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# RAMAN AND FTIR STUDIES OF SOME SOL-GEL BASED GLASSES IN THE ZnO-TiO$_2$-SiO$_2$ SYSTEM

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*Lucrarea studiază o serie de materiale vitroase din sistemul ternar ZnO-TiO$_2$-SiO$_2$ obţinute pe cale sol-gel, din precursori organici şi anorganici. Probele obţinute au fost analizate prin tehnici FTIR şi Raman, conducând la informaţii structurale la nivel molecular. Maximele de absorbţie în IR în transformată Fourier sunt identificate şi interpretate potrivit cu datele din literatură. Spectrele Raman, cu excitare laser Ga-As la lungimea de undă de 785 nm, pun în evidenţă modurile de vibraţie caracteristice pentru cei trei componenţi oxidici.*

*The paper studies a series of vitreous materials from the ternary ZnO-TiO2-SiO2 system obtained by sol-gel route from organic and inorganic precursors. The obtained samples have been analysed by FTIR and Raman techniques, leading to structural information at molecular level. The FTIR absorption maxima have been identified and interpreted according to literature data. The Raman spectra using Ga-As laser, at 785 nm, put in evidence the characteristic vibration modes for the three oxidic components.*

**Keywords**: Sol-gel based glasses, ZnO, TiO$_2$, SiO$_2$, FTIR spectra, Raman spectra.

## 1. Introduction

In the recent years the sol-gel method has gained enormous interest because of its applications and future possibilities [1,2]. The materials made by this route have very high purity, excellent homogeneity and compositions in the unaccessible domains [3-5] by conventional methods.

The glasses having compositions from the ternary system ZnO-TiO$_2$-SiO$_2$ show some great capabilities, due to their thermo-mechanical properties and chemical stability [3]. They can be utilised in the field of toxic waste management and also for protection coatings.

For molecular energy levels studies, two complementary techniques are used: the Fourier transform infrared absorption spectroscopy (FTIR) and Raman spectroscopy. For a vibration motion to be IR active, the dipole moment of the

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molecule must change [6]. For a transition to be Raman active there must be a change in the molecule polarizability.

In infrared spectroscopy only the asymmetric vibrations are active. The molecular IR spectra provide direct information about the discreet levels of energy of the molecule. The study of molecular vibration frequency permits the investigation of the interatomic bond forces and of the dissociation heat.

The Raman spectroscopy detects the symmetric vibrations in the sample. The energy variation due to the modification of the vibration and rotation energy provides useful information about the energy levels. The modification of the frequency corresponding to this energy variation is known as *Raman shift*. For several materials the Raman bands broaden and shift with decreasing of the nanocrystal size [7]. Shifts in the main Raman peaks are ascribed to stoichiometry changes [8] in the molecular species.

The purpose of this paper is to investigate the molecular structure of some glasses in the ternary system $ZnO-TiO_2-SiO_2$. The symmetric and asymmetric vibrations and rotations, the bonds bending and stretching as well as the first order distance in the studied materials are studied.

## 2. Experimental

The selected compositions for the study, denoted ZTS from I to X, are presented in Fig. 1. The compositions were chosen for various molar ratios of: $TiO_2/SiO_2$ ( 8/1 for the samples I and III, 3.6/1 for II and IV, and 1/1 for V, VI and X), $ZnO/SiO_2$ (2/1 for the compositions VI, VII and IX) and $ZnO/TiO_2$ (1/3.6 for the compositions VII and VIII).

The reagents were dihydrate zinc acetate p.a. (Chimica Dudesti), e.g. titanium (IV) chloride (Merck) and e.g. silicon tetrachloride (Merck).

The distilled water and also absolute ethyl alcohol were used as solvents. For pH modification several ammonia solutions in concentration from 1 to 4 M, and 0.1 M hydrochloric acid were used.

The solutions were prepared by zinc acetate dissolution in water and ethanol, at 50$^{o}$C, followed by the dropwise addition, of titanium and silicon tetra chloride, under continuous stirring.

The IR transmission spectra were recorded in the 4000 to 400 cm$^{-1}$ range with a Shimadzu FT-IR–620-JASCO spectrophotometer, accumulations 16, resolution 4 cm$^{-1}$.

The Raman spectra were plotted with a Raman System 2001 Ocean Optics equipment, using a 500 mW Ga-As laser diode, emitting at 785 nm, with a resolution under 8 cm$^{-1}$.

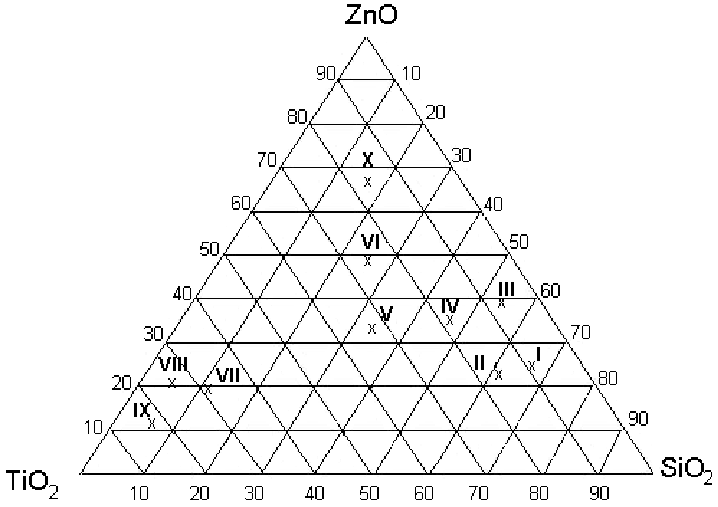

Fig.1. The selected compositions in the ternary system ZnO-TiO$_2$-SiO$_2$

## 3. Results and Discussion

For the chosen samples, thermally treated at 250, 870 and 1200°C the FTIR spectra were recorded, between 4000 and 400 cm$^{-1}$, and are presented in Figs 2 – 6.

