

QUALITATIVE MO TREATMENT OF THE γ -INDUCED PARAMAGNETIC CENTRES IN TITANIA BEARING SODIUM SILICATE GLASSES

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The unusual behaviour of EPR spectra of γ -irradiated titania bearing sodium silicate glasses with various contents of titania were qualitatively interpreted on the base of model molecular orbital calculations. As a model of the actual paramagnetic particles were chosen the clusters which indemnify the reasonable compromise between the model of cluster and exactness of calculation used. The results of the quantum chemical calculations show the preferential sensibilisation of Q^2 unit in comparison with Q^3 unit (the largest electron density in the vicinity of non bonding oxygens in Q^2 model). The bond strengths of Si-O bonds in the neighbourhood of non-bridging oxygens show to the preferential substitution of Si^{4+} for Ti^{4+} in the vicinity of the boundary of the cluster. The changes of the spin density distribution around the cluster after substitution of Si^{4+} for Ti^{4+} (the largest delocalization) explain the unusual behaviour of the g -tensor component with titania content in the glasses.

INTRODUCTION

Silicate systems containing titania represent important objects for glass technology as well as for ingenious petrology. Titania bearing silicate melts and glasses display unusual behaviour of various physical properties [1,2]. The reason for such extraordinary behaviour of titanium is the consequence of the various structural roles of titania, namely its net forming/modifying character as well as the changeable oxygen coordination number of Ti^{4+} ion [1-6].

The structural interpretation of the role of titania in the many component glasses is very controversial up to now. The tetrahedral coordination of Ti^{4+} is supposed from the results of EXAFS and Raman studies [7,8] for the various titania contents in alkali silicate glasses. This conclusion is in agreement with interpretation of spectral data of titania bearing alkali and alkali earth silicates [9-11]. The octahedral coordination of Ti^{4+} was assumed on the basis of interpretation of results of vibration spectra and X-ray measurements for another titania bearing alkali silicate glasses [4,12]. Recently Markgraf published [13] the assumption about the five coordination of Ti^{4+} ion in the glasses containing more than 10 mol.% of TiO_2 .

It is possible that such differences of structural behaviour of Ti^{4+} ion may reflect the composition of the glasses under study. The comprehensive paper of Mysen and Neuville (see [3] and references therein) summarised their own results as well as the results of other authors and they conclude that the role of titania in many component silicate glasses is open up to now. At present it is

impossible to elucidate the possibility of interpreting the role of Ti^{4+} at many component glasses in at least three ways:

1. Ti^{4+} ion substituted Si^{4+} in network tetrahedral coordination (network forming ion);
2. Ti^{4+} ion form clusters of TiO_2 type in which the Ti^{4+} is tetrahedral coordinated;
3. Ti^{4+} ions affect as a network modifier, probably occurring in the six fold or five fold coordination.

In the paper [14] we published the results of the quantitative decomposition of the EPR spectra of γ -irradiated titania bearing sodium silicate glasses. The results of EPR measurements show unusual changes of the content of HC_1 paramagnetic centres (assigned to centres arising from Q^2 structural units) and HC_2 paramagnetic centres (assigned to centres arising from Q^3 structural units) as well as unusual changes of the values of the main component of the g -tensor. The aim of this paper is to give some quantum chemical explanation of such unusual behaviour.

EXPERIMENTAL PART

EPR measurements

The glass samples were prepared with various TiO_2 content. The details of the sample preparation, the way of γ -irradiation (^{60}Co) and the EPR spectrum's measurements were described elsewhere [14]. The chemical compositions of the studied samples with the sample numbering convention are summarised in table 1. The

obtained spectra (figure 1) were decomposed into the shapes belonging to the individual paramagnetic species in the studied samples [15]. All the samples under study unambiguously indicate the presence of two types of paramagnetic particles with orthorhombic and axial symmetry respectively. These two types of radicals were classified as the HC₁ (orthorhombic) and HC₂ (axial symmetry) paramagnetic centres [14,16-19]. The decon-

volution analysis and its statistical characteristics show the correctness of the deconvolution method used. The relative abundance of the two mentioned paramagnetic centres does not show monotone dependency on the content of titanium in the sample (table 2 and figure 2). Also, the values of the main component of the *g*-tensor show analogic behaviour (table 2 and figures 3,4).

