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Stabilisation of metal ions in unusual oxidation states and electron dynamics in oxide glasses

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Abstract. The results of studies on the stabilisation of metal ions in unusual oxidation states in oxide glasses are surveyed. Attention is concentrated on the relation between the stabilisation of these ions and redistribution of the electron density, and on the disproportionation reactions accompanying it. The effect of reversible low-temperature disproportionation on niobium, titanium, vanadium, molybdenum, tungsten, and other ions is considered. The formation of metal clusters in oxide glasses is shown also to be associated with disproportionation. The bibliography includes 108 references.

I. Introduction

Current developmental chemistry is addressing the problems of producing new compounds and materials possessing valuable practical properties.

Metal ions in unusual oxidation states (UOS) arise in intermediate stages of redox processes including radiation-induced, catalytic, biochemical, mechanochemical, and other processes. Ions of this type have short lifetimes, and their steady-state concentrations are low. The fact that these ions are formed and their role in physicochemical processes have long remained obscure and their existence has been supported only by indirect data. Therefore, the physicochemical properties of these species could be inferred only from theoretical considerations. The appearance of matrix isolation methods in combination with various spectroscopic methods and techniques for the investigation of fast chemical processes have made it possible to begin an investigation of the properties of ions of various elements in UOS.

By the early 70s, studies devoted to the preparation of compounds containing metal ions in UOS in liquid or glassy aqueous media were published.[1,2] The UOS of metals were generated by radiation. Glassy media have been studied at 77 K by stationary methods, namely, EPR and optical spectroscopy.[3–6] The aqueous solutions at room temperature have been studied by pulse radiolysis using fast optical recording.[7,8] The information obtained made it possible to identify the regular variation of the physicochemical properties of metal ions in UOS as a function of their position in the Periodic Table and to embark upon solving the problem of their long-term stabilisation in inorganic glasses at 300 K.

It turned out that the solution of this problem is primarily associated with the elucidation of the role of the ligand environment of the metal ion, namely, the influence of the nature of ligands on the distribution of the electron density in the atomic orbital (AO) containing the electron that imparts to the ion the properties typical of ions in UOS. In the second place, solution of this problem is associated with the study of the physical properties of the solid glassy matrix itself, which contains modifying ions passing into UOS under various physical influences. Despite the great structural diversity of inorganic glasses, the problem actually reduces to the solution of a single fundamental problem, namely, to the study of localisation and delocalisation of electrons in the outer orbitals of atoms or ions as a function of the structure and properties of the solid matrix. Our review is devoted to this problem in relation to low-temperature glasses and inorganic oxide glasses (silicate, germanate, borate, and phosphate).

II. Ions in unusual oxidation states in oxide glasses

1. Frozen (glassy) solutions

In the late 1970s and the early 1980s, a series of studies was carried out at the Institute of Physical Chemistry of the RAS dealing with UOS of Period 4–6 metals obtained by low-temperature radiolysis in aqueous solutions of acids ($HClO_4$, HCl, H_2SO_4) or bases (NaOH, KOH) containing salts of these metals.[3–6,9–14] The choice of metals was determined by the fact that ions with the electron configuration $d^{10}s^1$, i.e. ions existing in a $^2S_{1/2}$ electronic state, are conveniently studied by the highly sensitive EPR method. These ions contain an unpaired electron in the outer *ns*-AO and arise upon single-electron reduction or oxidation of the central metal atom of an aqua, chloride, or other complex induced by γ-irradiation of frozen glassy solutions. The ions in UOS can be stabilised in glassy matrices at 77 K for an infinitely long period.

It has been shown[3–6,9–14] that the reactions of the initial ions with thermalised electrons (e_t^-) and $HO^\bullet$ radicals in low-temperature glasses make it possible to obtain Zn^{1+}, Cd^{1+}, Hg^{1+}, Ga^{2+}, In^{2+}, Tl^{2+}, Ge^{3+}, Sn^{3+}, Pb^{3+}, Sb^{4+}, and Bi^{4+} ions in the $^2S_{1/2}$ electronic state as well as Sn^{1+} and Pb^{1+} ions, which contain an unpaired electron in the outer *p*-orbital. The ions in a $^2S_{1/2}$ electronic state were shown to arise in the competing reactions of e_t^- with metal ions or with the hydroxonium ion. The Sn^{1+} and Pb^{1+} ions are also formed via the reduction of Sn^{2+} and Pb^{2+}

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with thermalised electrons. The relative rate constants for the reactions of e_t^- with Group IB–VB metal ions were determined.

$$H_3O^+ + e_t^- \longrightarrow H_2O + H^*, \quad (1)$$

$$M^{(Z+1)+} + e_t^- \longrightarrow M^{Z+}. \quad (2)$$

For the ions in a $^2S_{1/2}$ electronic state and for the Sn^{1+} and Pb^{1+} ions, g-factors, constants A_i of the isotropic hyperfine coupling (HFC), optical absorption bands, and the extinction coefficients were determined from EPR data and optical spectroscopy at 77 K (Table 1).