The ZTS I and ZTS III samples (Fig. 2), thermally treated at 250°C present the water specific vibrations [9], much more pronounced that in the case of samples treated at 1200°C (see the last Figs). These vibrations are more intense in the case of ZTS I sample, with increased silicon dioxide content. The ZTS I sample presents a more pronounced maximum for polymerized [SiO$_4$] group, at 1092 cm$^{-1}$. The specific maximum for un-polymerized [SiO$_4$] group, situated at 944 – 945 cm$^{-1}$[10], is more pronounced for the ZTS III sample, more rich in ZnO.

Regarding the samples thermal treated at 870°C, for ZTS III and ZTS V samples (Fig.3) comparatively to the ZTS I and ZTS II samples, two new maxima at 869 and 980 cm$^{-1}$ appear, which could be either the vibration for the Si-O-Ti bond or for the condensed [TiO$_4$] group. The difference could be due to the increased content of zinc, which leads to the titanium oxide polymerization. The vibration from 680 – 705 cm$^{-1}$ region decreases gradualy from ZTS I to ZTS II, ZTS III and ZTS V samples, a fact that can be assigned to un-polymerized [TiO$_6$] group.

This behavior suggests that the increase of the zinc oxide content, in some limits, leads to the decrease of the specific maximum for un-polymerized [TiO$_6$]

group, and also to the formation of zinc - titanium (and possible mixed titanium – silicon) networks. Furthermore, in IR spectra, the maxima at 900 – 932 cm$^{-1}$, which are attributed to condensed – polymerized [$TiO_4$] group increase from the ZTS I, ZTS II samples to ZTS III, ZTS V samples when zinc oxide content increases.

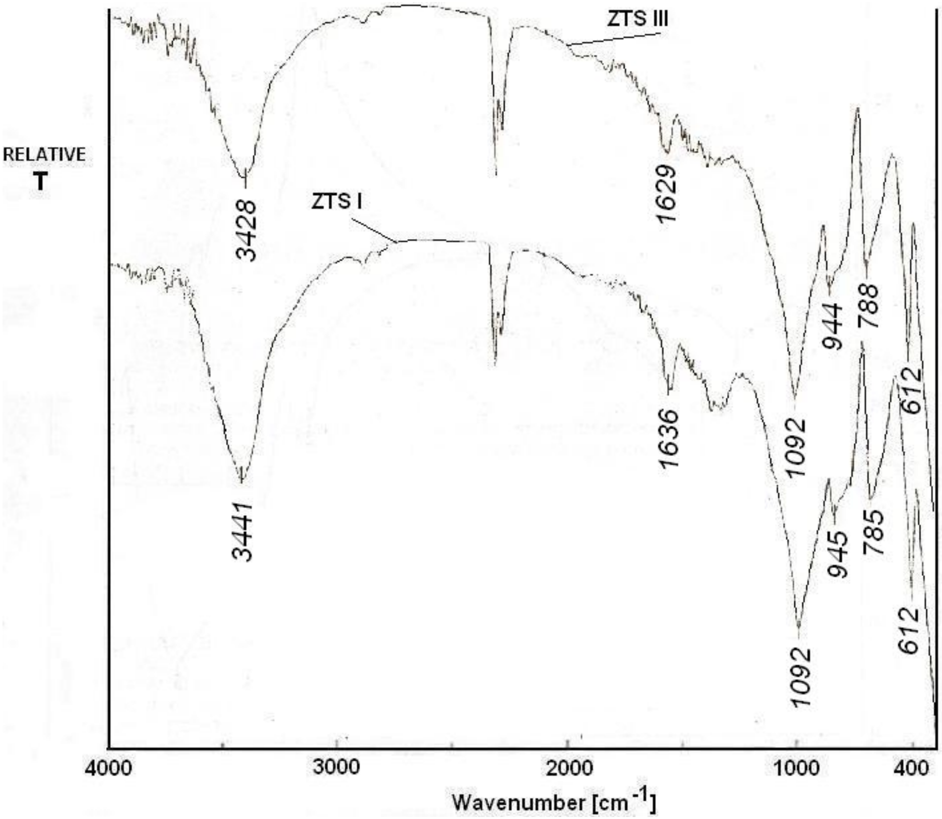

Fig.2. FTIR spectra for the ZTS I, and ZTS III samples, thermal treated at 250°C, one hour

This could be an evidence of the increased degree of polymerization for titanium oxide. The maximum for un-polymerized [$ZnO_6$] group, in 460 – 468 cm$^{-1}$ range decreases from ZTS I - ZTS II samples to ZTS III - ZTS V samples whereas the maximum for polymerized [$ZnO_4$] group, in 578 – 581 cm$^{-1}$ increases, respectively. This is an evidence that the zinc oxide also participates at formation of mixed networks, together with the titanium oxide and, possibly, with the silicon oxide. The maximum from 3420-3450 cm$^{-1}$, attributed to OH group [9], is more pronounced for the compositions more rich in ZnO and almost vanishes for the composition with high $TiO_2$ content.