Table 1. Chemical compositions of the glass samples investigated (mol.%).

glass	Na ₂ O	TiO ₂	SiO ₂
PS1	24.08	0.00	75.92
PS2	22.64	1.03	76.33
PS3	21.28	2.46	76.26
PS4	19.23	5.00	75.77
PK	32.66	9.92	57.43

¹⁾ Calculated as 100 % - % Na₂O - % TiO₂.

Table 2. The *g*-tensor components and the relative abundance of the HC₁ and HC₂ paramagnetic centres in the studied samples.

parameter	sample	PS ₁	PS ₂	PS ₃	PS ₄	PK
<i>g</i> ₁		2.0099	2.0195	2.0193	2.0190	2.0190
<i>g</i> _{//}	HC ₂	2.0115	1.9978	2.0073	2.0119	2.0113
<i>x</i> (HC ₂)		0.7439	0.1129	0.3146	0.9995	0.9999
<i>g</i> ₁		2.3369	2.1419	2.1456	2.1926	2.2139
<i>g</i> ₂	HC ₁	2.0086	2.0096	2.0095	2.0096	2.0097
<i>g</i> ₃		2.0035	2.0039	2.0039	2.0043	2.0044
<i>x</i> (HC ₁)		0.2561	0.8871	0.6854	0.0005	0.0001

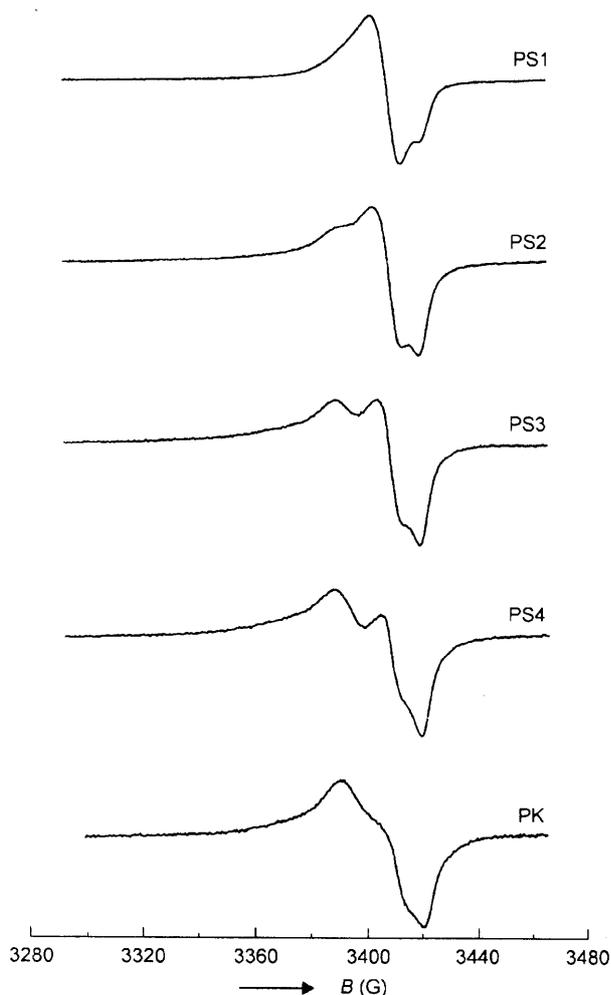


Figure 1. EPR spectra of γ -irradiated titanium bearing sodium silicate glasses.

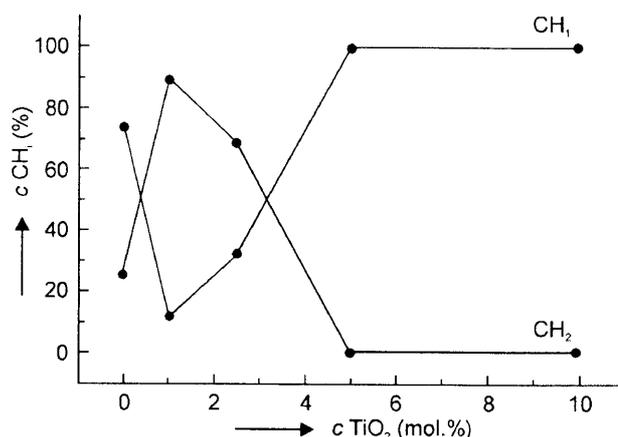


Figure 2. The relative abundance of the HC₁ and HC₂ centres as a function of titania content in the investigated samples.

