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Microstructure and dielectric properties of barium-vanadate glasses

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Abstract

The ac and dc conductivity in barium-vanadate glasses was investigated as a function of temperature and frequency with the use of impedance spectroscopy. The topography and microstructure of glasses were investigated by the means of X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods. The XRD results show that all samples are amorphous but microscopy investigation reveals that glasses with greater amount of V_2O_5 contain nanostructures. The influence of V_2O_5 quantity on dielectric properties was checked. The activation energy of dc conduction process was evaluated. On the basis of Jonscher universal dielectric response the temperature dependence of conductivity parameters were determined and compared to theoretical models collected by Elliott.

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Keywords: barium-vanadate glasses, small polaron hopping, overlapping polaron, impedance spectroscopy, glass nanocrystallization;

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1. Introduction

Glasses containing more than 5-10%mol of transition metal oxides (such as vanadium oxide), are electronic semiconductors. Their electrical properties are determined by the transition metal ions present in two different valence states V^{4+} and V^{5+} [1-5]. Conduction mechanism in this type of materials was described by Mott model of small polaron hopping between such ions [1].

Al-Hajry et al. [6] measured structural and electrical properties of barium-vanadate glasses. They suggested that these glasses contain single phase and are homogenous. The glass network is built up of mainly VO_4 polyhedra. They analyzed the high-temperature dc conductivity on the basis of Mott's small polaron theory and suggested that the conduction is due to the non-adiabatic hopping of polarons [6].

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The conductivity of vanadium-tellurite oxide glasses were investigated by Sankarappa et al. [7]. They confirmed that the temperature and frequency dependence of ac and dc conductivity exhibit a behavior similar to that predicted by Mott's small polaron hopping model in high temperature region. They analyzed data in terms of universal dielectric response (Jonscher [8]) and stated that it is not agree with models of quantum mechanical tunneling and correlated barrier hopping [7, 9].

Pietrzak et al. [10] studied electrical properties and microstructure of vanadium–phosphate glasses and found out that these glasses relatively easily undergo thermal nanocrystallization. The authors confirmed that appropriate thermal treatment (specific temperature and heating/cooling rate) changes the microstructure and significantly increases electrical conductivity. On the basis of "core–shell" model, they expected that due to nanocrystallization the concentration of V^{4+}–V^{5+} pairs responsible for electron hopping, is higher near the surfaces of the newly formed crystallites than inside the crystallites. Higher number of neighboring V^{4+}/V^{5+} hopping centers in the interfacial regions leads to smaller average distance between hopping centers, and consequently it causes an increase in conductivity [10].

The aim of the present study was to investigate the micro and nanostructure of barium-vanadate glasses and its influence on electrical properties.

2. Experimental

Samples of the composition of $xBaO$-$(100-x)V_2O_5$ where x= 30, 40 and 45 (in %mol) were prepared by the conventional melt quenching technique. Appropriate amounts of reagents: BaO (≥99.9%, P.P.H STANLAB Sp.J.) and V_2O_5 (≥99.9%, POCH) were thoroughly mixed in an agate mortar. The melting was performed in porcelain crucibles at 1273 K for 10–30 min, depending on glass composition. The melts were poured on preheated (to 393 K) brass plate and pressed by another plate to obtain flat circular pellets of 1-2 mm thickness and 10-20 mm in diameter.

The structure has been studied by the X-ray diffraction method with the use of a Philips X 'Pert Pro MPD system with the CuKα radiation. The XRD measurements were carried out on powder samples at room temperature. Scanning Electron Microscope FEI Quanta FEG 250 using 30kV beam accelerating voltage with SE-ETD detector (secondary electron - Everhart-Thornley detector) working in high vacuum mode (pressure 10^{-4} Pa) was used to observed the structure of the glasses. SEM measurements were conducted on samples fractures with 7nm gold coating.

The density of samples was measured at room temperature by Archimedes principle using kerosene as an immersion liquid.

For the electrical measurements gold electrodes were evaporated at the polished samples. Impedance measurements were carried out in the frequency range from 10 mHz to 1 MHz with the ac voltage of 1 V_{rms} in the temperature range from 153 K to 423 K with the Novocontrol Concept 40 broadband dielectric spectrometer.

