XRD Study of Amorphous P_2O_5-Na_2O-Nb_2O_5 Glasses

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*A set of amorphous $(P_2O_5)_{75-x}(Na_2O)_{25}(Nb_2O_5)_x$ **oxide glasses** (x=0, 5, 10 and 15) were investigated using XRD. The structural information of the first coordination shell in the short range order (SRO) were extracted using radial distribution analysis. The addition of niobium oxide **molecules were** found to replace the phosphate **groups** and changed the arrangement of the building units in both SRO and medium range order (MRO). In the SRO region the basic P-O **bonds** were arranged in the form PO_4 with an average P-O distance of 1.749(3) Å. The Na-O **bonds** were ordered in the form of distorted octahedral in a shortened atomic pair distance of 3.242(5)Å. The Nb-Nb pairs in the MRO **were found to be** at ~ 2.95(5) Å with a coordination number of 2.0. The introduction of Nb_2O_5 and Na_2O as a matrix modifier, both the peak shapes and peak positions exihibit considerable changes in both SRO and MRO ranges. The correlated Nb-Nb pairs may replace other phosphate correlated pairs such as P-Na in the SRO region with the increase of x. The structural modeling of the studied system was performed **and show** a good **agreement with** the observed and simulated results in the real space.*

1. Introduction:

Phosphate glasses have several advantages over conventional silicate and borate glasses due to their ***peculiar*** properties such as high thermal expansion coefficients, low melting and softening temperatures, and high ultraviolet transmission [1-6]. However, the poor chemical durability and high hygroscopic nature of phosphate glasses limited their technological applications. The physical properties and the chemical durability of phosphate glasses can be improved by introducing a number of glass formers and modifiers such as MoO_3, Fe_2O_3, Nb_2O_3, WO_3 [7-10]. The addition of tungsten oxide to phosphate glass improves its aqueous durability, increases the glass transition temperature, reduces its thermal expansion coefficient and improves its resistance to crystallization.

Investigations *of* different niobium phosphate glass systems mixed with a variety of transition metal ions like manganese, has been the subject of *enhanced* academic and technological interest. These glasses find a wide range of applications, such as glass fibers and optical lenses [11, 12], as electrodes [13], for radioactive waste immbolization [14], in hermetic sealing of metallic and ceramic materials [15] and as glass planar optical waveguides fabricated by ion exchange [16]. Further, these glasses are the most advantage materials for hosting lasing ions like manganese to give laser emission of high intensity with minimum beam divergence [17] and [14-17].

Rare-earth phosphate glasses with compositions in the metaphosphate-ultraphosphate region $(R_2O_3)_{0.25}(P_2O_5)_{0.75}$-$(R_2O_3)_{0.166}(P_2O_5)_{0.833}$ *are promising materials* in the laser and optoelectronics industry. Indeed, these materials have recently been under investigation for commercial application in fiber lasers [18]. ***This is most likely due to the fact that*** the rare-earth ions possess the required energy levels for achieving successful population inversion, and the non-linear refractive index is large enough to exhibit the required optical effects, without causing beam breakup and damage. Moreover, the particularly high concentration of rare-earth dopant present in these materials results in a myriad of exotic physical properties at low temperatures: negative thermal expansion and pressure dependence of bulk moduli [2] and unprecedented magnetic, magneto-optical and opto-acoustic phenomena [19-21]. The data described in this paper *[18]* represent the first successful complete neutron anomalous dispersion study on an amorphous material.

The objective of *the present* work is to investigate phosphate glasses; $(P_2O_5)_{75-x}(Na_2O)_{25}(Nb_2O_5)_x$ (x=0.0, 5.0, 10.0 and 15.0) using XRD with the application of radial distribution analysis in both SRO and MRO to throw some light on the role of niobium oxide introduced in the phosphate and constructing a three-dimensional model from the resulting observed RDF informations.

[N.B.: This work is mainly concerned with the given type of based phosphate glasses and I did not found a reported data on its RDF analysis and I think it's not of more importance to give a structural informations on its crystalline phase]

2. Experimental Work

2.1.1. Sample Preparation

Samples were prepared from reagent grade ammonium phosphate $(NH_4H_2PO_4)$, sodium carbonate (Na_2CO_3) and niobium oxide (Nb_2O_3) by mixing the reagents in appropriate proportion and heating in platinum crucibles

in an electric muffle furnace. To prevent excessive boiling and consequent loss of mass, water and ammonia $NH_4H_2PO_4$ were removed by pre-heating the mixture at 200 °C for several hours before fusion. The mixture was subsequently melted at 1150 °C for 1 h. The melt was then poured into a stainless steel mould and pressed between two stainless steel plates. The glass compositions were ***prepared according to this formula*** $(P_2O_5)_{75-x}(Na_2O)_{25}(Nb_2O_3)_x$; x=0, 5, 10 and 15 wt%.

