

THE STUDY OF THE VITREOUS MATERIALS OBTAINED BY THE SOL-GEL METHOD, IN THE TERNARY ZnO-V₂O₅-B₂O₃ SYSTEM

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The ternary zinc oxide-vanadium oxide-boron oxide system was studied in order to establish the compositional domain where glasses can be easily obtained by sol-gel method. The pH and temperature for optimal gelation is indicated. From infrared together with Fourier transformed infrared spectra it was concluded that, for some compositional domains, the boron oxide forms a mixed network together with the vanadium oxide. The thermogravimetric and differential thermal analysis revealed the temperatures for the vitreous transition and some crystalline transformation, and also the melting temperatures. The dielectric permittivity and dielectric loss were measured, and the dielectric loss factor calculated. The variation of dielectric properties to the electric field frequency and to composition is discussed. The variation curves of dielectric permittivity for 1 and 30 MHz were theoretically calculated and compared with the experimental ones, with good agreement.

INTRODUCTION

The sol-gel method, widely developed in the last 20 years, does not cessa to put at researchers disposal new technics, necessary for new development directions, such as the very high purity products realisation in oxidic systems that are hardly accesible by the classical methods, for applications in various domains: technical, strategical or vital for solving the problems concerning the annihilation of the undesired results from some industrial activities.^{1,2}

One of the vitreous systems that presents very interesting electrical and optical properties, that allow to obtain vitreous semiconducting layers, with applications in solid electrolites, nanocomposite electrods, infrared (IR) active layers or light modulators is the one that includes, together with the boron oxide, as network former, the vanadium and zinc oxide, which give to vitreous materials high polarizability and great dielectric permittivity, at lower dielectric losses than in the case of rich alkaline glasses, and also special optical properties, especially in the IR domain.³⁻⁶ Advanced purity vitreous materials are difficult to be obtained in this system by classical ways. The sol-gel method have permitted the obtaining and the studying of vitreous materials with various compositions, within this system.

The electrical permittivity, ϵ_r , also known as the dielectric constant, is related to the vitreous material polarizability by the classical relation Clausius-Mossoti:⁷

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} \sum N_i \alpha_i \quad (1)$$

where: ϵ_0 = the permittivity of vacuum;

N_i = number of the polarisable particles from i species;

α_i = the polarisability of i species;

The relation (1) can be written:⁸

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{4}{3} \pi N \alpha \quad (2)$$

where N is the number of the particles per volum unity, or, more simple: ⁸

$$\epsilon_r = 1 + 4\pi\alpha \quad (3)$$

The electrical polarizability is considered, in the case of glasses, that consists in four mechanisms, all based on electrical charge displacements on short distances, contributing to the total polarization: the electronic polarization (at frequency of 10^{15} Hz), the atomic polarization (frequency of 10^{12} - 10^{13} Hz), orientation polarization (10^3 - 10^{12} Hz) and interfacial polarization (10^{-3} - 10^3). ⁷ The heavy metals ions, among which it can be included the zinc, and the ions of the metals with multiple valence status, such as vanadium, can exhibit electronic polarization, and there for increasing the dielectric constant.

The dielectric constant of the vitreous materials is proportional to the second power of the refractive index, for very high frequency, according to Maxwell relation: ⁹

$$\epsilon_r = n^2 \quad (4)$$

where: n is the refractive index, and

to density, from the empirical relation of Hopkinson: ¹⁰

$$\epsilon_r = 2,2d \quad (5)$$

where: d is the density.

The zinc, due to its influence to the density and refractive index, as compared to usually silica-soda-lime glasses, increases the dielectric permittivity value, which is visible for the tabled coefficients, of the three properties. ^{8,9} For the vanadium oxide there are not available data of the influence coefficients, but it is known ¹⁰ that it increases the dielectric constant and leads to vitreous semiconducting materials.

The paper presents sol-gel preparation and electrical properties: the dielectric permittivity, ϵ_r and the dielectric loss, expressed as the loss angle tangent, $\text{tg } \delta$, for chosen compositions in the above mentioned system is studied. The influences of the composition and also of the electric field frequency on these properties were established. The theoretical calculation of the dielectric properties, based on literature constants, for boron and zinc oxides, and on an experimental data calculated constant, for the vanadium oxide, is presented.