To study metal ions in a $^2S_{1/2}$ electronic state by EPR, it is important to know the isotropic HFC constants for these species in the free state, $A_i^{(o)}$. Ershov and Aleksandrov [15] have suggested a semiempirical method for the calculation of the $A_i^{(o)}$ HFC constants for series of isoelectronic ions of Periods 4–6 of the Periodic Table existing in the $^2S_{1/2}$ electronic state. Comparison of these $A_i^{(o)}$ values obtained with the HFC constants A_i of these ions in a real medium permits determination of the character of their interaction with ligands. In fact, for a 'free' ion, $A_i^{(o)} = |\Psi_{ns}(0)|^2$, where $|\Psi_{ns}(0)|^2$ is the electron density at the nucleus caused by the electron in the outer ns-AO, while for the M^{Z+} ion in a real medium, $A_i \sim \Psi_{ns}$, where Ψ_{ns} is the electron density in the presence of a certain ligand environment. Thus, the $A_i/A_i^{(o)}$ ratio is the electron occupancy of the outer ns-AO that forms the chemical bond with the ligands of the complex.

It has been shown that the density of the unpaired electron at IIB–IVB Group metal ions, existing in the $^2S_{1/2}$ electronic state, in aqua and chloride complexes decreases with an increase in the charge of the metal ion within the same period.[9, 12, 14]

In a study of optical characteristics of these ions, it has been found that the energy of optical transitions at the maxima of absorption bands ($E_{\lambda_{max}}$) for the aqua complexes of IIB–IVB Group metal ions existing in UOS and in the $^2S_{1/2}$ electronic state increases regularly with an increase in the charge of the metal ion within the same period, while for the chloride complexes, this energy decreases. Semiempirical calculations of the energies of the a_{1g}^* and t_{1u}^* molecular orbitals for aqua complexes have shown that experimental $E_{\lambda_{max}}$ values are in agreement with $\Delta E = E(t_{1u}^*) - E(a_{1g}^*)$; this confirms the fact that the optical absorption bands are due to the $a_{1g}^* \longrightarrow t_{1u}^*$ transition.

It has been shown that in the case of chloride complexes, optical absorption bands are due to the $1t_{1u} \longrightarrow a_{1g}^*$, $2t_{1u} \longrightarrow a_{1g}^*$, and $3t_{1u} \longrightarrow a_{1g}^*$ electron transitions. The energies of these transitions decrease with increase in the charge on the central metal ion in isoelectronic series.[12] The antiparallel courses of the variation of the energies of optical transitions in aqua and chloride complexes of metal ions in an isoelectronic series are accounted for by the crucial role of the ligand environment. Unlike the optical transition in aqua complexes, which is caused by the transfer of an electron from the central ion to the ligands (H_2O molecules), the optical transition in the chloride complexes

Table 1. Spectroscopic parameters of metal ions in unusual oxidation states in aqueous solutions of their salts at 77 K (low-temperature glasses).

