) doublets in the Mössbauer spectra, ** measured at 300K, nm means not measured.

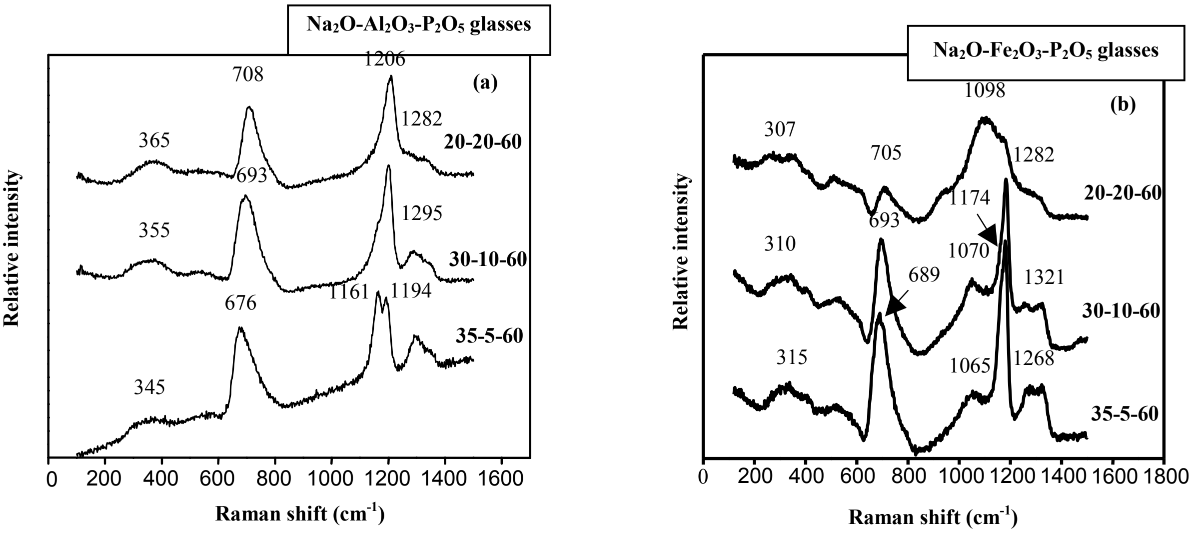
Na₂O-Al₂O₃-P₂O₅ glasses
(a)
Relative intensity
708
1206
1282
365
20-20-60
693
355
1295
30-10-60
676
1161
1194
35-5-60
345
0 200 400 600 800 1000 1200 1400 1600
Raman shift (cm⁻¹)
Na₂O-Fe₂O₃-P₂O₅ glasses
(b)
1098
307
705
1282
20-20-60
693
1174
310
1070
689
1321
30-10-60
315
1065
1268
35-5-60
0 200 400 600 800 1000 1200 1400 1600 1800
Raman shift (cm⁻¹)

Fig. 2.

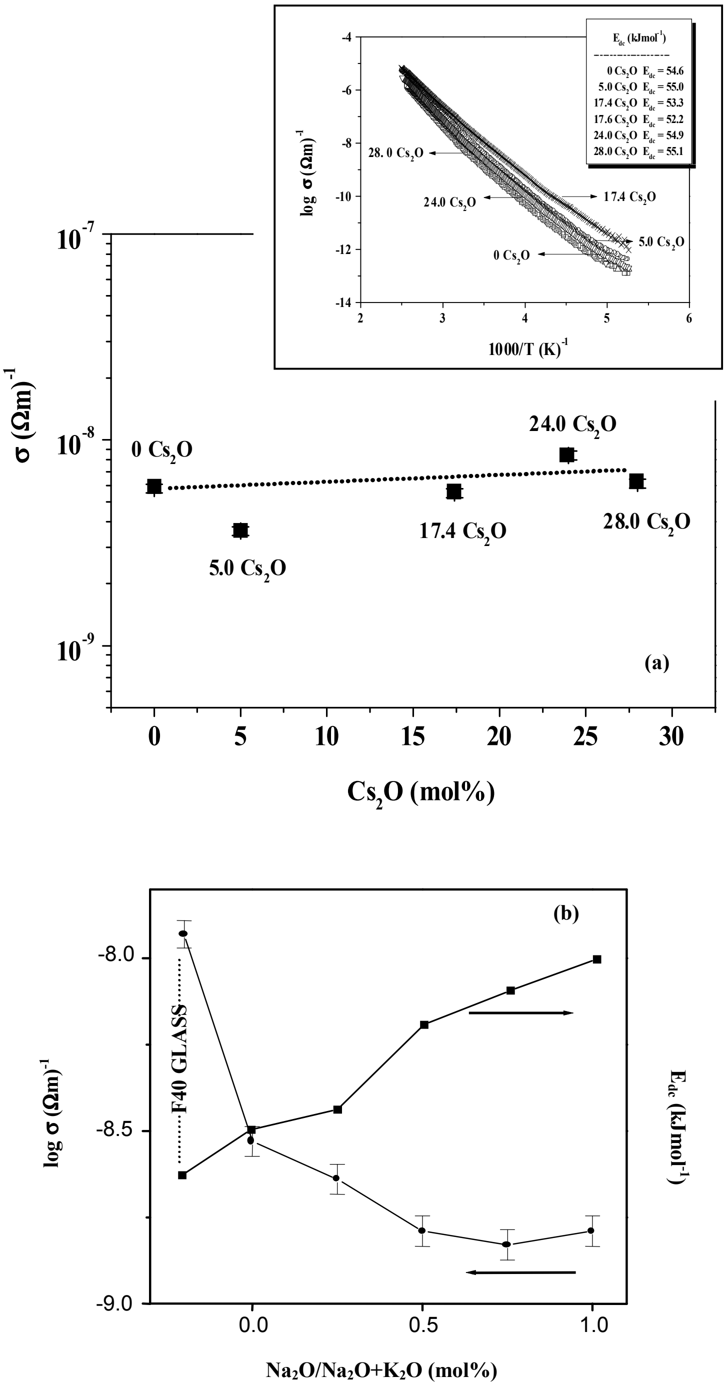
E_dc (kJmol⁻¹)
0 Cs₂O E_dc = 54.6
5.0 Cs₂O E_dc = 55.0
17.4 Cs₂O E_dc = 53.3
17.6 Cs₂O E_dc = 52.2
24.0 Cs₂O E_dc = 54.9
28.0 Cs₂O E_dc = 55.1
log σ (Ωm)⁻¹
28. 0 Cs₂O
24.0 Cs₂O
17.4 Cs₂O
5.0 Cs₂O
0 Cs₂O
-4 -6 -8 -10 -12 -14
2 3 4 5 6
1000/T (K)⁻¹
σ (Ωm)⁻¹
10⁻⁷
10⁻⁸
10⁻⁹
0 Cs₂O
5.0 Cs₂O
17.4 Cs₂O
24.0 Cs₂O
28.0 Cs₂O
(a)
0 5 10 15 20 25 30
Cs₂O (mol%)
(b)
log σ (Ωm)⁻¹
-8.0
-8.5
-9.0
F40 GLASS
E_dc (kJmol⁻¹)
0.0 0.5 1.0
Na₂O/Na₂O+K₂O (mol%)

Fig. 3.