3. Results

All as received samples are amorphous, as can be seen in XRD patterns showed in Fig. 1. The topography of glass fractures is presented in SEM microscopy images in smaller (Fig. 2) and bigger magnification (Fig. 3). Figures 2a, b and c show the microstructure when Fig. 3a, b and c present the nanostructure of respectively: $45BaO$–$55V_2O_5$, $40BaO$–$60V_2O_5$ and $30BaO$–$70V_2O_5$ (in %mol) samples. It can be seen that sample with the lowest amount, 55% of V_2O_5 does not exhibit any visible features both in micro and nanoscale. Samples containing 60% and 70% of V_2O_5 consist of randomly distributed micro and nanostructures. The dimension of detected structures are larger in sample with higher amount of V_2O_5. The shape of detected nanostructures is substantially circular.

Fig. 4 and 5 present the real part of conductivity versus frequency measured at different temperatures for all glasses. The plots consist of two regions: dc plateau dominating in the low frequency region and ac component increasing with frequency in a linear fashion in log-log scale. In samples with 55% (Fig. 4 (a)) and 60% V_2O_5 (Fig. 5 (a)) the frequency independent dc region at 153 K and 183 K temperatures is masked by ac conductivity. In glass containing 70% V_2O_5 (Fig. 5 (b)) only dc region is visible in temperature range from 303 K to 423 K.

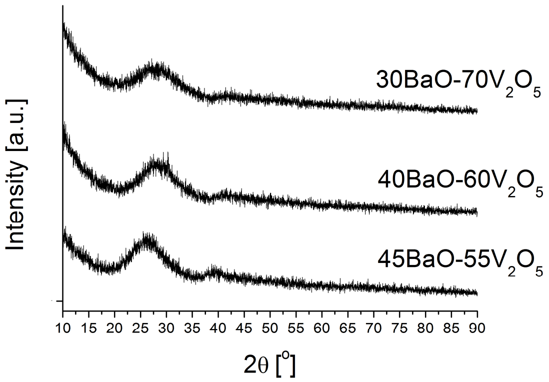

Fig. 1. XRD patterns for investigated samples.

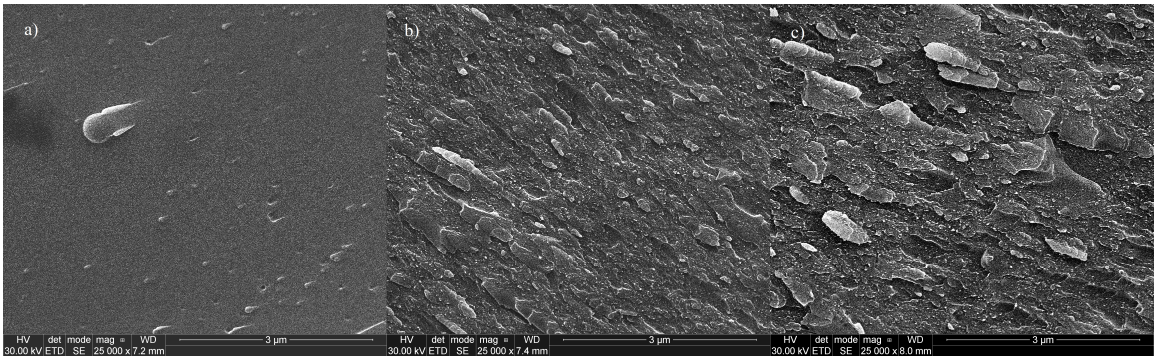

Fig. 2. SEM microscopy images of (a) $45BaO–55V_2O_5$, (b) $40BaO–60V_2O_5$ and (c) $30BaO–70V_2O_5$ (in %mol) glasses fractures, in microscale.

Fig. 3. SEM microscopy images of (a) $45BaO–55V_2O_5$, (b) $40BaO–60V_2O_5$ and (c) $30BaO–70V_2O_5$ (in %mol) glasses fractures in nanoscale.