EXPERIMENTAL

The chosen compositions, in molar and gravimetric per centages, together with the molar ratio of vanadium oxide versus zinc oxide (V/Z), are presented in Table 1.

Table 1

The studied compositions, for the sol-gel glass obtaining, in the system B_2O_3 -ZnO- V_2O_5

Sample	V/Z	Composition [molar %]			Composition [grav %]		
		B_2O_3	ZnO	V_2O_5	B_2O_3	ZnO	V_2O_5
I	2	3	4	5	6	7	8
I	1/1	30	35	35	18,57	25,08	56,35
II	1/1	20	40	40	11,74	27,18	61,07
III	1/1	10	45	45	5,58	29,08	65,34
IV	1/2	20	53,33	26,67	13,24	40,85	45,9
V	2/1	20	26,67	53,33	10,55	16,28	73,16
VI	-	46	-	54	24,8	-	75,2
VII	-	27,3	-	72,7	12,6	-	87,4

The raw materials used were zinc acetate, a.g., $Zn(CH_3COO)_2 \cdot 2H_2O$, Chimopar, vanadium penta-oxide, e.g., Merck and boron acid, e.g., H_3BO_4 , Chimopar. The solvents used were distilled water and absolute ethilic alcohol, Silal. The ammonia solution, between 0.1 and 1.4 molar concentration, and chloric acid, 0.1 N concentration, were used for the pH adjustment. The solutions were prepared at the National Glass Institute, from the e.g. solutions, Silal.

The solutions were prepared by the dissolution of zinc acetate in water and ethanol, at 50°C, suited by the pH adjustment and the drop by drop adding of the vanadium and boron acid solutions. The pH was then finally adjusted. The pH measurements were achieved with the aid of a digital pH-meter, PH 100 type.

The drying was performed in controlled humidity and temperature, in a 200 dm³ stove, China. The thermal treatments, at high temperatures were made in electrical fours, equipped with kanthal resistance, silite elements and superkanthal elements, in aluminous crucibles.

The infrared transmission spectra were plotted with the aid of a spectrophotometer SPEKORD M 80 type, and the Fourier transformed infrared transmission with a Shimadzu spectrophotometer. The viscosity measurements were realised with the ROTOVISCO viscosimeter, and the thermal analysis with a MOM type analyzer. The TESLA BM 311G Q-meter, resonance method, was utilised for the dielectric permittivity and dielectric loss measurement. The measurements were performed at three values for the electrical field frequency, 100 KHz, 1 MHz and 30 MHz, for the study of its influence on the electrical properties of the realized glasses.

RESULTS AND DISCUSSION

The Figure 1 presents the domains from the ternary system in which, by classical melting, at temperatures over 1000°C, glasses and partially or total crystallized materials can be obtained.

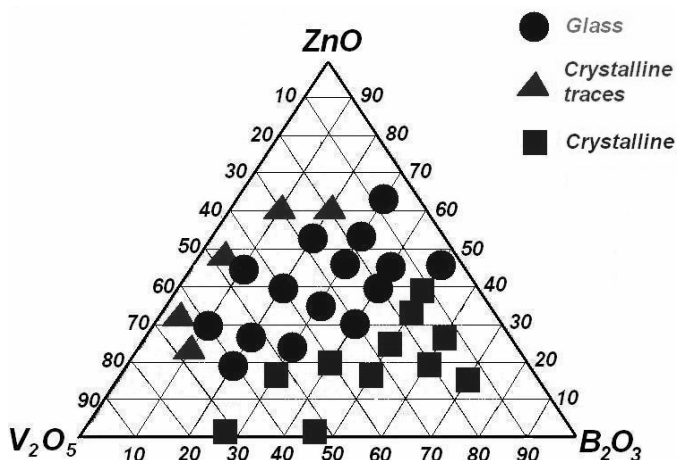


Fig. 1 – The domains in which glasses, slight crystallized and total crystallized materials can be obtained.

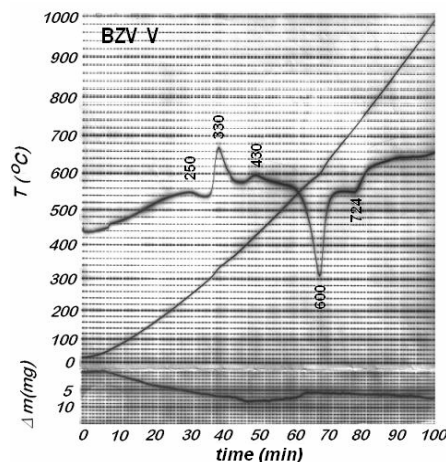


Figure 2. The DTA/TGA curves, for the BZV V composition, dried sample, for the temperature domain 20-1000°C.