2.1.2. RDF Formulation Analysis

The total structure factor of a glass is given ***by***

$$S(K)= \{ I(K)-[<f^2>-<f>^2]\}/ <f>^2 \qquad (1)$$

where I(K) is being the scattered corrected X-ray intensity of the atomic species constituting the given specimen, f is the atomic scattering factor, $K=4\pi\sin\theta/\lambda$ is the magnitude of the scattering vector and λ is being the wavelength of the applied radiation. The term $[<f^2>-<f>^2]$ is known as the Laue diffraction. The Laue term is of more significant at small angle (2θ) of scattering. The observed S(K) is related to the deviation from the average number density $\rho_\circ$ by a sine transform [18].

$$S(K)=4\pi/K \int r[\rho(r) - \rho_\circ]\sin(Kr)dr \qquad (2)$$

The integration limit is from zero to infinity and experimentally it will be replaced by $0-K_{max}$ and $\rho(r)$ is the atomic density as a function of the radial distance r. Here

$$\rho_{\circ =} \rho N/A \times 10^{24} \qquad (3)$$

where ρ is the sample density in gm/cm^3, N is the Avogadro's number, A is being the sample atomic weight. RDF is given as

$$4\pi r^2 \rho(r) = r G(r)+ 4\pi r^2 \rho_\circ \qquad (4)$$

where G(r) is the reduced RDF, so

$$G(r) = 4\pi r [\rho(r)-\rho_\circ] = 2/\pi \int K[S(K)-1]\exp(-\alpha^2 K^2)\sin(Kr)dK \qquad (5)$$

The term $4\pi r^2\rho_\circ$ ***in eq. (4)*** is of asymptotic form and α^2 in eq. (5) is the disordering parameter of value $\approx 0.01 Å^2$ mainly used to reduce the effect of spurious details in the high K-range in the measured data. The applied programs for calculating RDF and extracting the required informations in both SRO and MRO ranges are given by V. Petkov [22] and a package programs of "Synchrotron Radiation" [LURE-France] [23].

2.1.3. XRD Experimental Setup

The present data were collected using Philips (X'pert MPD) diffractometer *using* the Bragg-Brentano para-focusing technique. Highly monochromated Cu-radiation (wavelength= 1.54051Å) was used. The step scan mode was applied in the 2θ-range (4-157.4612°). The step size $\Delta 2\theta$ *was* 0.04° and the counting time was 10 seconds for each reading. The corresponding accessible maximum scattering vector magnitude, K, was 8.0 Å^{-1}. The air scattering was avoided by a suitable applied arrangement of XRD system. The receiving and divergence slits were properly chosen in both small and large 2θ-ranges, in order to improve the qualities of data collected.

3. Results and Discussion

The scattered intensity in the K-space are corrected for the polarization and absorption, scaled and normalized to get on the self scattered intensity and the structure factor S(K) [24-27]. Table 1 gives some physical parameters of the studied glasses depicting a reflection of the increased sample densities and oxygen *content* with adding Niobium oxide.

Table (1) Some Physical Parameters of the Studied amorphous $(P_2O_5)_{75-x}(Na_2O)_{25}(Nb_2O_5)_x$

Parameter	P	Na	Nb	O	Sampl	Samp2	Samp3	Samp4	Comments
Density $\rho(gm/cm^3)$	1.83	0.971	8.57	1.429	8.947	9.621	10.295	10.969	Calculated density
f' (λ=1.54051Å)	0.283	0.128	-0.25	0.045	------	-------	-------	-------	E(Cu-k$_\alpha$)=8.0477keV
f" (λ=1.54051Å)	0.433	0.124	2.452	0.032	------	-------	-------	-------	
f "(k$_\alpha$;λ=0.748Å)	0.106	0.028	0.686	0.007	------	-------	-------	-------	E(Nb-k$_\alpha$)=16.581keV
f "(k$_\beta$; λ=0.666Å)	0.083	0.022	0.551	0.005	------	-------	-------	-------	E(Nb-k$_\beta$)=18.614keV
Atomic no. Z	15	11	41	8	------	-------	-------	-------	
Atomic Weight A	31	23	93	16	122	128.2	150.4	140.6	
μ/ρ (cm^2/gm)	76.6	30.21	146.9	11.63	79.50	101.08	113.19	146.12	For Samp1
$\rho_\circ$ Atoms/Å^3	-----	------	-----	-----	0.049	0.0497	0.0453	0.0517	For Samp2
Elemental Concentration	0.381	0.094	0.00	0.525	------	-------	-------	------	For Samp3
	0.339	0.089	0.073	0.499	------	-------	-------	------	For Samp4
	0.268	0.077	0.124	0.532	------	-------	-------	-------	
	0.265	0.082	0.198	0.455	------	-------	-------	-------	

Figure (1) shows the total structure factor S(K) in the K-space for the studied samples. The first distinct peak was located at ~ 1.70Å^{-1} having a composite structure with the introduction of niobates in the matrix. The second broadened peak is observed around 4.70Å^{-1}, which reflects the presence of MRO in the amorphous matrix. There is no, observed further peaks in the