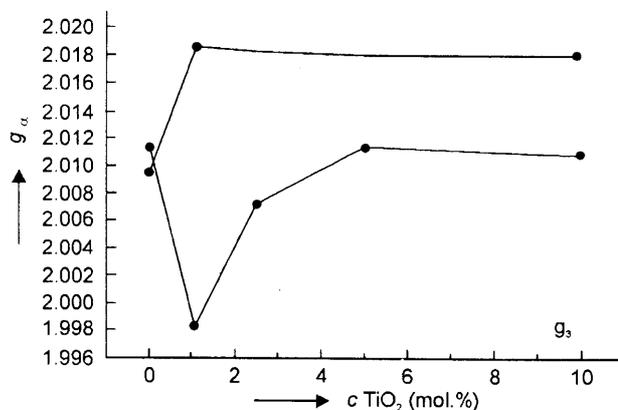


Figure 3. The dependence of the values of the main components of the *g*-tensor on the titania content in the HC₁ paramagnetic centres.

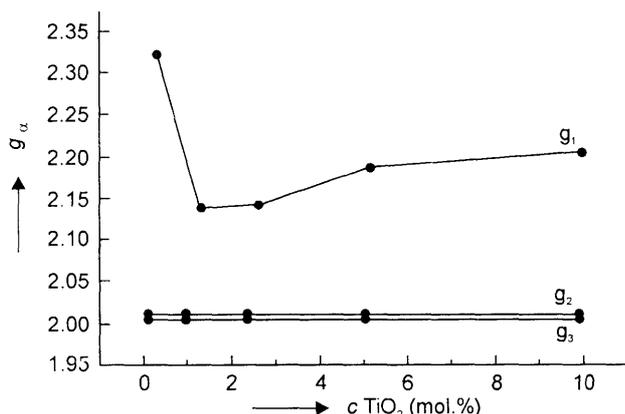


Figure 4. The dependence of the values of the main components of the g -tensor on the titania content in the HC_2 paramagnetic centres.

Method of calculation

Understanding the relationship between the molecular structure and the physical and chemical properties of silicates is one of the most significant topics in material science because of the ubiquitous nature of silicon-oxygen containing compounds in the geosphere and biosphere [20]. In contrast to many X-ray and spectroscopic experimental results [21,22] there have been only a few attempts to correlate the molecular structure of silicates with their physical and chemical properties at a quantum mechanical level up to the present [23-29].

At present quantum chemistry has to the disposition a wide scale of various computational methods from ab-initio up to semiempirical ones (see for example [30,31]). The computational time increases for ab-initio methods [30] as well as for cluster size, i.e. the number of atoms in a model molecular cluster while the quality (physical reality) of these methods is strongly dependent on the greatness of orbital basis set used. On the other hand there are many semiempirical methods [31] which, by the appropriate parametrisation, grant physically accepted results with only a modest increase in computational time.

In the region of theoretical investigation of silicates with the amorphous structure (glasses, ceramics) the cluster entrance has predominated, i.e. the calculations of models of the solid phase of the final magnitude - clusters. The cluster model of the solid phase represents a selection of the certain fragment from the solid state and therefore, also the interruption of some chemical bonds at the boundaries of the cluster. Therefore, atoms in the boundaries of the cluster show considerable changes of their electron structure and binding properties unlike the same atoms from the inside of the cluster. Therefore it is very important to choose a sufficient size

for the cluster (minimisation of the number of boundaries' atoms) and also the convenient termination of the cluster in such a way that the boundaries effects will be minimised.