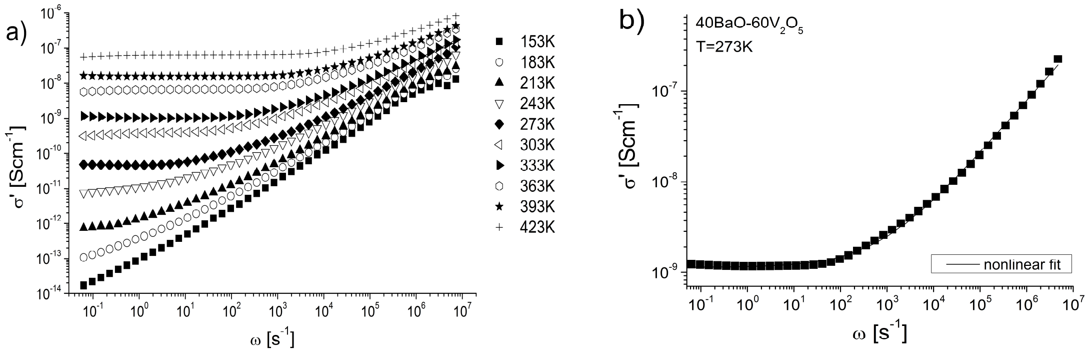

Fig. 4. (a) Real part of conductivity versus frequency measured at different temperatures for 45BaO–55V_2O_5 glass; (b) example of the results of power law fitting procedure to measured real part of conductivity.

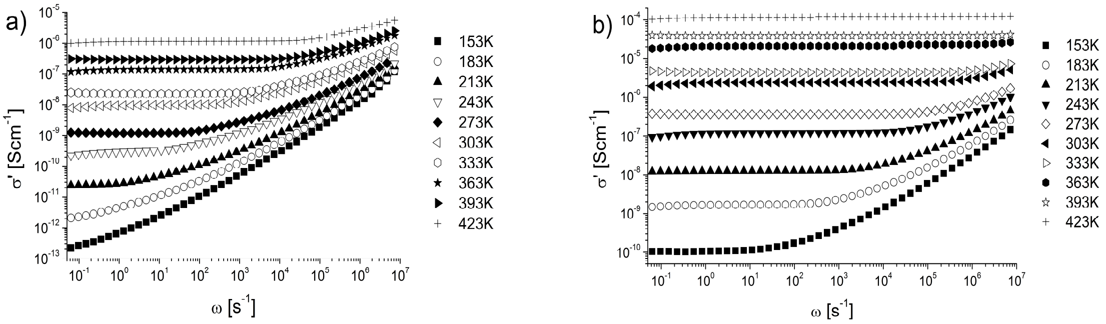

Fig. 5. Real part of conductivity versus frequency measured at different temperatures for (a) 40BaO–60V_2O_5 and (b) 30BaO–70V_2O_5 (in %mol) glass samples.

4. Discussion

The 45BaO-55V_2O_5 sample does not exhibit any specific nano and microstructure, when 40BaO-60V_2O_5 and 30BaO-70V_2O_5 samples consist of microstructures and nanogranules randomly distributed within the glass matrix (Fig. 2 and 3). It can be noticed that between 45BaO-55V_2O_5 and 40BaO-60V_2O_5 samples, there is only slight difference of 5%mol V_2O_5 in composition but this small change significantly influences the material microstructure. We believe that between these two compositions there is a limit of maximum amount of vanadium oxide for which the sample stays homogenous. Pietrzak et al. [10] investigated the microstructure of nanocrystallized V_2O_5-P_2O_5 glasses. The SEM micrographs of glasses with 90% of V_2O_5 and heat-treated in the 548 K, were similar to obtained in our glasses with 60% and 70% V_2O_5. They also checked that the crystalline phase which developed under heating corresponds to XRD spectrum of V_2O_5 [10]. On the basis of this observation, we may suppose that also in our glasses some amount of vanadium ions form the nanostructures and the rest bond with barium ions and form the glass matrix. The size of nanostructures increases with the increase in V_2O_5 amount. The nanostructures are not visible in XRD spectra and are probably amorphous.

The composition dependence of the density, molar volume, concentration of vanadium ions and average distance between them are presented in Tab.1. The value of molar volume was calculated from the density and composition. The average distance R, between the vanadium ions was calculated from the relation $R=N^{-1/3}$, where N is the concentration of vanadium ions per unit volume, calculated from batch composition and the measured density. The calculations were made assuming a uniform distribution of vanadium ions. It may be observed that glass density and average distance between vanadium ions decrease gradually when molar volume and the concentration of these ions increase with the increase of V_2O_5 amount. Similar trends were noticed in Al-Hajry et al. [6] and Sen et al. [9] works. They suggested that these monotonous changes indicate that the topology of the network does not significantly change with composition and may be explained as due to the replacement of a heavier cation (Ba) by a lighter one (V). However the values of density and molar volume which we obtained are respectively lower and higher than in the literature [6, 9]. Moreover we noticed that the micro and nanostructure of our samples significantly changed above 55% of V_2O_5 quantity. We think that in our samples the decrease of density and increase of molar volume may be also caused by nano-arrangement of vanadium ions.