extended K-space which indicates the presence of only the first ordered shells in SRO and MRO.
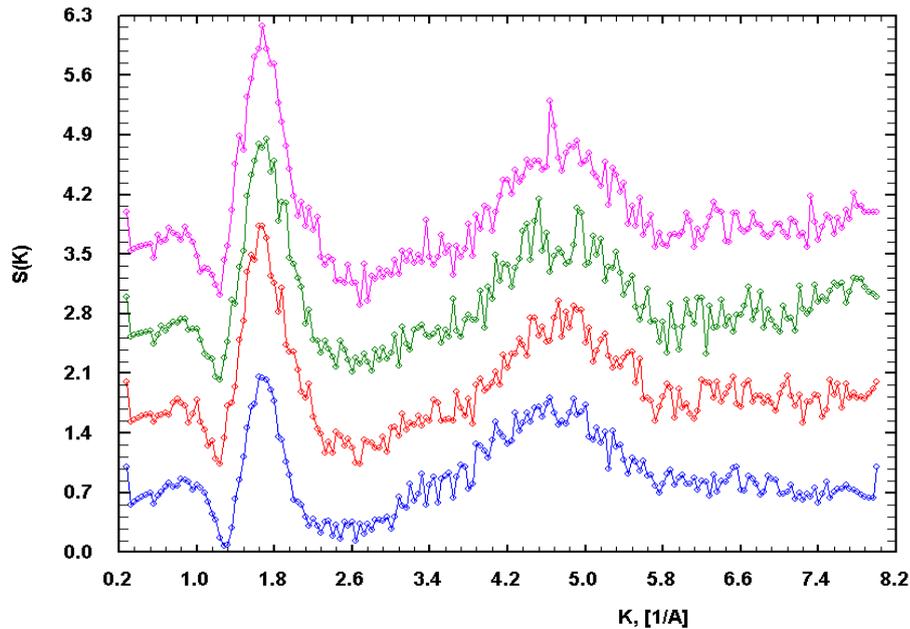
Fig. (1): The Total Structure Factor in the K-space of the Amorphous $(75-x)P_2O_5-25$ $Na_2O-xNb_2O_5$ with x=0.0, 5, 10 and 15 Weight % (from bottom to top) with XRD Source of Wavelength 1.54051 Angstrom.

Figure(2) gives the RDF versus the radial distance for the given samples. In the first sample (x=0.0), the first coordination shell was located at 1.732Å with a coordination number 5.122($\pm$0.2). This shell had a shoulder at about 2.30Å. This shell belongs to P-O pairs arranged in the form PO_4 units and the post shoulder revealing the presence of P-P correlated pairs of a coordination number about 1.0. The coordination shell centered at 3.26Å which belongs to Na-O atomic pairs arranged in the form of distorted octahedral blocks of a coordination number ~ 4.74. For this specimen of zero percent niobates non-extended real information depicted in the RDF.

In the second sample x=5.0, the first RDF peak was observed at the same position as in the first sample at 1.732Å with the absence of the observed post shoulder at 2.30Å which means a good Gaussian shape of this peak in x=5.0 *is evolved and the absence of P-P pairs due to the absence of the previous shoulder*. This observed first shell is due to also to P-O linked pairs. The P-O pairs are still linked in form of PO_4 units and the introduction of niobates in the matrix increases the possibility of niobium atoms to replace phosphorus atoms at a larger distance of ~ 2.60Å. The possibility of formation

of Nb-O pairs at about 2.30Å instead of P-P and/or P-Nb pairs is of small weight due to the high weight percent of P_2O_5 as a glassy former in the given system. The second shell in the second sample(x=5.0) was observed at 3.212Å with a smaller distance compared to its value in the first sample by about 0.05Å and with a decreased coordination number to be~ 3.80. This change of Na-O coordinated pairs of octahedral to tetrahedral coordinated atoms is mainly due to the introduction of niobates in the given amorphous system. As a consequence, a new formed pairs linked with a referenced niobium atom may be evolved instead of sodium atom.
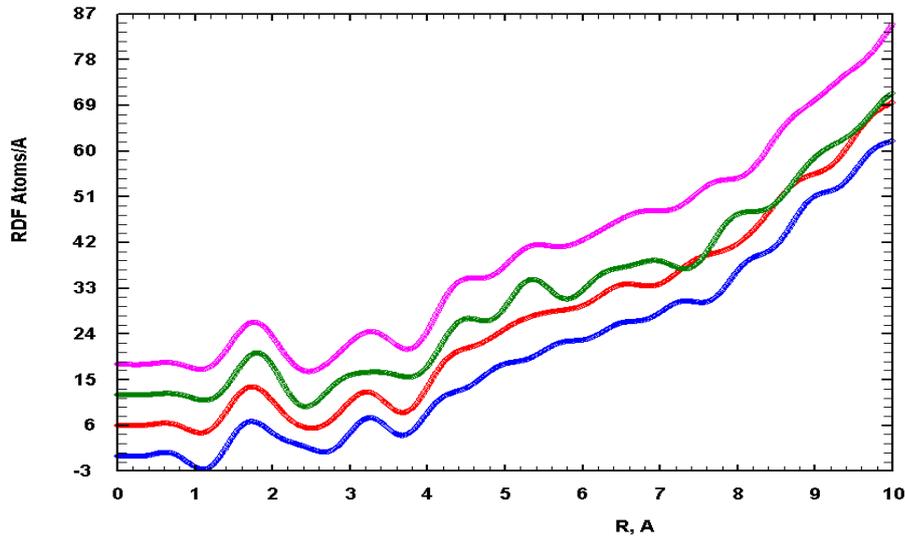
Fig. (2): The Total RDF of Amorphous P_2O_5 Na_2O-Nb_2O_5 Versus R for Doped Nb_2O_5 with 0.0, 5, 10.0 and 15.0 Weight % Respectively Replacing Phosphate (From bottom to top)