There was established that in the domain of 25–55 molar% of ZnO the gels can be easily obtained, in the chosen synthesis conditions. The gelation speed was minimum at the pH around 1 and at the temperature of 50°C.

The differential thermal analysis, for sample BZV V is plotted in Figure 2. The following thermal effects were observed: the endothermal effect due to vitreous transition, at 250°C; the exothermal effect due to crystallization, at 330°C; the exothermal effect due to the polymorphic transformation, at 430°C; the endothermal effect of the eutectic melting, at 600°C; the endothermal effect for the secondary melting, around 724°C. A slight weight loss is also observed in the 20–500°C range, assigned to adsorbed water and structural OH⁻ elimination. The increase of weight at 500°C could be assigned to V⁴⁺ ions oxidation.

The infrared transmission spectra, for the samples BZV I, II, IV and V, are presented in the Figure 3.

There are put in evidence the characteristic vibration bands² for B₂O₃ depolymerized, at 1350 cm⁻¹, boroxol group, at 700 cm⁻¹, [ZnO₆] and [ZnO₄]¹, at 450-300 cm⁻¹, besides with the characteristic vibration band for V-O-V bonds, at 920 cm⁻¹. The maximum for the boron oxide vibration band decreases with the vanadium oxide content increase, which indicates the forming of mixed boron oxide – vanadium oxide network. The sample BZV V presents the transmission sensible higher than the other samples, in the 1500-1000 cm⁻¹ domain, due to higher vanadium oxide content.

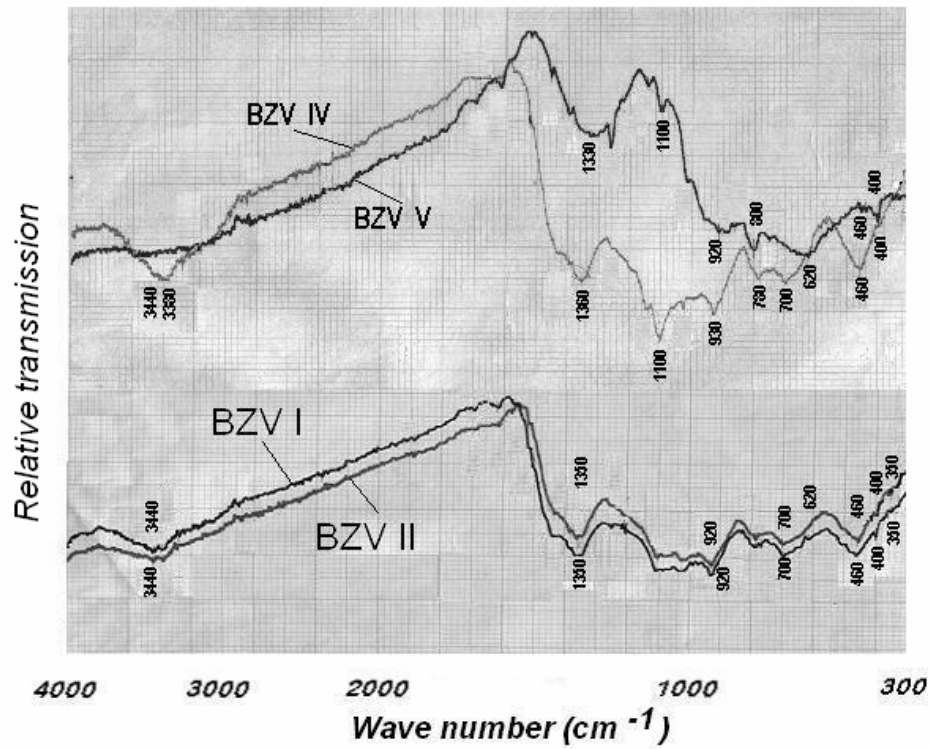


Fig. 3 – The IR transmission spectra for the xerogels, with composition code BZV I, BZV II, BZV IV and BZV V, thermal treated at 120°C.