The quasi-relativistic LCAO MO SCF INDO method [32] was used for the quantum chemical calculations of model systems for Q^2 and Q^3 units. The appropriate clusters were elected in order to minimise border effects by unsaturated border bonds. For a model of Q^2 unit the cluster containing 31 atoms (figure 5) was chosen. Such a type of cluster contains only 6 unsaturated oxygen bonds which were saturated by adding hydrogen atoms (the total numbers of cluster atoms were 37 atoms). The model of Q^3 unit includes 50 atoms (figure 6) and contains only 3 unsaturated oxygen bonds which were saturated by hydrogen atoms. In this way the reasonable compromise between the greatness of the cluster used (the convenience of the model) and the exactness of the method of calculation will be reached. For both types of clusters molecular species (with total charge of the cluster $Q = -2$ for Q^2 unit and $Q = -1$ for Q^3 unit; spin multiplicity $S = 1$ for both molecular models) were cal-

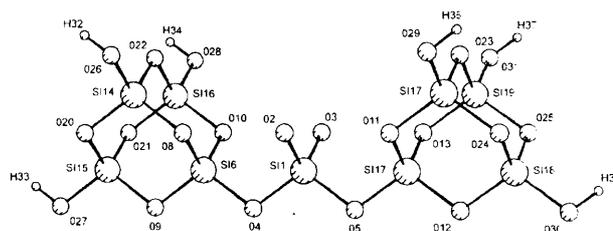


Figure 5. The scheme of the investigated model for the Q_2 centres.

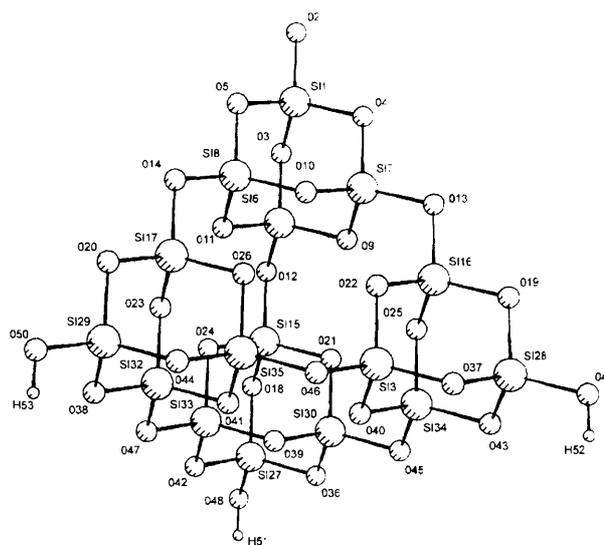


Figure 6. The scheme of the investigated model for the Q_3 centres.

culated and also the radiation induced paramagnetic species (with total charge $Q = -1$ for Q^2 unit and $Q = 0$ for Q^3 unit; spin multiplicity $S = 2$ for both radical models). Also, for all models the systems with gradually substituted Si^{4+} ions for Ti^{4+} ions were calculated. For the model of Q^2 unit two equivalent positions for such gradual substitution are possible, while for the model of Q^3 unit there are three such possibilities.

The calculated Wiberg indices [33] which characterised the strength of various bonds are summarised in tables 3 and 4. The charges on the atoms for Q^2 and Q^3 units and also for the competent model of radicals are collected in tables 5 and 6. The distributions of the unpaired electron density for both models of paramagnetic species are also shown (tables 7 and 8).

Table 3. Wiberg indices if the crucial bonds in the model of Q^2 cluster.

bond	molecule			radical		
	no - Ti	1 - Ti	2 - Ti	no - Ti	1 - Ti	2 - Ti
1-2	1.155	1.123	1.090	0.758	0.718	0.703
1-3	1.155	1.123	1.090	0.758	0.718	0.703
1-4	0.424	0.466	0.467	0.707	0.677	0.768
1-5	0.424	0.417	0.467	0.707	0.809	0.768
4-6	0.963	1.575	1.571	0.608	1.315	1.137
5-7	0.963	0.969	1.571	0.608	0.568	1.137
6-8	0.678	1.008	1.008	0.697	1.080	1.123
6-9	0.678	1.008	1.008	0.697	1.114	1.123
6-10	0.678	1.008	1.009	0.697	1.114	1.123
7-12	0.678	0.679	1.009	0.697	0.633	1.123
7-12	0.678	0.679	1.009	0.697	0.633	1.123
7-13	0.678	0.679	1.009	0.697	0.638	1.123