In the third sample (x=10.0), a large changes are observed in RDF peaks in both SRO and MRO regions. The first RDF coordination shell is elongated and revealed at 1.80Å having an increased coordination number 6.85. Also, the second shell is shifted to 3.23Å with an increased coordination number of 4.73. This second peak was in *the* form of broad composite peaks of an average maximum of about 3.30Å. This gives an evidence of PO_4 formation followed by P-Nb arranged pairs of trigonal form. The next two longer r-observed peaks (MRO) are positioned at 4.53Å and 5.35Å with coordination numbers 10.16 and 20.28, respectively. These two peaks are mainly due to second shell coordination's of Nb-Nb and Na-Na respectively, each of which having a layered structure. One can observe, in the third sample(x=10.0), the increased order of the correlated atomic pairs giving an extended RDF information in the real space. The last fourth sample (x=15.0), had only the first two ordered RDF

shells with a maxima at 1.753Å and 3.265Å and coordination numbers 7.87 and 4.92 respectively. The previous two maxima are belonging to P-O and Na-O connected pairs (The sum of atomic radii of both Na and O is about 3.27Å). Table(2) collects the observed RDF structural information's of the investigated $(P_2O_5)_{75-x}(Na_2O)_{25}(Nb_2O_5)_x$ glasses.

Table (2) : RDF Structural Parameters of the Investigated Amorphous $(P_2O5)_{75-x}$ $(Na_2O)_{25}(Nb_2O_5)_x$; x = 0.0, 5.0, 10.0 and 15.0 by Weight Percent.

Sample,x(w%)	r_1 Å	N_1	r_2 Å	N_2	r_3 Å	N_3	r_4 Å	N_4	O/P
0.0	1.732	5.122	3.260	4.736	-----	-----	-----	-----	2.667
5.0	1.729	4.615	3.212	3.800	-----	-----	-----	-----	2.786
10.0	1.800	6.85	3.230	4.730	4.527	10.160	5.350	20.280	2.923
15.0	1.753	7.870	3.265	4.920	-----	------	-----	------	3.083
Pair Correlation	P-O		Na-O						

$r_1 \pm 0.03$ Å, $N_1 \pm 0.2$, $r_2 \pm 0.05$, $N_2 \pm 0.45$, $r_3 \pm 0.055$Å, $N_3 \pm 0.55$

Comparing obtained RDF results with those published by J.M. Cole et al. for the glassy system $(Sm_2O_3)_{0.205}(P_2O_5)_{0.795}$ studied by anomalous dispersion neutron diffraction [18], our first ordered shell of P-O pairs is elongated by about 0.185Å which is due to the presence of Na_2O as a matrix modifier in the given weight (0.25), but a good agreement is found of P(O) coordination number (~ 4.0). The observed shift of the first peak post shoulder towards 3.0Å indicates to the evidence of Nb-Nb correlated pairs instead of those P-P pairs at a shorter distance (~2.30Å) which means clearly the ability of niobates to replace the phosphates inside the amorphous matrix with increasing percents of x (Nb_2O_3). The decreasing of the second shell coordination number in case of x=5.0 (second sample) which belongs to Na-O arranged pairs may reflect the *formation* Nb…X new pairs, X may be Na or Nb atom.

The composite peaks structure of this complex ternary phosphate compound can not be specifically revealed with the application of normal XRD, and in the next section the structural modeling of this amorphous matrix may give a good discrimination of different connected atomic pairs ordered in 3-dimensional space.

4. Structural Modeling of Amorphous $(P_2O_5)_{75-x}$ $(Na_2O)_{25}$ $(Nb_2O_5)_x$:

The importance of the structural modeling of an amorphous system is to detect clearly the arranged polyhedra representing the different connected atomic pairs in the three dimensional space. The good approach between the observed RDF and the calculated one will give good assessment of the obtained