The maximum at 573-574 cm$^{-1}$, attributed to polymerized [ZnO$_4$] group [11], increases with zinc oxide content (Fig.4) in the order: ZTS I-ZTS III-ZTS X; simultaneously, an important decrease of the maximum at 480 - 486 cm$^{-1}$, specific to un-polymerized [ZnO$_6$] group [12] is noticed.

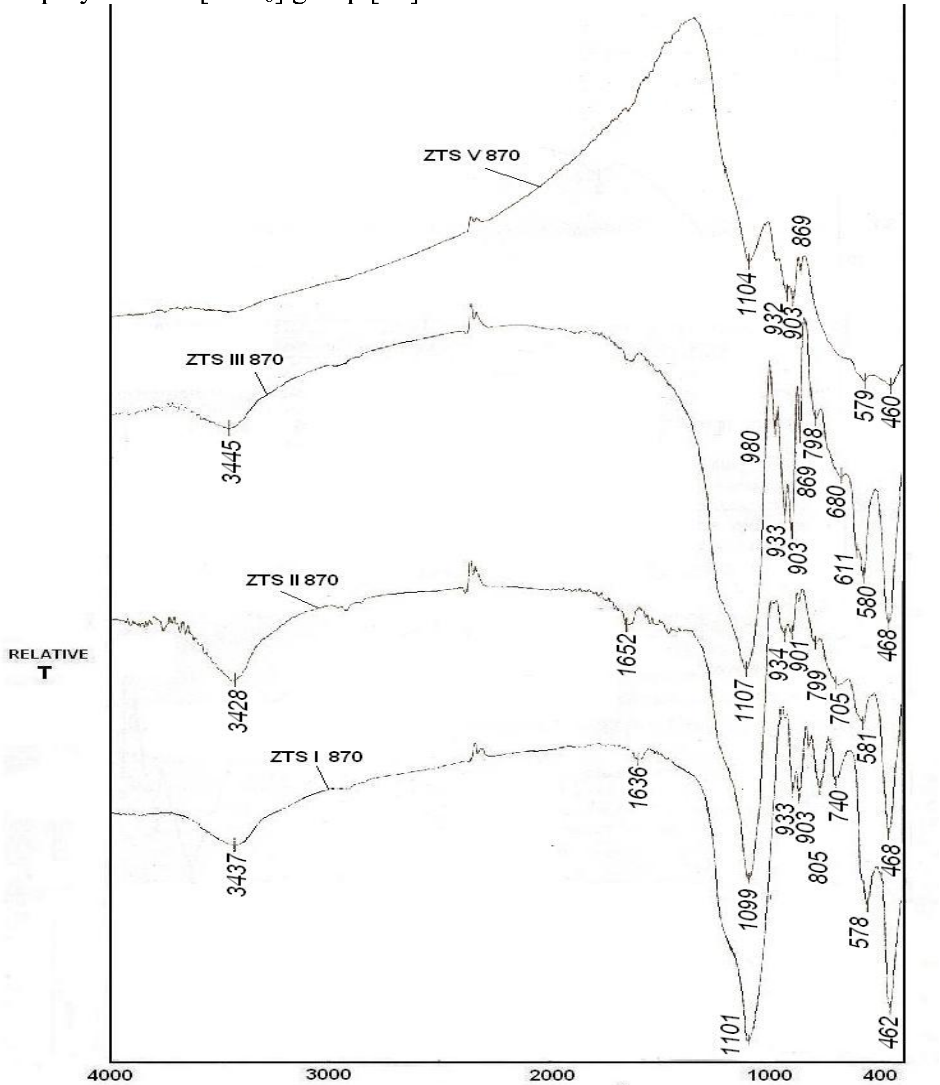

Fig.3. FTIR spectra for ZTS I, ZTS II, ZTS III, and ZTS V samples, thermally treated for one hour at 870°C

It means that zinc oxide polymerizes when its content increases, for a relatively constant silicon oxide content. On the other hand, the specific vibration in 617 - 618 cm$^{-1}$ region, due to the un-polymerized titanium oxide, vanishes with the zinc oxide content increase. This confirms the polymerization of titanium oxide, probably in mixed networks, together with zinc oxide. The absorption maximum attributed to polymerized [$SiO_4$] group [13], from 1095 - 1096 $cm^{-1}$, diminishes from sample ZTS I to ZTS III and disappears completely in the case of sample ZTS X, with very high zinc oxide concentration.

From Fig. 5 it can be seen that the maximum from 577 - 578 $cm^{-1}$, assigned to the polymerized [$ZnO_4$] group, gradually decreases from ZTS VI sample to ZTS VII sample and disappears in the case of ZTS II sample.