The Fourier transform infrared transmission spectra, for the samples code BZV II, BZV III and BZV IV, are presented, comparatively, in Figure 4 and the characteristic vibration band position in Table 2.

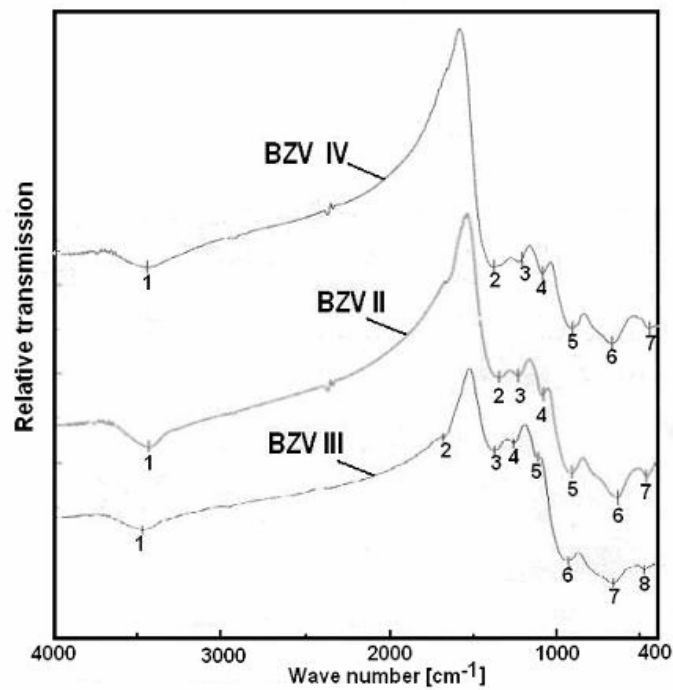


Fig. 4 – The FTIR spectra for samples code BZV II, III, IV.

Table 2

Characteristic vibration bands position from the FTIR spectra

Sample	Position of vibration bands [cm^{-1}]							
	1	2	3	4	5	6	7	8
BZV II	3430.32		1343.39	1230.40	1078.38	909.29	637.26	468.28
BZV III	3440.25	1654.35	1343.33	1230.34	1086.33	908.21	641.19	459.20
BZV IV	3448.33		1382.33	1213.34	1090.32	912.26	675.25	451.26

From the FTIR spectra it can be seen that, for the vanadium content below 50 molar %, the transmission maximum, in the $1600\text{-}1400\text{ cm}^{-1}$ domain, decreases with vanadium content increasing. The absorption maximum from 650 cm^{-1} , assigned to cyclic boron, boroxol type, increases with the vanadium content, parallel with the maximum at 1350 cm^{-1} decreasing, for depolymerised boron, for those three compositions. Those observations confirm the supposition that the boron oxide and the vanadium oxide could form together a mixed network. The maximum for octahedral coordination of the zinc $[\text{ZnO}_6]$ decreases with the zinc content increasing, for this compositional domain.

The Table 3 presents the electrical properties values for the glasses code BZV I, BZV II, BZV IV and BZV V, for electrical field frequency of 100 KHz, 1 and 30 MHz.

Table 3

The electrical properties for glasses BZV I, BZV II, BZV IV and BZV V, for electrical field frequencies of 100 KHz, 1 MHz and 30 MHz

Frequency	Property	Glass sample code			
		BZV I	BZV II	BZV IV	BZV V
100 KHz	Dielectric permittivity ϵ_r	9,74	12,55	8,05	17,22
	Dielectric loss $\text{tg } \delta$	24×10^{-3}	193×10^{-3}	$3,86 \times 10^{-3}$	646×10^{-3}
	Loss factor	0.23	2.42	0.031	11,12
1 MHz	Dielectric permittivity ϵ_r	8,84	10,26	8,55	13,13
	Dielectric loss $\text{tg } \delta$	$13,53 \times 10^{-3}$	$54,4 \times 10^{-3}$	$4,44 \times 10^{-3}$	$155,6 \times 10^{-3}$
	Loss factor	0,12	0,56	0,04	2,04
30 MHz	Dielectric permittivity ϵ_r	9,8	14,6	8,47	13,74
	Dielectric loss $\text{tg } \delta$	$4,8 \times 10^{-3}$	$6,93 \times 10^{-3}$	$6,6 \times 10^{-3}$	$13,9 \times 10^{-3}$
	Loss factor	0,05	0,10	0,06	0,19

The electrical properties variation *versus* electrical frequency, for the four chosen samples of vitreous materials, are presented in Figures 5 and 6. The frequency values for the determinations were of 100 Hz, 1 MHz and 30 MHz.