model. Also, with the increase of the applied structural parameters in the fit process the ability to simulate the observed peaks in its exact shape will be *evident*. The RDF fit of the first two coordination shells of the given amorphous $(P_2O_5)_{75-x}$ $(Na_2O)_{25}$ $(Nb_2O_5)_x$ was given in **Fig.** *(3-6)* **with** two different trials. In this performed fit the calculated Fourier transform was done shell by shell and in the second trial was done in one-run step; i.e. to calculate the total RDF for the first two coordination shells taking N, r and σ (Coordination number, correlation atomic pair distance and the disorder parameter) as the main parameters of fit and K_{max} around $8.0Å^{-1}$.
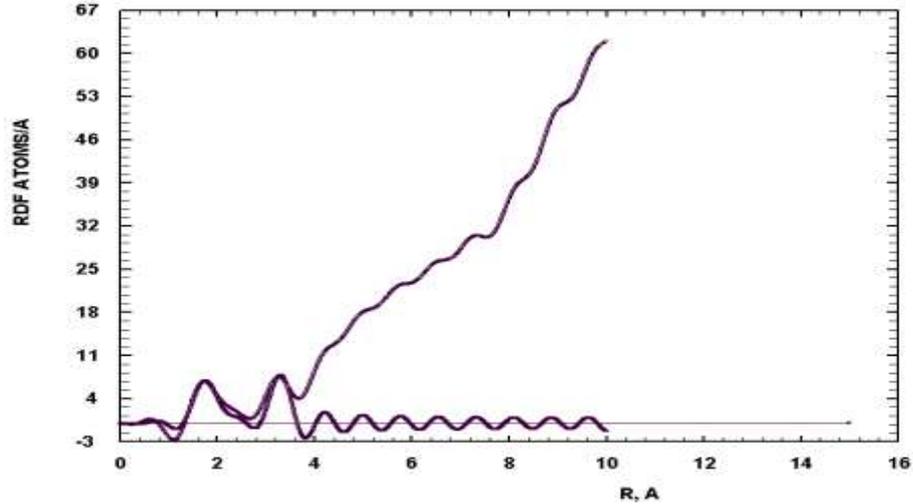
Fig. (3): The RDF Fit of the First Two Coordination Shells (one shot) of Amorphous Sodium Phosphate Doped with Niobate ($Nb_2O_5=0.0$); the Lower curve (extended wavy shape) is for the RDF (Calc.) and the Upper One is for RDF (Obs.)