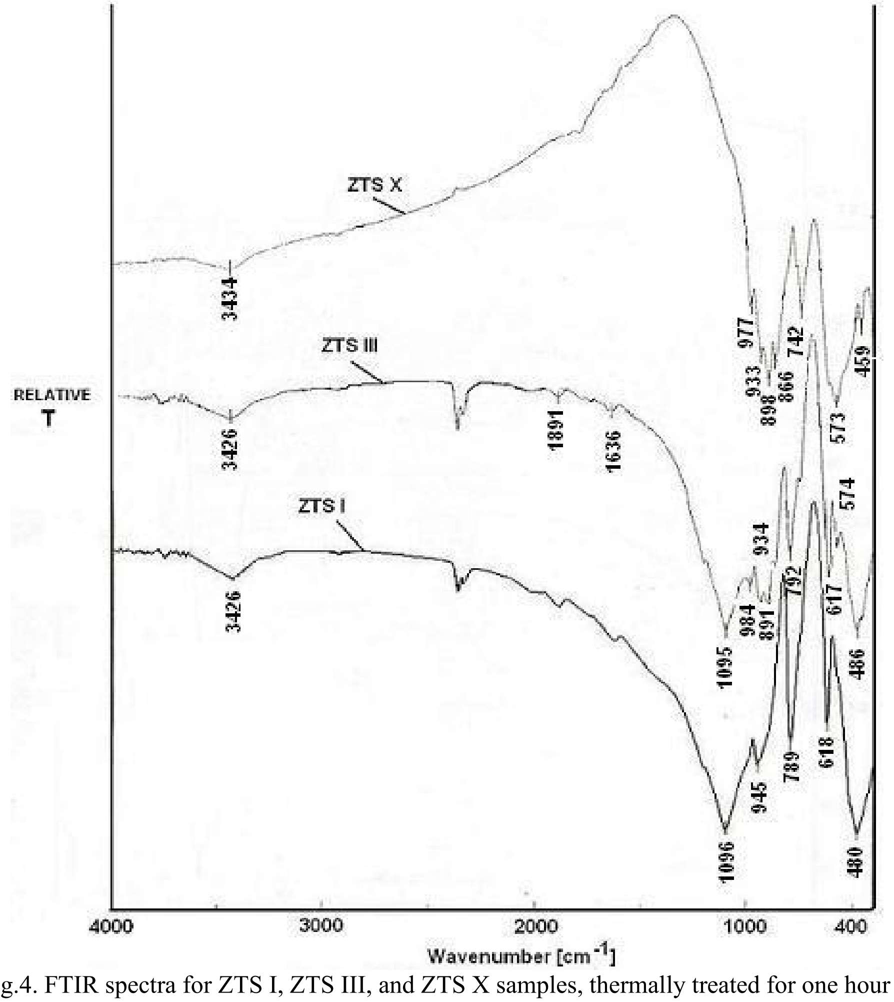

Fig.4. FTIR spectra for ZTS I, ZTS III, and ZTS X samples, thermally treated for one hour at 1200°C

Although the ZTS II and ZTS VII samples have equal concentration of zinc oxide, the above discussed maximum appears only in the case of ZTS VII sample, with high titanium oxide content and not for the ZTS II sample with high silica content. This fact proves the different behavior of the zinc oxide, which is responsible for the occurence of mixed networks with titanium oxide, but it behaves as network modifier for the silicon oxide. The specific maximum for un-polymerized [ZnO$_6$] group is very pronounced in the case of ZTS II sample, confirming the previous assumptions. For the ZTS VI sample, rich in ZnO, the characteristic maximum for un-polymerized [ZnO$_6$] group also appears. However, it is less important that in the case of ZTS II sample, unlike for the ZTS VII sample for which this maximum vanishes, meaning that ZnO is totally polymerized.

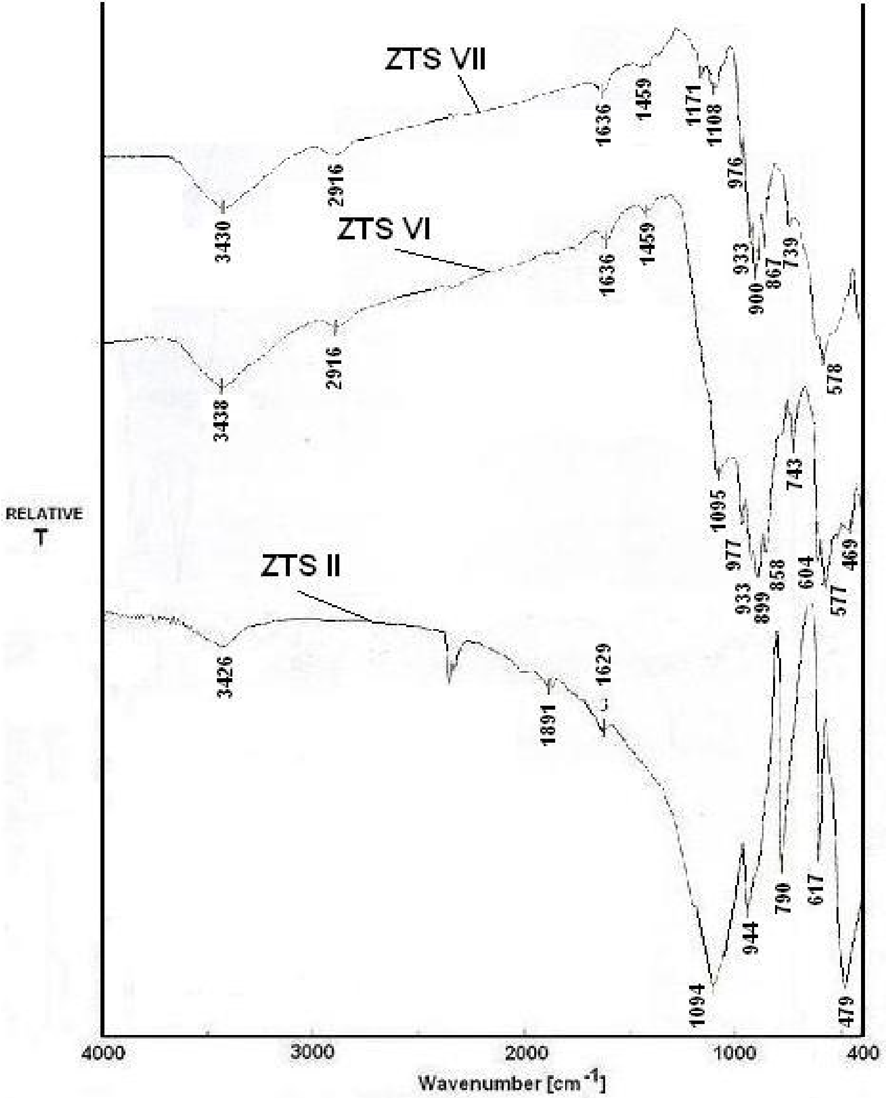

Fig 5. FTIR spectra for the ZTS II, ZTS VI and ZTS VII samples, thermally treated one hour at 1200°C