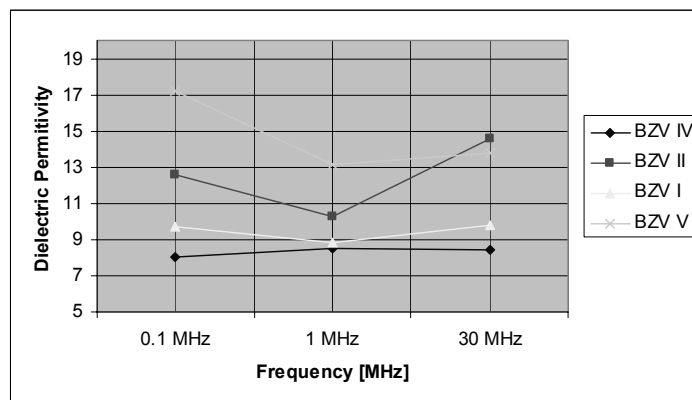


Fig. 5 – The dielectric permittivity variation with the electrical frequency, for the four representative samples

The variation of the dielectric permittivity with electrical field increase is different for different compositions: for the sample IV, with the V/Z ratio of 1/2, there appear a slight and continuous increase of the permittivity with the frequency increase; the compositions with V/Z ratio of 1/1 (samples I and II)

presents a minimum of the permittivity at 1MHz frequency and a rise at 30 MHz frequency, more pronounced for the lower boron content (sample I); the sample with the molar ratio of 2/1 (composition V) presents the same minimum at 1MHz frequency, but it has lower permittivity at 30 MHz than at 0.1 MHz.

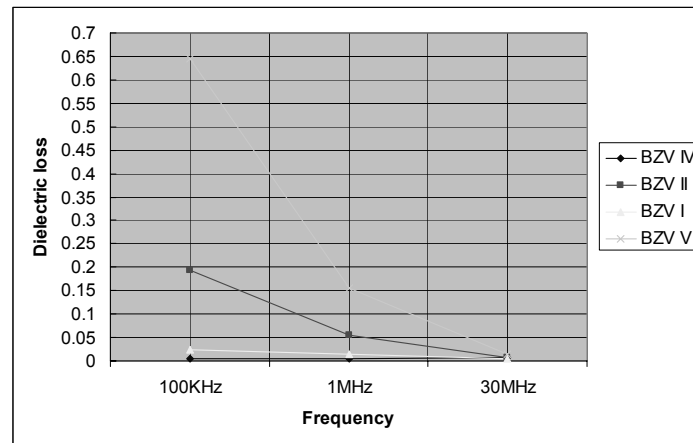


Fig. 6 – The variation of dielectric loss, expressed as $\text{tg } \delta$, to the frequency, for the vitreous materials code BZV I, II, IV and V

The dielectric loss, for three from the four tested compositions, have a similar variation, showing a sharp decrease as the frequency increase. The sample IV, which is rich in ZnO, have a different behaviour, recording a slight increase of the $\text{tg } \delta$, to frequency raising. The compositions rich in vanadium oxide, at low frequency, present sensibly higher dielectric loss values.

The variation of dielectric properties with the samples composition, for the three testing frequency values is plotted in Figures 7 and 8.

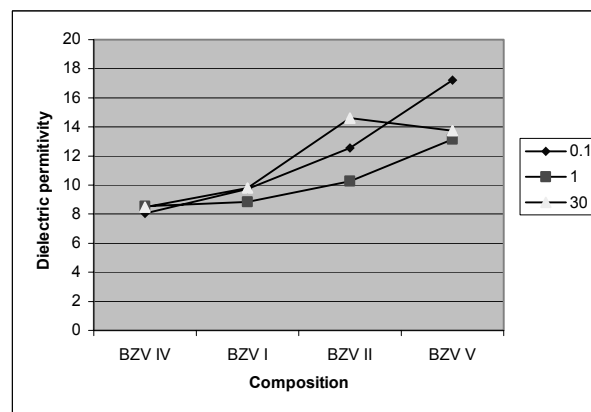


Fig. 7 – The variation of dielectric permittivity to composition, for the frequency of 100 KHz, 1 MHz and 30 MHz