Ion in UOS (J)[a]	Solution	g-factor of the ion in UOS	$A_i/A_i^{(o)}$	λ_{max}/ nm	ε/ 10^3 dm^6 mol^{-1} cm^{-1}	Ion in UOS (J)[a]	Solution	g-factor of the ion in UOS	$A_i/A_i^{(o)}$	λ_{max}/ nm	ε/ 10^3 dm^6 mol^{-1} cm^{-1}
Zn^{1+} ($\frac{5}{2}$)	8 M HCl	1.997		230	7.0	Hg^{1+} ($\frac{1}{2}$)	5 M H_2SO_4	1.986	0.750		
	6 M $HClO_4$			290	6.5		5 M D_2SO_4	1.996			
Ga^{2+} ($\frac{3}{2}$)	9–10 M HCl	2.001	0.391	260			5 M H_3PO_4	1.979	0.765		
	7 M $HClO_4$	2.001	0.562	245	9.2			(1.987)[b]			
Ge^{3+} ($\frac{9}{2}$)	8–10 M HCl	2.003		270	5.0						
						Tl^{2+} ($\frac{1}{2}$)	8 M HCl	2.002	0.398	210	
Cd^{1+} ($\frac{1}{2}$)	6–10 M HCl	1.987	0.697	220	9.0					280	
				300	6.0		7 M $HClO_4$	2.002	0.594	225	13.6
	6 M $HClO_4$	1.989	0.633	270	13.6			2.002	0.477		
	5 M H_2SO_4	1.989	0.650								
	5 M D_2SO_4	1.997	0.617			Pb^{3+} ($\frac{1}{2}$)	6–10 M HCl	2.005	0.359	220	
	5 M H_3PO_4	1.980	0.650							300	13.0
		(1.986)[b]	(0.622)[b]							430	9.0
In^{2+} ($\frac{9}{2}$)	6–10 M HCl			245			5–8.5 M $HClO_4$	1.999	0.533	200	
				310			10 M NaOH	1.991 ($g_\perp$),	0.274		
	6 M $HClO_4$			235	14.3			2.004 ($g_\parallel$)			
Sn^{3+} ($\frac{1}{2}$)	6–10 M HCl	2.005	0.413	275		Sn^{1+} (see[c])	6–10 M HCl	1.993 (g_{aver})			
				360			5–8 M $HClO_4$	1.824 (g_1),		210	
	5–8 M $HClO_4$	1.995	0.428	215				2.196 (g_3)			
	5 M H_2SO_4	1.996	0.516				5 M H_2SO_4	1.812 (g_1),			
	10 M NaOH	1.989 ($g_\perp$),	0.267	310				2.174 (g_3)			
		2.001 ($g_\parallel$)					10 M NaOH	1.989 (g_{aver})			
Hg^{1+} ($\frac{1}{2}$)	6–10 M HCl	1.981	0.660	200		Pb^{1+}	6 M $HClO_4$			300	
				270	12.0		6–10 M NaOH			275	2.3
	6 M $HClO_4$	1.982	0.785	240	17.6					360	1.8
		(1.991)[b]	(0.840)[b]								

[a] The nuclear spin for the odd isotope of an ion in a $^2S_{1/2}$ electronic state is given in parentheses. [b] The g-factor of the ion at another stabilisation site. [c] For Sn^{1+} ion, $g_{aver} = (g_1 + g_2 + g_3)/3$ or those values of g-factors that could be determined in the experiment, for example, g_1 and g_3, are given.

is due to the electron transfer from the ligand (Cl^- ion) to the central ion.

A regular variation of the $E^0[M^{(Z+1)+}/M^{Z+}]$ redox potentials as a function of the charge on the cation existing in an unusual oxidation state has been found:[14, 16] the $E^0[M^{(Z+1)+}/M^{Z+}]$ values increase as the charge on the cation increases within one Period, whereas within one Group, i.e. for ions having the same charge, they increase with increase in the number of the Period. The theoretical grounds for these regularities have been reported.[17]

The above results reflect a fundamental feature of metals (in particular, of metals in UOS having the $d^{10}s^1$ electron configuration), namely, that their physicochemical properties vary monotonically with the atomic number.

These conclusions refer also to the ions in UOS arising at room temperature. At 300 K in aqueous solutions, these species disappear over periods of $10^{-6}-10^{-4}$ s, the time for their destruction being determined by the diffusion mobility. Their properties can be conveniently studied by pulse radiolysis with fast optical recording,[18-22] which makes it possible to determine the positions of optical absorption bands and the extinction coefficients and to measure the rate constants for the reactions of these ions with short-lived species such as hydrated electron (e^-), the $CO_2^{\bullet-}$ radical anion, the $HO^\bullet$ radical, and the $O^{\bullet-}$ radical anion in aqueous solutions. Based on the characteristics of the optical spectra recorded in the initial stages of chemical transformations over various time intervals (up to 10^{-4} s), the formation of monosubstituted hydroxo- and chloride complexes of IB–IVB Group metals in UOS and in a $^2S_{1/2}$ electronic state was established, and the instability constants for these complexes were determined; these constants were found to vary monotonically in the series of isoelectronic ions in UOS as a function of the position of the metal in the Periodic Table.

When low-temperature glasses are defrosted, the ions in UOS disappear irreversibly due to the intensification of the diffusion of cations and anions in the matrix. This is why the authors cited above did not answer the question of how hydrogen-like ions with the $d^{10}s^1$ electron configuration form stable chemical compounds. However, the results of studies on the influence of the ligand environment on the properties of metal ions in UOS suggest the possibility of preparing solid glasses in which metal ions in UOS will be stable over periods of time from microseconds to months and even longer. The physicochemical parameters of these glasses should vary as functions of the properties of the stabilised ion.

2. Stabilisation of metals in unusual oxidation states in oxide glasses

As noted above, ions in UOS can exist over extended periods in low-temperature glasses at 77 K. However, it is obvious that these frozen aqueous solutions containing ions in UOS are of no practical interest, since the unusual properties imparted to them by metals in UOS disappear irreversibly when the temperature is slightly raised. Therefore, the logical pathway to the development of new materials with new unusual properties caused by the presence of ions in UOS is the preparation of solid-state materials based on 'true' molten glasses, which are capable of stabilising these species in their matrices.