The vibration maximum in the 1094 – 1095 $cm^{-1}$ domain, specific for polymerized [$SiO_4$], decreases strongly from ZTS II sample to ZTS VI sample, as ZnO content increases. It disappears for the ZTS VII sample, where it seems to be possible the formation of mixed network of zinc oxide - titanium oxide, illustrated by the maxima recorded at 867, 900, 933 and 976 $cm^{-1}$. The vibration from 790 $cm^{-1}$, due to un-polymerized [$TiO_6$] group decreases and almost disappears from ZTS II sample to ZTS VII sample as the titanium oxide content increases, whereas the maximum for polymerized [$TiO_4$], at 900 $cm^{-1}$ is more pronounced.

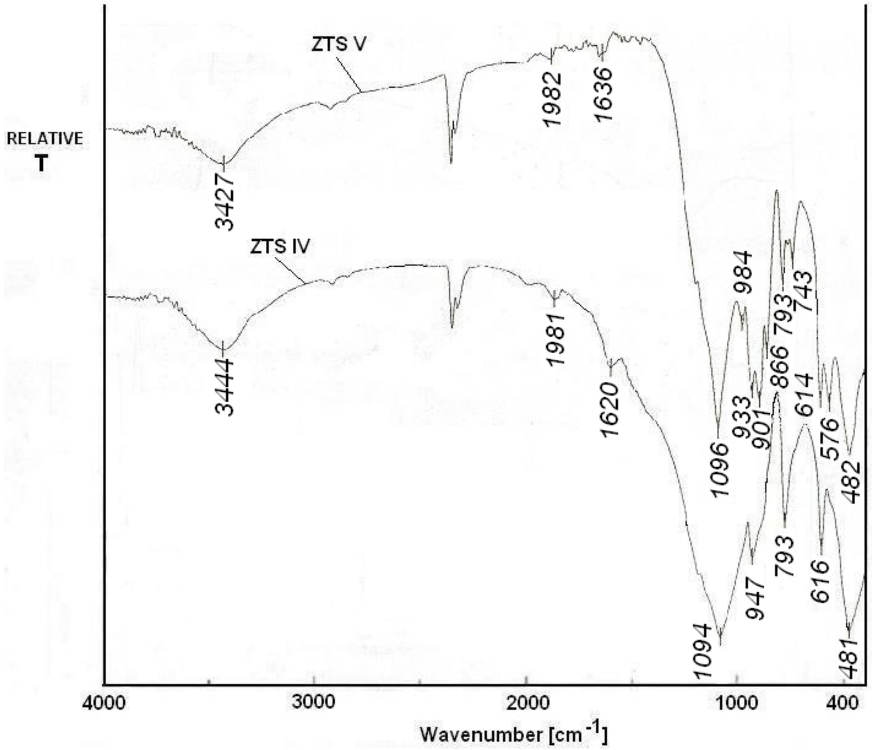

Fig. 6. FTIR spectra for samples ZTS IV and ZTS V, thermally treated for one hour at 1200°C

The spectra from Fig. 6 show a maximum for polymerized ZnO at 576 $cm^{-1}$, if the titanium oxide content increases. At the same time, the maximum characteristic for un-polymerized [$ZnO_6$], in the 481 – 482 $cm^{-1}$ region, diminishes. This behavior also proves the possibility of forming mixed networks of titanium oxide - zinc oxide. As the titanium oxide concentration increases several maxima assigned to the Si-O-Ti bond vibration and to the condensed [$TiO_4$] group appear, at 866 – 924 $cm^{-1}$, indicating the possible formation of titanium oxide – silicon oxide mixed network. The maximum at 947 $cm^{-1}$ shifts and splits into two maxima when the titanium oxide content increases. These two maxima assigned to condensed – polymerized [$TiO_4$] group [14], at 901 and 933 $cm^{-1}$, respectively, may supplementary indicate the presence of more complex network, including zinc oxide.

The Raman spectra for ZTS I, ZTS II, ZTS III and ZTS V samples, shown in Fig. 7 have the specific shape of vitreous state for the samples. There are present the characteristic Raman maxima for vitreous Si-O boson [15], in the domain 41.04 – 90.28 $cm^{-1}$, as well as for symmetric Si-O-Si bending ν2 [16], for species $Q_2$ and $Q_3$, in 303.66 – 333.76 $cm^{-1}$ and 430.87 – 496.53 $cm^{-1}$ ranges. The specific Raman maxima for asymmetric bending ν4 [16] appear in the 519.79 – 566.29 $cm^{-1}$ domain and for stretching Si-O vibrations, assigned to Q2 type tetrahedron [17] as trimeric ring [18] at 596.38 – 607.32 $cm^{-1}$. The symmetric ν1 stretching for Si-O [16] appears at 811.14 – 848.07 $cm^{-1}$ and the asymmetric Si-O stretching ν3 [16] for species Q2 [17] at 852.17 – 1086.08 $cm^{-1}$. For the species Q3 [17] the symmetric stretching maximum appears at 1099.76 – 1105.23 $cm^{-1}$.