The permittivity values, for all testing frequencies, increase with the vanadium oxide content, in the order: BZV IV (26.67 molar% of V_2O_5)-BZV I (35 molar% of V_2O_5)-BZV II (40 molar% of V_2O_5)-BZV V (53.33 molar% of V_2O_5). The only decrease of the permittivity to vanadium oxide content that appears, for the frequency of 30 MHz, is the one from 40 to 53.33 molar% vanadium oxide. If it is accepted that the mixed network of boron and vanadium oxides is formed, in which the boron and the vanadium are tetra-coordinated, this behaviour could be explained by the apparition of hexa-coordinated vanadium in excess, that leads to the decrease of the permittivity at high temperatures. The zinc content have less influence that the vanadium to the permittivity value, proved by the lowest level of the permittivity for the BZV IV sample, which have the zinc content of 53.33 molar%.

The replacement of 10% boron oxide with 5% zinc oxide and 5% vanadium oxide (sample I-sample II) have a spectacular effect to the permittivity level; for all the tested frequencies it appears in this case a rise of 25% for the dielectric constant.

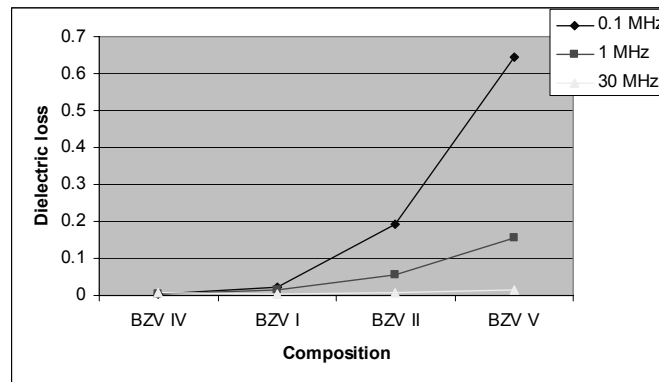


Fig. 8 – The dielectric loss, expressed as $\text{tg } \delta$, versus composition, for the frequencies of 0.1, 1 and 30 MHz.

The dielectric loss increases with the vanadium oxide content, more important for small frequencies than for the higher ones. From the dielectric permittivity and the dielectric loss values it was calculated the dielectric loss factor. The variation curves for the dielectric loss factor, for the four compositions and the three frequency values, of 0.1, 1 and 30 MHz, are presented in Figure 8. The loss factor decreases with the frequency increasing, for the samples richer in vanadium oxide and presents an inverse tendency, of slight increase, for the sample no. IV, richer in zinc oxide. From the Figure 9 it can be observed the increase of the loss factor to vanadium oxide content increasing, for all the three frequencies, more important at lower frequencies.

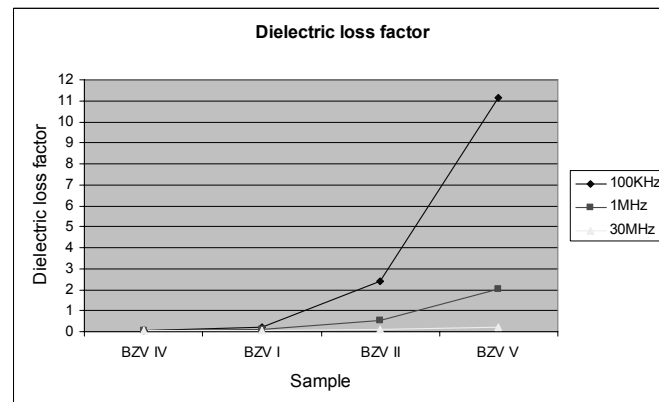


Fig. 9 – The dielectric loss factor versus composition, for the frequencies of 0.1, 1 and 30 MHz.

It is interesting to remarks the behaviour of the sample with the zinc to vanadium of 2/1 ratio, the only sample for which the dielectric permittivity and dielectric loss increase slightly to electric field frequency increasing. For all the other samples the increase of the frequency leads to the decrease of the dielectric loss. The dielectric permittivity has complex variation to frequency, for the samples rich in vanadium, due to the mixt network boron-vanadium forming, for some compositional domains, and to the changes of the coordination number, for the boron, which pass from 3 to 4, and also for the vanadium, from 6 to 4.