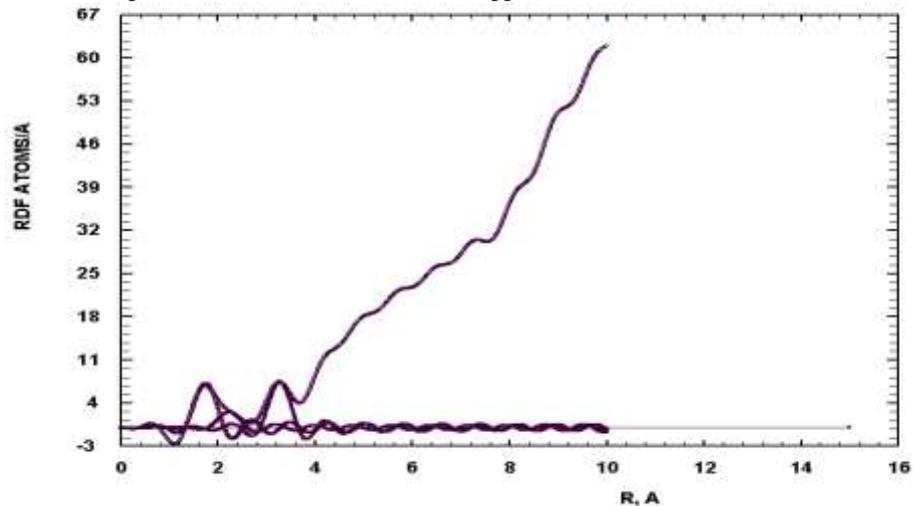
Fig. (3b): The RDF Fit of the First Two Coordination Shells of the Amorphous $(P_2O_5)_{75-x}(Na_2O)_{25}(Nb_2O_5)_x$, Shell by Sheel for x=0.0; (the Upper curve is for $RDR_{(Obs.)}$ and the Lower One is for $RDF_{(Cals.)}$
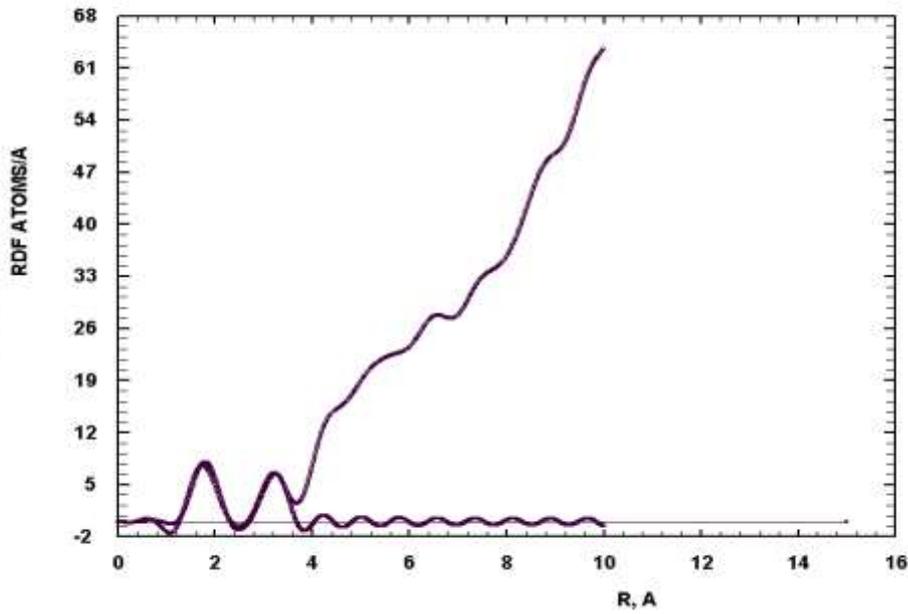
Fig. (4a): The RDF Fit of the First Two Coordination Shells (one shot) of Amorphous Sodium Phosphate Doped with Niobate $(Nb_2O_5=5.0)$; the Lower curve (extended wavy shape) is for the RDF (Calc.) and the Upper One is for RDF (Obs.)
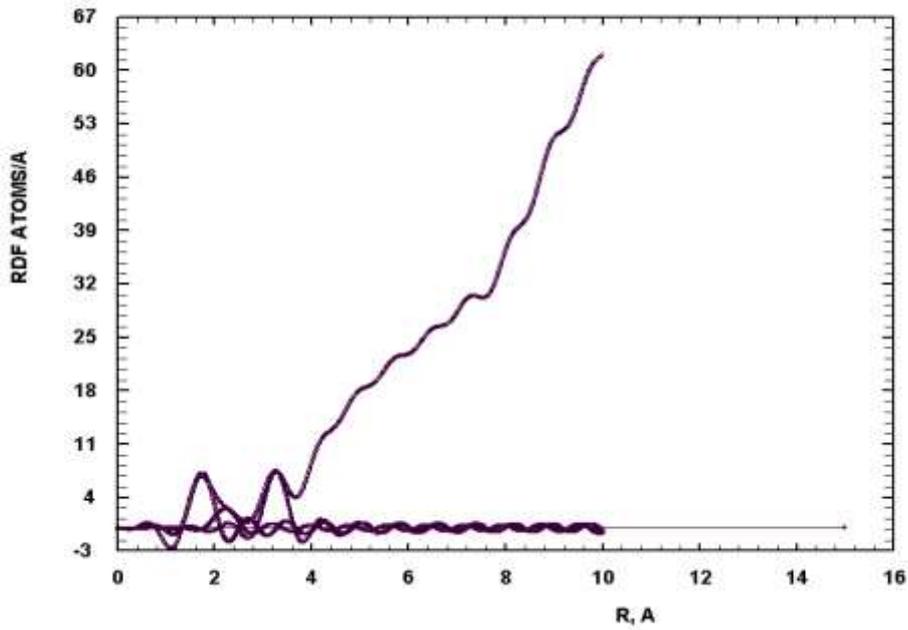
Fig. (4b): The RDF Fit of the First Two Coordination Shells of the Amorphous $(P_2O_5)_{75-x}(Na_2O)_{25}(Nb_2O_5)_x$, Shell by Sheel for x=5.0; (the Upper curve is for $RDR_{(Obs.)}$ and the Lower One is for $RDF_{(Cals.)}$
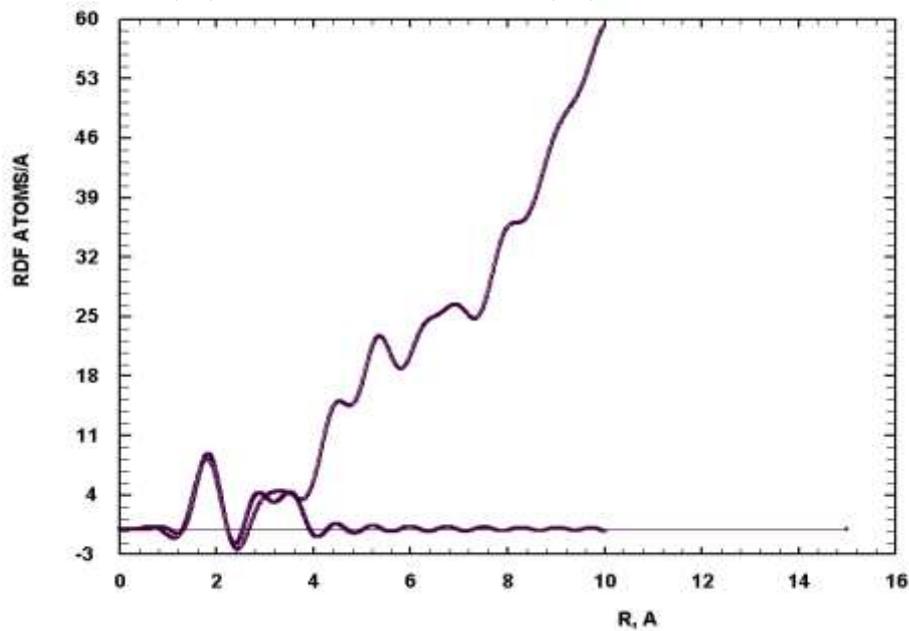