Table 1. Density, molar volume, concentration of vanadium ions, average distance and polaron radii.

Composition (in %mol)	d $^{+}/_{-}0.01$ (gcm^{-3})	V_m $^{+}/_{-}0.2$ (cm^{3}mol^{-1})	N $^{+}/_{-}0.01$ (x10^{22} cm^{-3})	R $^{+}/_{-}0.01$ (Å)	r_0 $^{+}/_{-}0.01$ (Å)
30BaO-70V_2O_5	3.52	49.3	0.86	4.89	1.96
40BaO-60V_2O_5	3.72	45.8	0.79	5.03	2.01
45BaO-55V_2O_5	3.82	44.3	0.75	5.11	2.04

The dependence of the ac conductivity on angular frequency in amorphous materials is usually found to obey the form (so called Jonscher law or universal dynamic response) [8]:

$$\sigma(\omega) = \sigma_{DC} + A\omega^{s(T)} \tag{1}$$

where σ_{DC} is the dc conductivity and $\sigma_{AC}=A\omega^{s(T)}$ is the ac component. The first term (dc conductivity) dominates in the low frequency region and the second one (power law behavior) in the high frequency region. All our samples fulfill the Jonscher law. The dc conductivity and the exponent *s* are determined using a numerical fitting of the above equation to the measured data. Example result of the fitting procedure is showed in Fig. 4 (b).

Tab. 2 presents calculated values of σ_{DC} at 303K. It can be noticed that glass dc conductivity increases with increase of V_2O_5 amount. Change the glass composition of 15 %mol of V_2O_5 increase the conductivity value by four orders of magnitude.

Schnakenberg has presented a model for non-adiabatic regime of small polaron hopping. The conductivity versus temperature may be described by [11]:

$$\sigma = \frac{A}{T}\left[\sinh\left(\frac{h\nu_0}{kT}\right)\right]^{\frac{1}{2}} \times \exp\left[-\left(\frac{4W_H}{h\nu_0}\right)\tanh\left(\frac{h\nu_0}{4kT}\right)\right] \times \exp\left[-\left(\frac{W_D}{kT}\right)\right] \tag{2}$$

where: W_H is polaron energy, υ_0 is the longitudinal optical phonon frequency and W_D is the disorder energy defined as the mean difference of electronic energies between two hopping sites.

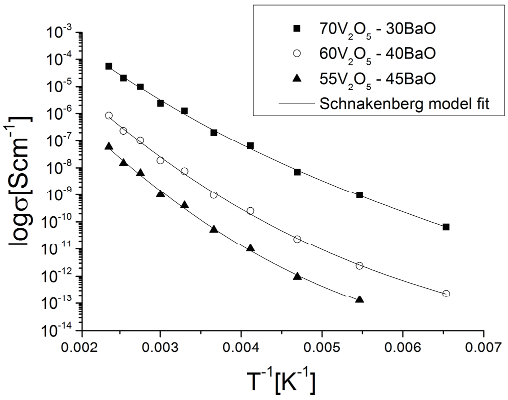

Fig. 6. Dc conductivity versus 1/T.

Fig. 6 presents the temperature dependence of log dc conductivity with numerical fitting of above relation. It can be seen that the relation is in a good agreement with experimental data. Tab. 2 shows the obtained parameters and values of adjusted R-square. The change of W_D indicates that the degree of disorder increases with the increase of V_2O_5 amount. W_H behaves inversely to W_D. For the stronger localization small polaron radius r_0 will decrease and it will follow the increase of W_H [1, 12]:

$$W_H = \frac{e^2}{4\varepsilon_p r_0} \tag{3}$$

It is well known that structural disorder leads to the localization of the charge carriers in amorphous semiconductors. It corresponds to the so called "Anderson localization" [1, 12].

The obtained values of $h\upsilon_0$ appear reasonable and are similar to results presented in Sen et al. work [14].