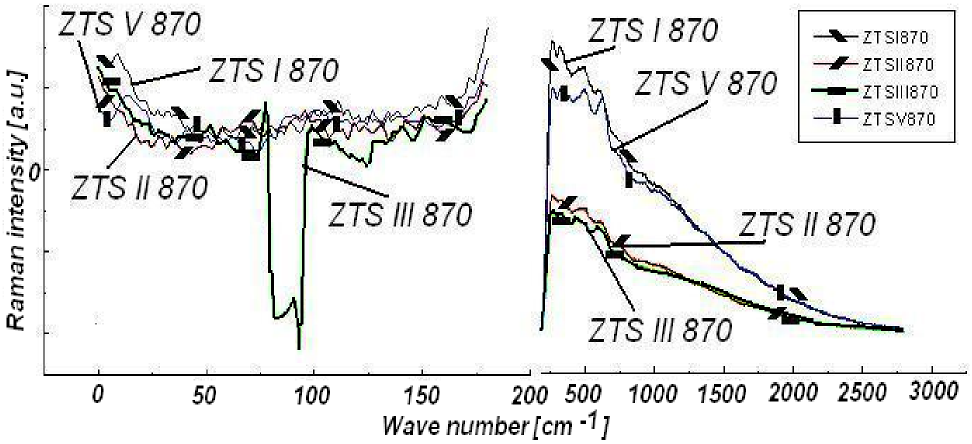

Fig.7. Raman spectra for the ZTS I, II, III and ZTS V sample, thermally treated one hour at 870°C

The increased $TiO_2$ content for the ZTS II and V samples, in comparison with ZTS I and ZTS III samples, leads to an increased number of maxima for Si-O vibrations. This could be explained assuming that Si-O and Ti-O are able to form mixed network. The increase of the zinc oxide content leads to Raman shifts toward lower wave numbers.

For Zn-O bond the Raman active phonons can be identified as E2 type [19] in the domains 95.75 - 103.96 $cm^{-1}$ and 432.24 - 436.35 $cm^{-1}$ [20] as well as E1 type phonons, at 403.52 - 418.56 $cm^{-1}$ and 581.34 – 585.44 $cm^{-1}$. In the case of ZTS V sample with increased titanium oxide content, having also equal molar percentages from each compound, the E1 maximum shifts to lower energy, due to the ternary networks occurence.

The literature data for $TiO_2$ indicate the characteristic Raman phonons for Eg type vibrations, which are specific for anatase at 144-145 $cm^{-1}$ [21], 195-198 $cm^{-1}$ [22], and 638-640 $cm^{-1}$ [22]. Supplementary, B1g type anatas vibrations at 397-399 $cm^{-1}$ [23] and 514-518 $cm^{-1}$ and also A1g type vibrations at 514-518 $cm^{-1}$ [22] were identified. Comparatively, for the rutil type the literature indicates the characteristic vibrations at 143 $cm^{-1}$ [23] for B1g, at 424-448 $cm^{-1}$ [24] for Eg, at 610-621 $cm^{-1}$ [24] for A1g and at 826 $cm^{-1}$ [23], for B2g type.

The Raman diagrams from Fig. 7 exhibits the characteristic maxima for titanium oxide for all four compositions. These maxima are shifted towards lower energies for all A, B and E type vibrations, especially in the case of ZTS III and ZTS V samples, indicating the mixed network formation.

The Raman spectra for ZTS I, ZTS II, and ZTS VII samples, for ZTS III and ZTS V samples, and for ZTS VI and ZTS X samples, all thermal treated at 1200°C, for 1 hour, are presented in Figs. 8, 9 and 10, respectively.

The Fig. 8 shows that for all three samples the higher thermal treatment temperature leads to the increase of the maxima corresponding to titanium dioxide, situated at around 428 and 600 $cm^{-1}$, respectively. Both maxima are close to those attributed to the rutil. The shift is toward lower energies, more pronounced in the case of ZTS VII sample (which is very rich in titanium dioxide), where the maxima were recorded at 424.04 and 599.12 $cm^{-1}$. This can be explained by the binary and ternary networks formed by titanium dioxide together with silicon dioxide and zinc oxide, respectively.

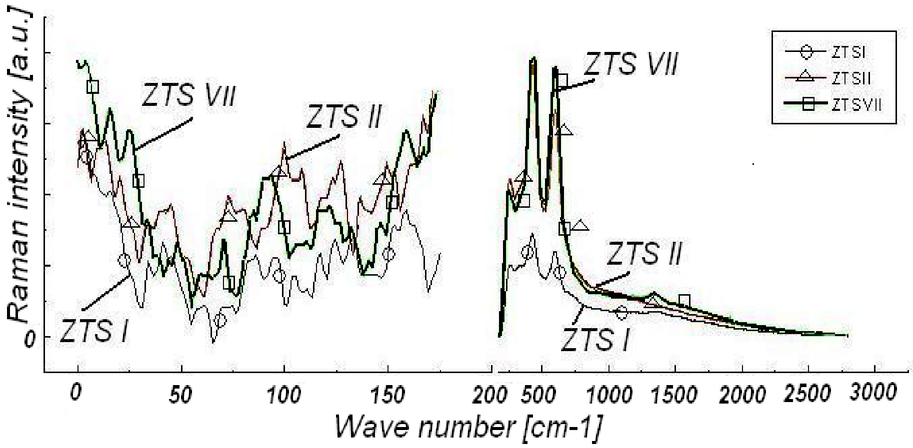

Fig.8. Raman spectra for the ZTS I, II and VII sample, thermally treated 1 hour at 1200°C