Table 4. The Wiberg indices of the crucial bonds for the Q^3 cluster models.

bond	molecule				radical			
	no - Ti	1 - Ti	2 - Ti	3 - Ti	no - Ti	1 - Ti	2 - Ti	3 - Ti
1-2	0.748	1.046	1.064	1.092	0.753	0.749	0.765	0.752
1-3	0.721	0.670	0.640	0.607	0.712	0.766	0.767	0.757
1-4	0.721	0.640	0.640	0.607	0.712	0.714	0.767	0.757
1-5	0.721	0.640	0.607	0.607	0.712	0.714	0.710	0.757
3-6	0.911	1.309	1.303	1.306	0.699	1.178	1.132	1.115
4-7	0.911	0.898	1.303	1.306	0.699	0.728	1.132	1.115
5-8	0.911	0.898	0.898	1.306	0.699	0.728	0.743	1.115
6-9	0.735	1.144	1.104	1.063	0.696	1.144	1.096	1.074
7-10	0.735	0.756	1.104	1.063	0.696	0.730	1.112	1.074
8-11	0.735	0.756	0.727	1.063	0.696	0.730	0.740	1.074
6-11	0.735	1.144	1.104	1.063	0.696	1.144	1.111	1.074
7-9	0.735	0.736	1.104	1.063	0.696	0.730	1.098	1.074
8-10	0.735	0.765	0.727	1.063	0.696	0.730	0.738	1.074
6-12	0.736	1.051	1.045	1.036	0.715	1.131	1.180	1.170
7-13	0.736	0.703	1.045	1.036	0.715	0.735	1.177	1.170
8-14	0.736	0.703	0.695	1.036	0.715	0.735	0.755	1.170

Table 5. The charges on the crucial atoms in the Q^2 model cluster.

atom	molecule			radical		
	no - Ti	1 - Ti	2 - Ti	no - Ti	1 - Ti	2 - Ti
Si ₁	+0.763	+0.834	+0.904	+0.994	+1.079	+1.203
O ₂	-0.602	-0.625	-0.626	-0.335	-0.321	-0.302
O ₃	-0.602	-0.625	-0.626	-0.335	-0.321	-0.302
O ₄	-0.520	-0.515	-0.518	-0.487	-0.491	-0.483
O ₅	-0.520	-0.523	-0.518	-0.487	-0.495	-0.483
Si ₆ /Ti ₆	+1.098*	+0.643**	+0.636**	+1.018*	+0.703**	+0.686**
Si ₇ /Ti ₇	+1.098*	+1.102*	+0.636**	+1.018*	+0.918*	+0.686**
O ₈	-0.531	-0.464	-0.538	-0.556	-0.478	-0.561
O ₉	-0.531	-0.535	-0.538	-0.556	-0.547	-0.561
O ₁₀	-0.606	-0.530	-0.490	-0.576	-0.539	-0.548
O ₁₁	-0.606	-0.605	-0.490	-0.576	-0.587	-0.548
O ₁₂	-0.606	-0.530	-0.490	-0.576	-0.539	-0.548
O ₁₃	-0.606	-0.605	-0.490	-0.576	-0.587	-0.548

* The competent atom is Si; ** The competent atom is Ti.

Table 6. The charges on the crucial atoms in Q³ model cluster.