The r_0 values were also determined on the basis of values of average distance between vanadium ions and the Bogomolov et al. equation for nondispersive system (Tab. 1) [13]:

$$r_0 = \left(\frac{\pi}{6}\right)^{\frac{1}{3}} \frac{R}{2} \tag{4}$$

The values of polaron radii obtained by two methods are different. The r_0 values calculated from simple density measurements decrease with V_2O_5 content increase, similarly as in Sen et al. work [14] but are significantly higher than in the literature [6, 14]. On the other hand the r_0 values evaluated from electrical measurements for 45BaO-55V_2O_5 and 40BaO-60V_2O_5 samples are lower while this for 30BaO-70V_2O_5 sample is more than two times higher than in the literature [6, 14]. The possible reason for these differences is that Bogomolov et al. [13] equation (4) is oversimplified for a complex system and calculations obtained from density measurements imply a uniform distribution of vanadium ions in glasses when estimations from electrical measurements show effective distances of the centers of hopping.

Al-Hajry et al. [6] stated that the small value of activation energy for sample with the highest amount of V_2O_5 suggests that dc conduction process is controlled by small polaron hopping. They also stated that the small values of polaron radii suggest that the polarons are highly localized [6]. Our results show low values of polaron radii for 45BaO-55V_2O_5 and 40BaO-60V_2O_5 samples but 30BaO-70V_2O_5 sample exhibits the polaron radius very similar to the value of average distance between vanadium ions. This big value may suggest different conduction mechanism: overlaping large polaron hopping.

Table 2. Dc conductivity parameters.

Composition (in %mol)	$\sigma_{DC\,(T=303K)}$ (Scm^{-1})	W_H (eV)	W_D (eV)	$h\upsilon_0$ (eV)	R^2	r_0 (Å)
$30BaO\text{-}70V_2O_5$	$2.40*10^{-6}$	0.365 $(^{+}/_{-}0.006)$	0.214 $(^{+}/_{-}0.004)$	0.0879 $(^{+}/_{-}0.002)$	0.94	4.77 $(^{+}/_{-}0.08)$
$40BaO\text{-}60V_2O_5$	$9.16*10^{-9}$	0.618 $(^{+}/_{-}0.006)$	0.134 $(^{+}/_{-}0.004)$	0.0838 $(^{+}/_{-}0.001)$	0.94	1.22 $(^{+}/_{-}0.01)$
$45BaO\text{-}55V_2O_5$	$3.76*10^{-10}$	0.718 $(^{+}/_{-}0.006)$	0.114 $(^{+}/_{-}0.004)$	0.0864 $(^{+}/_{-}0.001)$	0.93	1.40 $(^{+}/_{-}0.01)$

Fig. 8 shows the temperature dependence of the frequency exponent *s* (equation 1) for all samples. Its dependence on temperature were compared to the models collected by Elliot [9]. On the basis of literature [1-8], it was difficult to clearly define which ac conduction mechanism exist in these glasses. Therefore the values of s for the most expected models were presented in Fig. 7 and compared with measured data. Values of the exponent s characteristic for small-polaron quantum-mechanical tunnelling SP model may be described by [9]:

$$s = 1 - \frac{4}{\ln\left(\frac{1}{\omega\tau_0}\right) - \frac{W_H}{kT}} \tag{5}$$

where: W_H is energy for polaron transfer, τ_0 is the characteristic relaxation time.

Values of the exponent s characteristic for correlated-barier hopping CBH model may be described by [9]:

$$s = 1 - \frac{6kT}{W_M - kT\ln\left(\frac{1}{\omega\tau_0}\right)} \qquad W = W_M - \frac{e^2}{\pi\varepsilon\varepsilon_0 R} \tag{6}$$

where: W_M is the maximum height of the energy band and ε_0 is the permittivity of free space.

Values of the exponent s characteristic for overlaping large-polaron tunnelling OLP model may be described by [9]:

$$s = 1 - \frac{4 + \frac{6W_{H0}r_0'}{kTR_\omega'^2}}{R_\omega'\left(1 + \frac{W_{H0}r_0'}{kTR_\omega'^2}\right)} \qquad W_H = W_{H0}\left(1 - \frac{r_0}{R}\right) \tag{7}$$

where: W_{H0} is reduced polaron hopping energy, R is average distance between the vanadium ions, r_0 is polaron radius, R_ω is tunnelling distance at frequency ω, $R_\omega'=2\alpha R_\omega$ and $r_0'=2\alpha r_0$ are reduced quantities, α is tunneling factor (the ratio of wave function decay).