For the same ZTS VII sample the characteristic boson for vitreous Si-O-Si group is shifted to higher energies, meaning that the Si-O-Si bond is replaced by Si-O-Ti bond. The maximum assigned in literature to E2 type Zn-O vibration, at 100 $cm^{-1}$, appears at lower wave number for the sample more reach in $SiO_2$ (ZTS I sample), that is at 95.75 $cm^{-1}$, comparatively to the sample more reach in $TiO_2$ (ZTS II sample), located at 99.85 $cm^{-1}$.

For ZTS I and ZTS II samples, the increase of the temperature from 870 to 1200°C has shifted the maximum for the symmetric bending ν2 of Si-O bond from 322.81 $cm^{-1}$ to higher energies, at 337.86 and 344.7 $cm^{-1}$, respectively; on contrary, the shift of the maximum for asymmetric bending ν4 is towards lower energies, from 548.51 to 522.52 $cm^{-1}$ for both samples. The characteristic maxima for the Q2 species of $SiO_2$ tetrahedron, located at 950 – 1000 $cm^{-1}$, are less numerous for the ZTS I and ZTS II samples burned at 1200°C, comparatively with those treated at 870°C. In the same conditions the maximum for the Q3 species, at about 1100 $cm^{-1}$, disappears.

For ZTS III and ZTS V samples (Fig. 9), with higher content in zinc oxide than ZTS I and II samples, the E2 vibration for Zn-O bond is put in evidence at higher wave numbers, 116.27 and 117.64 $cm^{-1}$, respectively. The characteristic bosons for vitreous silica are present as two and three maxima, at 42.40 and 51.98 $cm^{-1}$ for ZTS III, and 38.30, 45.14 and 49.24 for ZTS V. The influence of increased titania is evidenced in the case of ZTS V sample by the occurence of the third maximum.

Similar to the case of ZTS I and ZTS II samples, the thermal treatment at 1200°C of ZTS III and ZTS V samples leads to increased amplitude of the specific two maxima for titania, at 429.51 (430.87 for ZTS V) and at 600.49 $cm^{-1}$ (for both maxima) and shifted to lower wave numbers comparatively to those for rutil; this also indicates the forming of mixed networks.

For these ZTS III and ZTS V samples, comparatively to the same samples, burned at 870°C, the same shifting to lower energies appears for those maxima characteristic to titania vibrations.

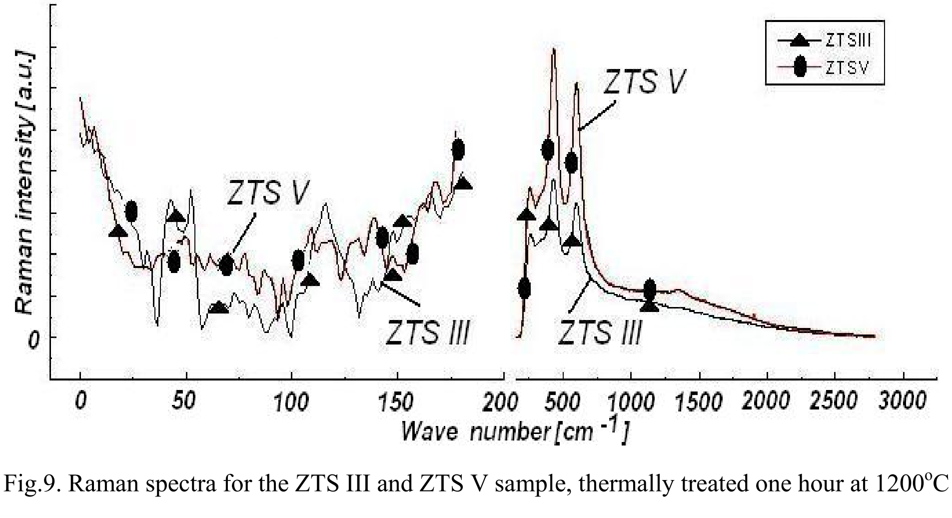

Fig.9. Raman spectra for the ZTS III and ZTS V sample, thermally treated one hour at 1200°C

The increased content of zinc oxide for samples burned at 1200°C influences the maximum for asymmetric stretching of Si-O bond by shifting it to lower energies: 952.03 cm$^{-1}$ for ZTS III and ZTS V samples, comparatively to 956.13 cm$^{-1}$ for ZTS I and ZTS II samples. The same maximum is displaced to higher energies for the ZTS III and ZTS V samples burned at 1200°C, comparatively to the same samples thermally treated at 870°C. Moreover, for these ZTS III and ZTS V samples the increased content of zinc oxide leads to the reappearance of the maximum for Q3 species of silica tetrahedron at 1105.23 cm$^{-1}$, and at 1110.7 cm$^{-1}$, respectively.