atom	molecule				radical			
	no - Ti	1 - Ti	2 - Ti	3 - Ti	no - Ti	1 - Ti	2 - Ti	3 - Ti
Si ₁	+1.004	+1.011	+1.039	+1.070	+1.018	+1.088	+1.173	+1.239
O ₂	-0.473	-0.488	-0.504	-0.531	-0.256	-0.256	-0.262	-0.272
O ₃	-0.579	-0.535	-0.531	-0.529	-0.518	-0.512	-0.507	-0.505
O ₄	-0.579	-0.573	-0.531	-0.529	-0.518	-0.532	-0.507	-0.505
O ₅	-0.579	-0.573	-0.566	-0.529	-0.518	-0.532	-0.507	-0.505
Si ₆ /Ti ₆	+1.119*	+0.670**	+0.704**	+0.736**	+1.030*	+0.708**	+0.735**	+0.768**
Si ₇ /Ti ₇	+1.119*	+1.144*	+0.704**	+0.736**	+1.030*	+1.111*	+0.735**	+0.768**
Si ₈ /Ti ₈	+1.119*	+1.144*	+1.170*	+0.736**	+1.030*	+1.111*	+1.190*	+0.768**
O ₉	-0.542	-0.560	-0.480	-0.478	-0.544	-0.534	-0.463	-0.460
O ₁₀	-0.542	-0.560	-0.555	-0.478	-0.544	-0.534	-0.538	-0.460
O ₁₁	-0.542	-0.584	-0.555	-0.478	-0.544	-0.573	-0.538	-0.460
O ₁₂	-0.534	-0.461	-0.463	-0.463	-0.516	-0.441	-0.457	-0.451
O ₁₃	-0.534	-0.527	-0.497	-0.463	-0.516	-0.482	-0.466	-0.451
O ₁₄	-0.534	-0.527	-0.497	-0.463	-0.516	-0.482	-0.466	-0.451

* The competent atom is Si.

** The competent atom is Ti.

Table 7. The distribution of the spin density in the crucial atoms and absolute values of the spin densities in individual planes in the Q² model cluster.

atom	no - Ti	1 - Ti	2 - Ti
Si ₁	-0.151	-0.146	-0.126
O ₂	+0.934	+1.079	+1.136
O ₃	+0.934	+1.079	+1.136
O ₄	-0.244	-0.082	-0.125
O ₅	-0.244	-0.281	-0.125
Si ₆ /Ti ₆	+0.031*	+0.010**	-0.008**
Si ₇ /Ti ₇	-0.031*	-0.034*	+0.008**
O ₈	+0.043	+0.045	-0.011
O ₉	+0.043	-0.009	-0.011
O ₁₀	+0.043	-0.009	-0.011
O ₁₁	-0.043	-0.045	-0.011
O ₁₂	-0.043	-0.009	-0.011
O ₁₃	-0.043	-0.009	+0.011

plane	no - Ti	1 - Ti	2 - Ti
1	0.151	0.146	0.126
2-3	1.136	1.079	0.939
4-5	0.244	0.182	0.125
6-7	0.031	0.022	0.008
8-13	0.043	0.021	0.011
14-19	0.027	0.050	0.127
20-31	0.039	0.063	0.098

* The competent atom is Si.

** The competent atom is Ti.

Table 8. The distribution of the spin density in the crucial atoms and absolute values of the spin densities in individual planes in the Q³ model cluster.

atom	no - Ti	1 - Ti	2 - Ti	3 - Ti
Si ₁	-0.175	-0.140	-0.125	-0.123
O ₂	+1.307	+1.295	+1.280	+1.270
O ₃	-0.564	+0.055	+0.097	+0.057
O ₄	+0.564	+0.492	+0.097	-0.057
O ₅	+0.564	-0.492	-0.272	-0.057
Si ₆ /Ti ₆	+0.067*	-0.014**	-0.020**	+0.012**
Si ₇ /Ti ₇	-0.067*	-0.065*	-0.020**	-0.012**
Si ₈ /Ti ₈	-0.067*	+0.065*	-0.030*	+0.012**
O ₉	+0.510	-0.145	-0.010	-0.005
O ₁₀	-0.510	-0.145	+0.159	+0.005
O ₁₁	-0.510	+0.200	+0.010	-0.005
O ₁₂	-0.608	-0.250	+0.016	+0.078
O ₁₃	+0.608	+0.553	+0.016	+0.078
O ₁₄	-0.608	+0.553	+0.359	+0.078

plane	no - Ti	1 - Ti	2 - Ti	3 - Ti
2	0.175	0.140	0.125	0.123
1	1.307	1.295	1.280	1.270
3-5	0.564	0.346	0.155	0.057
6-8	0.067	0.048	0.023	0.012
9-14	0.559	0.308	0.097	0.042
15-17	0.073	0.034	0.021	0.011
18-26	0.505	0.482	0.440	0.384
27-35	0.054	0.065	0.085	0.098
36-50	0.434	0.468	0.510	0.530

* The competent atom is Si.