Fig. (5a): The RDF Fit of the First Two Coordination Shells (one shot) of Amorphous Sodium Phosphate Doped with Niobate (Nb_2O_5=10.0); the Lower curve (extended wavy shape) is for the RDF (Calc.) and the Upper One is for RDF (Obs.)
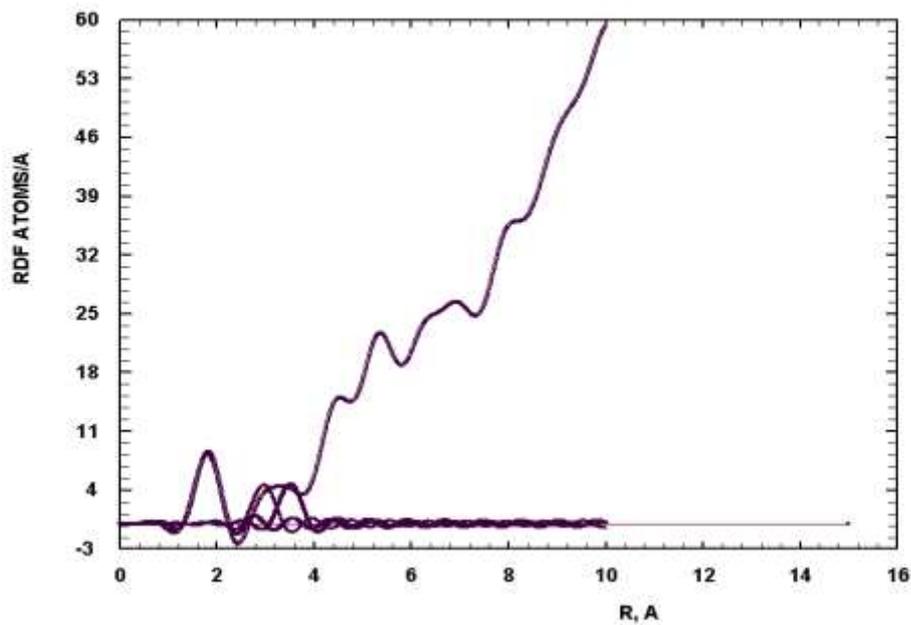
Fig. (5b): The RDF Fit of the First Two Coordination Shells of the Amorphous $(P_2O_5)_{75x}(Na_2O)_{25}(Nb_2O_5)_x$, Shell by Sheel for x=10.0; (the Upper curve is for RDR$_{(Obs.)}$ and the Lower One is for RDF$_{(Cals.)}$
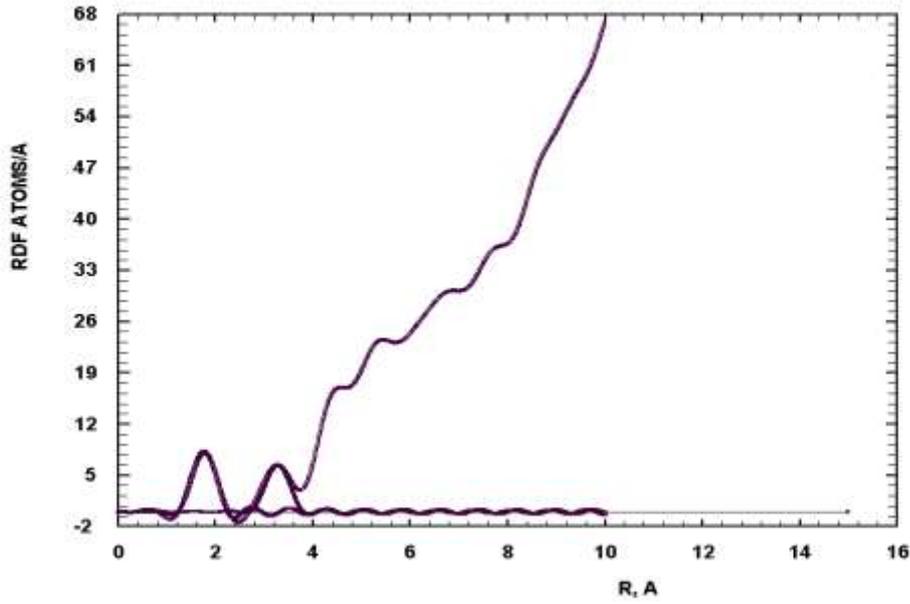
Fig. (6b): The RDF Fit of the First Two Coordination of the Amorphous $(P_2O_5)_{75-x}(Na_2O)_{25}(Nb_2O_5)_x$, Shell by Sheel for x=15.0; (the Upper curve is for RDR$_{(Obs.)}$ and the Lower One is for RDF$_{(Cals.)}$
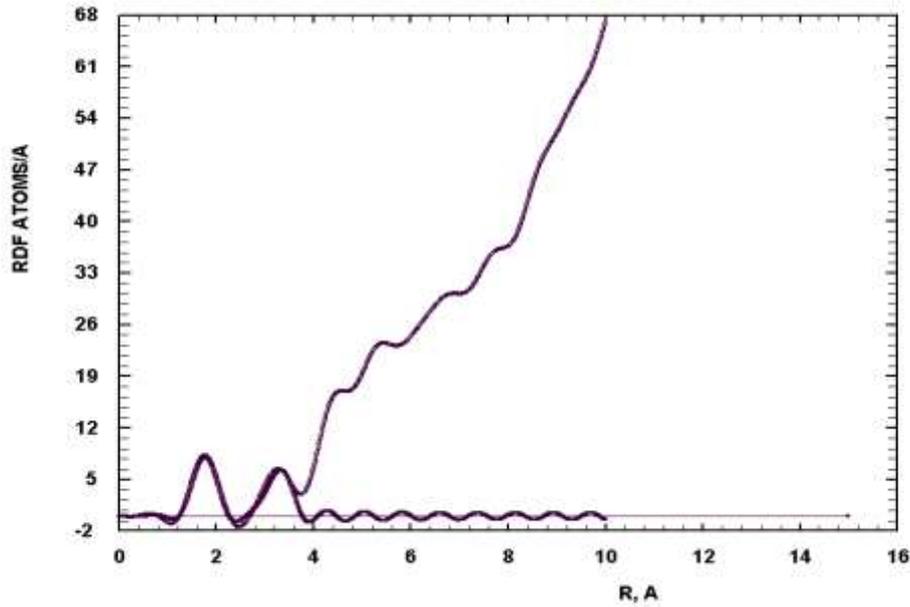
Fig. (6a): The RDF Fit of the First Two Coordination Shells (one shot) of Amorphous Sodium Phosphate Doped with Niobate (Nb_2O_5=15.0); the Lower curve (extended wavy shape) is for the RDF (Calc.) and the Upper One is for RDF (Obs.)