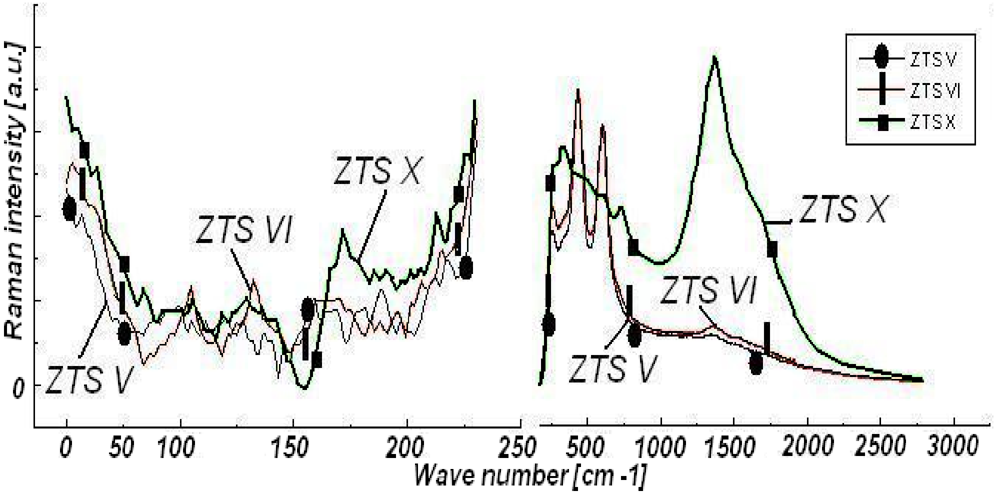

Fig.10. Raman spectra for the ZTS V, VI and X samples, thermally treated one hour at 1200°C

The Raman spectra (Fig. 10), for these samples treated at 1200°C for 1 hour, have the same shape as spectra for the other samples (Figs. 8 and 9), for ZTS VI sample, but a different shape for ZTS X sample. This shape difference is due to the increased basicity of the ZTS X sample, which has the greatest concentration of zinc oxide.

The specific vibration for titanium oxide of ZTS V sample, located at 430.87 cm$^{-1}$, shifts to higher energies (433.61 cm$^{-1}$) for ZTS VI sample, whereas for ZTS X sample the shift is towards lower wave number, i.e. at 428.14 cm$^{-1}$. This behavior shows that for high zinc oxide content a mixed network of titanium oxide together with zinc oxide is formed, rather the simple network of titanium oxide. This assumption is also supported by the displacement of the maximum from 600.49 cm$^{-1}$ in the case of the ZTS V and ZTS VI samples, to 604.59 cm$^{-1}$ for the ZTS X sample.

The maximum of the specific bosons for vitreous silica, at 45.14 $cm^{-1}$ for ZTS V, shifts to higher wave numbers for ZTS VI and ZTS X samples, which have an increased zinc oxide content. The symmetric bending ν2, the asymmetric bending ν4 and the asymmetric stretching ν3, all specific for the silicon oxide, shift toward lower energies as the zinc content increase, in the order ZTS V, ZTS VI and ZTS X samples. The same behavior was registered for the Q3 species of the $[Si-O_4]$ tetrahedron, the corresponding positions being: 1110.7 $cm^{-1}$ for ZTS V sample, 1099.76 $cm^{-1}$ for ZTS VI sample and 1090.18 $cm^{-1}$ for ZTS X sample.

The maximum for the E2 vibration, specific for zinc oxide, moves towards higher wave numbers as zinc oxide content increases, in the order: ZTS V - 117.64 $cm^{-1}$, ZTS VI – 120.37 $cm^{-1}$, ZTS X – 121.74 $cm^{-1}$. The same behavior was noticed for the overtone of the zinc oxide A1 vibration, which shifts from 1157.21 $cm^{-1}$ in the case of the ZTS V sample, to 1166.78 $cm^{-1}$ in the case of the ZTS X sample.

## 4. Conclusions

The present study of some sol-gel glasses based on $ZnO-TiO_2-SiO_2$ system has succeded to put in evidence the influence of each oxidic component and also of the thermal treatment on the recorded FTIR and Raman spectra.

The maxima in FTIR spectra for un-polymerized $[SiO_4]$ group raise their amplitude for the samples more rich in zinc oxide, thermally treated at 250°C, showing the expected unfavorable influence of ZnO on silicon dioxide polymerization. For the samples treated at 870°C, the appearance of new maxima specific for both condensed $[TiO_4]$ group and Si-O-Ti bond shows that the increased ZnO content leads to titanium oxide polymerization. The decrease of the maximum for un-polymerized $[ZnO_6]$ group and the increase of the peak for polymerized $[ZnO_4]$ group confirm the participation of ZnO in mixed network together with titanium oxide.

In the case of samples burned at 1200°C, the absorption maximum attributed to polymerized $[SiO_4]$ group decreases with ZnO content and even disappears for the sample with the highest zinc oxide content, proving that ZnO acts as network modifier.

The displacement to lower energies of the maxima assigned to titanium oxide, exhibited in Raman spectra for the samples thermally treated at 870°C, is more pronounced for the samples more rich in zinc oxide. In the case of samples treated at 1200°C the maxima for the characteristic bosons for vitreous silica shift to higher energies, which means that the Si-O-Si bonds may be replaced by Si-O-Ti bonds.

For high zinc oxide content, the maxima for titanium oxide in Raman spectra move to lower wave numbers; this can signify the appearance of binary and ternary mixed network. The different shape of the Raman curve for the sample with the greatest amount of zinc oxide treated at 1200°C can be assigned to the increased basicity of the sample.

Both FTIR spectroscopy and Raman spectroscopy indicate that the composition with equally molar percentages of the three compounds, ZnO, $TiO_2$, and $SiO_2$ has the most significant tendency to form ternary networks.

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