Using the tabled coefficients from other papers⁸, ponderated, for the influence of boron and zinc oxide on dielectric permittivity and a calculated from experimental data coefficient at the frequencies of 1 and 30 MHz, for the vanadium oxide, the dielectric permittivity was calculated for the above frequencies. The obtained data, for the four compositions, are presented in the Table 4. The curve of calculated variation of the dielectric permittivity, as compared with the experimental curve, for the frequencies of 1 and 30 MHz, are presented in Figures 10 and 11.

Table 4

The dielectric calculated permittivity, for the frequencies of 1 and 30 MHz

Frequency	BZV IV	BZV I	BZV II	BZV V
1 MHz calculated	8.70	9.45	10.62	12.55
30 MHz calculated	8.26	9.89	11.07	13.89

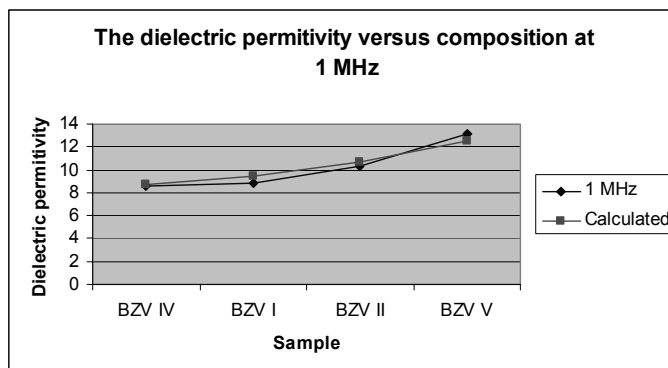


Fig. 10 – The comparison of the calculated and experimental curves, for dielectric permittivity, at 1 MHz.

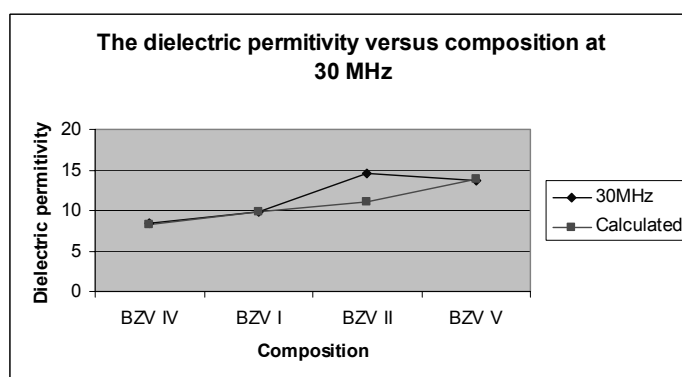


Fig. 11 – The calculated and experimental curves for the dielectric permittivity, at the frequency of 30 MHz.

As it can be seen from the above figures, the calculated curves fit well to the experimental ones, for the two frequencies of 1 and 30 MHz, with one exception, the sample code BZV II, at 30 MHz, about which we proposed an explanation previously.

CONCLUSIONS

Sol-gel glasses in the $\text{ZnO-V}_2\text{O}_5\text{-B}_2\text{O}_3$ system were prepared.

In the ternary system $\text{ZnO-V}_2\text{O}_5\text{-B}_2\text{O}_3$, the minimum for the gelation rate is found at low pH, in acid compositions, around $\text{pH} = 1$.

The IR and FTIR spectra provided precious information, which support the idea that the boron, together with the vanadium, form mixed network, in the compositional domain of high vanadium content, above 40 molar%, in the ternary studied system.

About the influence of the composition to the electrical properties, it was clearly revealed the increase of the dielectric permittivity and dielectric loss to the vanadium oxide content increasing. The dielectric loss factor decreases to the increase of frequency, for the compositions rich in vanadium and increases significantly to the vanadium content increasing.

Using the tabled constants for the deduction of theoretical variation curves for the dielectric permittivity, at several compositions, was difficult, because it were not available the constants for the vanadium coordinations.

There were plotted the theoretical curves of the permittivity variation versus the vanadium oxide increase, for the frequencies of 1 and 30 MHz, based on theoretical calculations, using the tabled ponderated data for the boron and zinc oxide, and the medium experimental deduced coefficients, for the vanadium oxide. The concordance to experimental data was good, but it must be effectuated the correlation with others researchers data, in order to establish the practical possibility to use the theoretical additive calculation methods for the dielectric properties in such compositional domains.

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