The main extracted RDF parameters of the applied model are N, r, and σ are listed in Table (3). The fit of the first sample (x=0.0) is not highly sounded due to the asymmetric shape (non-Gaussian form) of the first RDF observed peak and also highly disordered second peak.

The fit of the next three samples(x=5.0, 10.0, and 15.0) respectively is highly sounded giving a very good approach between the observed and calculated RDF real space correlations. The table.1 will give all the collected data in the form of r, N and σ; the correlation distance of a certain atomic pair, the corresponding coordination number and the disordering parameter. Table 3 gathering the observed RDF extracted parameters and those calculated from the proposed model with nearly the same standard deviations for both r and N values of their observed and calculated values.

Table (3): Structural Modeling of the First Ordered Shells of Amorphous $(P_2O_5)_{75-x}$ $(Na_2O)_{25}(Nb_2O_5)_x$; x = 0.0, 5.0, 10.0 and 15.0 Weight Percent

	N_1 (Sim.)	r_1 (Sim.)Å	$σ_1$ (Sim.)Å	N_2(Sim.)	r_2 (Sim.)Å	$σ_2$(Sim.)Å	N_3(Sim.)	r_3(Sim.)Å	$σ_3$(Sim.)Å
Samp1; x = 0.0	3.0+1.25	1.720+2.2	0.08+0.01	2.90+1.56	3.24	0.045	--------	------	---------
	N_1(Obs.)	r_1(Obs.)Å	$σ_1$ (Obs.)Å	N_2(Obs.)	r_2(obs.)Å	$σ_2$ (Obs.)Å	N_3(Obs.)	r_3(Obs.)Å	$σ_3$ (Obs.)Å
	5.122	1.732 (with Shoulder)	0.089	4.736	3.26	0.0887	--------	-------	---------
Pair Type	P-O and P-P			Na-Na					
Samp2; x = 5.0	N_1 (Sim.)	r_1 (Sim.)Å	$σ_1$ (Sim.) Å	N_2 (Sim.)	r_2 (Sim.) Å	$σ_2$ (Sim.) Å	--------	------	--------
	3.80+0.80	1.71	0.185	3.30	3.21	0.089	--------	-------	---------
	N_1 (Obs.)	r_1 (Obs.)Å	σ1 (Obs.) Å	N_2 (Obs.)	r_2 (Obs.) Å	$σ_2$ (Obs.)Å	--------	-------	--------
	4.615	1.729	0.089	3.80	3.212	0.15	--------	-------	--------
Pair Type	P-O			Na-Na					
Samp3; x=10.0	N_1 (Sim.)	r_1 (Sim.)Å	$σ_1$ (Sim.)Å	N_2 (Sim.)	r_2 (Sim.)Å	$σ_2$(Sim.)Å	N_3(Sim.)	r_3(Sim.)Å	$σ_3$(Sim.)Å
	4.25	1.786	0.16	2.00	2.95	0.09	2.00	3.499	0.09
	N_1(Obs.)	r_1(Obs.)Å	$σ_1$ (Obs.)Å	N_2(Obs.)	r_2(obs.)Å	$σ_2$ (Obs.)Å	N_3(Obs.)	r_3(Obs.)Å	$σ_3$ (Obs.)Å
	4.0	1.785	0.115	1.998	2.96	0.091	2.00	3.501	0.086
Pair Type	P-O			Nb-Nb			Na-Na		
Samp4; x = 15.0	N_1 (Sim.)	r_1 (Sim.)Å	$σ_1$ (Sim.)Å	N_2(Sim.)	r_2 (Sim.)Å	$σ_2$(Sim.)Å	N_3(Sim.)	r_3(Sim.)Å	$σ_3$(Sim.)Å
	4.35+3.0	1.74	0.19	3.75	3.26	0.19	---------	------	--------
	N_1(Obs.)	r_1(Obs.)Å	$σ_1$ (Obs.)Å	N_2(Obs.)	r_2(obs.)Å	$σ_2$ (Obs.)Å	--------	-------	--------
	7.87	1.753	0.089	4.92	3.265	0.089	--------	------	--------
Pair Type	P-O & Nb-O			Na-O			--------	------	--------

$σ_t = \sqrt{σ_{th}+σ_{stat.}}$; Both of $σ_{th}$ and $σ_{stat}$ are observed disorder parameters with noticing that the first thermal disorder parameter is more larger than the second static disorder term which is related inversely with K_{max}.

Conclusions:

1. The amorphous given based phosphate glasses doped with Niobium oxide in an increased percent, the niobium atoms will replace the phosphorus atoms in the SRO region.

2. Due to the presence of Na_2O in the matrix, some structural changes concerning the distance correlations and pair coordination numbers are observed; such as the P-O elongated distance and its changed coordination number with the change of x (niobium oxide percent).

3. It was observed in case of x=10.0 an increased order in the amorphous matrix in its MRO structure which means that a more stability in the investigated glasses concerning its energy distribution and also an improved conducting behavior.

4. The proposed model giving a good fit with the observed RDF structural information's which means a good realistic information's of the SRO and MRO collected data.

5. The sodium atoms (or ions) are arranged in form of distorted octahedral by oxygen atoms at a distance of about 3.23Å.

6. In case of samples 3 and 4(x=10.0 and 15.0), the first two coordination shells are of composite structure (P-O & Nb-Nb) with distances at 1.75Å and 2.70Å and having a coordination number of 4.0 and 3.0 respectively (in the form PO_4 and NbO_3 units).

Acknowledgement

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