** The competent atom is Ti.

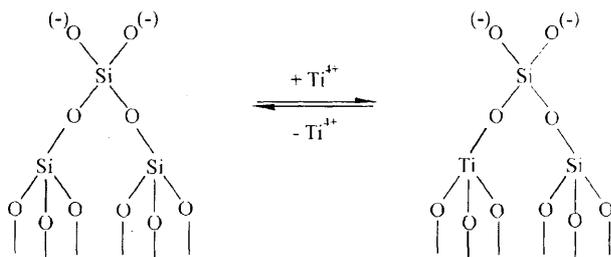
DISCUSSION

The deconvolution analysis of EPR spectra of γ -radiation induced paramagnetic species in the measured samples showed two types of various paramagnetic centres in all samples [14,16-19]:

1. HC_1 centre with orthorhombic EPR spectrum;
2. HC_2 centre with axially symmetric EPR spectrum.

These paramagnetic centres are generated as electron holes in lone pairs of non-bridging oxygens in tetrahedral SiO_4 units. These units are known as Q^i units, where i represent a number of bridging oxygens connecting the competent tetrahedron with its nearest neighbourhood tetrahedron. Considering symmetry requirements, the HC_1 radicals may be generated from Q^2 units, which have only two-fold symmetry axes. On the other hand the HC_2 radicals may be generated from Q^3 units with three-fold symmetry axes. By this assumption the experimentally obtained relative abundance of these two types of paramagnetic species in the PS_1 sample (sample without titanium) is in contradiction with the conclusion of Mysen and Frantz [34]. These authors, using the Raman spectroscopy, found $x(Q^4) = 0.340$, $x(Q^3) = 0.652$ and $x(Q^2) = 0.007$ for sodium trisilicate glass. The great differences between these values and the experimentally obtained ones ($x(CH_1) = 0.256$, $x(CH_2) = 0.744$) (see table 2 and figure 2) indicate the significant difference between the quantum yields of CH_1 and CH_2 generation. The different quantum yields of these two types of paramagnetic centres may be caused as a consequence of larger localisation of electron density on the Q^2 structural unit as opposed to the Q^3 unit. The results of quantum chemical calculations show that the total charge on the respective SiO_4 tetrahedron in Q^2 unit (table 5) is $Q_{SiO_4} = -1.481$, while the similar value for the Q^3 unit (table 6) is only $Q_{SiO_4} = -1.206$.

At low titania content (under the 1 mol.%) the structure of the glass remains practically unchanged with respect to Q^i units distribution. When titanium enters the structure of silicate glass the quantum yield of radiation generation is due to the great absorption cross-section of Ti^{4+} strongly enhanced in its vicinity. The strong increase of HC_1 centres compared to HC_2 centres (table 2, figure 2) indicates the preferable sensibilisation of Q^2 units at low titania contents. The results of MO calculations show that Si^{4+} in the neighbourhood of the Q^2 unit is the weakest bonded. The largest probability of substitution of Si^{4+} for Ti^{4+} is just in the vicinity of the Q^2 unit.



The sum of the Wiberg indices which characterise the competent bonds of the mentioned Si^{4+} , are after substitution for Ti^{4+} , changed from the value $W = 3.032$ to the value $W = 4.601$. The resulting effect of the bond strengthening for Q^3 unit is only from the value $W = 3.364$ into $W = 4.641$. These results show that the effect of the bond strengthening in the Q^3 units is smaller than the similar effect in the Q^2 units. Therefore it may be supposed the preferential substitution of Si^{4+} for Ti^{4+} in the vicinity of the non-bridging oxygens in the Q^2 units in comparison with Q^3 units.

For the greater content of TiO_2 the structural changes induced by titania in silicate network overwhelm the above discussed effect. In the case of high content of titania, it leads to the substitution of TiO_2 for the Na_2O , what means that it has the role of the network-modifier. On the other hand, TiO_2 also shows the partially network-forming activity. Therefore in the glasses with great TiO_2 content (say more than 5 mol.%) there are only axially symmetric CH_2 centres present.