The first two models: SP and CBH were approximated using the value of $\omega\tau_0$ 10^{-9}. It may be seen that they are not in agreement with our results. The behavior of the frequency exponent s showed the greatest similarity to OLP model for all glasses. Therefore this model was chosen to analyze electrical properties of our samples and parameters of this model were fitted using the relation (7). Figure 7 presents the temperature dependence of the frequency exponent s with OLP model fit. It can be seen that for samples with 55% and 60% V_2O_5 the measured data is in good agreement with this model. Glass containing 70%V_2O_5 behaves differently. It was possible to determine s parameter only in temperature range from 153 K to 243K. Table 3 shows the parameters calculated from fitting and values of adjusted R-square. The fitting for sample with 70%V_2O_5 shows quite low value of adjusted R-square, because of a small number of points. The obtained values of reduced polaron hopping energy, reduced polaron radius and the tunneling factor α for all samples appear reasonable. Murawski [15] measured the ac conductivity of phosphorous-vanadate glasses and suggested that in these glasses the ac conduction mechanism is due to OLP. The calculated values of reduced polaron radius for glasses with 50%, 60% and 70% V_2O_5 was respectively: 2.5, 2.0, 2.0 and reduced polaron hopping energy: 0.67, 0.60, 0.51. Our samples containing similar amount of V_2O_5 and with BaO instead P_2O_5 show slightly lower values of estimated parameters.

Summing up, on the basis of obtained results and relations we may state that dc conductivity is in good agreement with Schnakenberg relation which described non-adiabatic small polaron hopping mechanism. On the other hand, ac conductivity parameter s is well approximated by overlaping polaron hopping mechanism. However both models are only approximations and do not take into account multiple interactions with optical as well as acoustic phonons [16]. A much more general model of non-adiabatic hopping conductivity process was proposed by Gorhan-Bergeron and Emin [17].

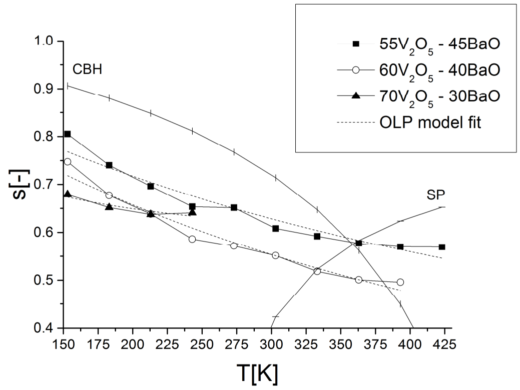

Fig. 7. Temperature dependence of the frequency exponent s with example of OLP, CBH, SP models fit for xBaO – (100-x) V_2O_5 glasses.

Table 3. Ac conductivity parameters.

Composition	W_{H0}	r_0'	R_ω'	R^2
(in %mol)	(eV)	(-)	(-)	
$30BaO-70V_2O_5$	0.45	1.51	8.84	0.784
	$(^{+}/_{-}0.08)$	$(^{+}/_{-}0.26)$	$(^{+}/_{-}0.13)$	
$40BaO-60V_2O_5$	0.49	1.64	3.78	0.959
	$(^{+}/_{-}0.07)$	$(^{+}/_{-}0.25)$	$(^{+}/_{-}0.71)$	
$45BaO-55V_2O_5$	0.56	1.95	4.32	0.932
	$(^{+}/_{-}0.12)$	$(^{+}/_{-}0.39)$	$(^{+}/_{-}1.26)$	

5. Conclusions

To conclude, barium-vanadate glasses were prepared. XRD measurements confirm their amorphous nature. However samples with greater than 55% of V_2O_5 contains nanostructures. The size of nanostructures increases with the increase in V_2O_5 amount.

The ac conductivity fulfil the Joncher law for amorphous materials. Dc conductivity increases and activation energy decrease with increase of V_2O_5 amount. On the basis of dc conductivity dependence on frequency, we suppose that the conduction process is due to small-polaron hopping, while the ac conductivity behavior is in agreement with the overlapping polaron hopping.

Acknowledgements

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