As indicated, the probability of Ti^{4+} location in the neighbourhood of the particular Q^i units is the largest. However the details of the chemical bonds may significantly influence the electron structure of the resulting paramagnetic centres. The values of the main component of the g -tensor are very sensitive on such redistribution of electron density. It may be seen that addition of titania to the glass brings about to the great changes of the values of the main component of the g -tensor (figures 2 and 3). In both cases we can see the extraordinary irregularities in the region of low titania content (near the value of 1 mol.%). These irregularities are manifested with the expressive local minima of the $g_{||}$ and g_{\perp} in the case of HC_1 and HC_2 centres, respectively. The molecular orbital calculation of Ti^{4+} substituted models show the considerable changes of the unpaired electron density of the cluster. After the substitution of Si^{4+} for Ti^{4+} in the closed vicinity of Q^2 or Q^3 units comes considerable delocalisation of the spin density in the given cluster. In the tables 7 and 8 are the spin densities on the individual atoms of the central SiO_4 unit as well as its absolute values for the various planes of the cluster. From this table it can be seen, that Ti^{4+} acts as a spin density transmitter for the large space volume. This effect is the consequence of inclusion of 3d atomic orbitals to the chemical bonds. The mentioned effect causes the significant changes of the main component of the g -tensor after substitution of Si^{4+} for Ti^{4+} .

CONCLUSIONS

The qualitative quantum chemical model calculations were used for the explanation of the changes of the EPR spectra of the titania bearing sodium silicate glasses with various contents of titania. The reasonable compromise between the model used (the greatness of the cluster

used) and the exactness of method of calculation was chosen.

The results of the molecular orbital calculations show that the preferential sensibilisation of the Q^2 unit is a consequence of the largest local electron density in the region of SiO_4 tetrahedron with non-bonding oxygens in the Q^2 cluster in comparison with the Q^3 cluster. Therefore the quantum yield of the HC_2 paramagnetic centres generation is significantly greater in comparison with quantum yield of the HC_1 centres generation.

The estimation of the bond strengths of individual Si-O bonds (using the Wiberg indices) leads to the preferential substitution of Si^{4+} for Ti^{4+} in the nearest neighbourhood of the non-bridging oxygens.

The changes of the spin density distribution around the cluster (greater delocalisation) after substitution of Si^{4+} for Ti^{4+} explain the unusual behaviour of the main component of the g -tensor with content of titania in samples. This effect is caused by the inclusion of 3d atomic orbitals of titanium into the chemical bonds.

It must be said that obtained results have only a qualitative character. For more exact conclusions it will be necessary to provide the direct quantum chemical calculations of the g -tensor components for various models of local environment of the pertinent Q^1 unit. This will be a part of our future work.

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KVALITATÍVNA MO ŠTÚDIA γ -INDUKOVANÝCH PARAMAGNETICKÝCH CENTIER V SODNO KREMIČITANOVÝCH SKLÁCH OBSAHUJÚCICH OXID TITANIČITÝ

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Na základe modelových kvantovochemických výpočtov sa kvalitatívne interpretovala neobvyklá závislosť EPR spektier γ -žiarením ožiarených sodno kremičitých skiel obsahujúcich titán. Ako model príslušných paramagnetických častíc sa použili klastre, ktoré sú vyváženým kompromisom medzi exaktnosťou výpočtu a veľkosťou použitého klastra. Výsledky MO výpočtov ukázali na preferenčnú senzibilizáciu Q^2 jednotiek v porovnaní s Q^3 jednotkami (vyššia elektrónová hustota v susedstve neväzbových kyslíkov v Q^2 jednotke). Väzbová sila Si-O väzieb v susedstve neväzbových kyslíkov ukazuje na preferenčnú substitúciu Si^{4+} za Ti^{4+} v blízkosti hranice klastra. Zmeny distribúcie spinovej hustoty v objeme klastra po substitúcii Si^{4+} za Ti^{4+} (vyššia delokalizácia) vysvetľujú neobvyklé chovanie sa zložiek g -tenzora v sklách obsahujúcich titán.