In fact, the absence of symmetry in their structure and their isotropic properties make glasses identical to liquids, whereas the elasticity of shape makes glasses similar to solids. A glass is considered to be a true solution in which a relationship exists between the composition, the structure, and the properties. At present, articles of glass and glassy materials are used in virtually all branches of industry.[23] Therefore, to confer on these objects new properties specified beforehand is a significant and urgent problem.

In recent years, investigations of glassy media have been vigorously pursued, although the background for these studies was laid long ago by D I Mendeleev,[24] who suggested the polymeric concept of the structure of glass, and by Lebedev and Zakhariasen,[25, 26] who developed the ideas of microheterogeneity and network structure of glass. Even now these works stimulate studies aimed at controlling the properties of glasses both by varying the structure of glass with a particular elemental composition[27] and by introducing ions to modify its properties.[28] The modifying ions can alter the properties of a glass both during its synthesis (glass melting) and when a finished (solid) glass is exposed to a certain influence (heat, light, radiation).[29, 30] Oxide glasses have found the widest practical application.

Oxide glasses can be divided conventionally into four main classes (according to the main glass-forming compound), namely, borate, silicate, germanate, and phosphate glasses. These groups of glasses differ in microstructure and, consequently, their physicochemical properties are also dissimilar. The introduction of modifying ions into these glasses extends considerably the range of existing properties.[31] Stabilisation of these ions in a glass matrix is associated with redistribution of the electron density of the ligands surrounding the ions and with local variations of the glass structure.

Since the 1970s, studies have been carried out dealing with chemically active species generated by various kinds of treatment and stabilised in glassy matrices as colour centres (CC), paramagnetic centres (PMC), and luminescence centres.[27-31] The physicochemical properties of these centres have been studied by stationary and pulse methods.[27-31] However, all the information obtained at that time referred to the matrix centres of the main classes of glasses. The studies were concerned with the optical and kinetic properties of these centres, i.e., they reduced to utilitarian investigation of the radiation sensitivity of glasses by a trial-and-error method. This approach did not conform completely to the modern state of development of the physical chemistry of the glassy state. Therefore, systematic studies are needed that would take into account the properties of elements incorporated in glasses, depending on their position in the Periodic Table.

Apparently, glasses capable of stabilising the modifying ions as well as ions in UOS should contain a wide range of valence states of atoms and ions, which would permit the glassy system to reach an equilibrium after the introduction of ions in metastable states. Borate, silicate, germanate, and phosphate glasses have been studied.[32-47] Particular attention was focused on three-component alkali glasses: lithium, sodium, and potassium borate, germanate, phosphate, and silicate glasses as well as on the barium aluminophosphate glasses (BAPG). The content of metal oxide in these glasses varied from 3 to 30 mol %. Other glass-forming systems have also been studied; they are mentioned below.

As a rule, after irradiation at 77 and at 300 K, the systems under study containing admixtures of metal oxides exhibited EPR signals and optical absorption bands (AB) differing from those typical of the known electron and hole sites in borate, silicate, and germanate glasses and also from those exhibited by PO_4^{2-} and PO_3^{2-} radical anions in the phosphate glasses.[32-43] The intensity of these additional EPR signals and of the absorption bands depends on the amount of the oxide introduced, on the ratio of all the glass components, and on the method used for the synthesis of the glass.

For glasses containing cadmium, mercury, gallium, thallium, and lead oxides, it has been found that the increase in the intensity of the additional EPR signals in the magnetic field region corresponding to the g-factor for the free electron (g_e) is accompanied by an increase in the intensity of the high-field (450–700 mT) EPR signals. The latter signals are due to the hyperfine coupling of the electron spins in the outer ns-AO with the $J \neq 0$ nuclear spins of the odd isotopes of the metals added.[36] The ratio of the normalised surface of the high-field signals to the surface of the signals in the g_e region corresponds to the ratio of the percentage of metal isotopes with $J = \frac{1}{2}$ or $\frac{3}{2}$ to the percentage of isotopes with $J = 0$. This indicates that the additional EPR signals in question are associated with the metals introduced and proves unambiguously that these signals refer to UOS of metals in

the $^2S_{1/2}$ electronic state, namely, Cd^{1+}, Hg^{1+}, Ga^{2+}, Tl^{2+}, Sn^{3+}, and Pb^{3+}. The spectral parameters for these species are listed in Table 2.

In the case of glasses containing zinc, antimony, and germanium oxides (for odd isotopes of these metals, $J = \frac{5}{2}$, $\frac{7}{2}$ and $\frac{9}{2}$, respectively), additional signals typical of Zn^{1+}, Ge^{3+}, and Sb^{4+}, have also been detected in the EPR spectra after γ-irradiation. The parameters of these signals are also presented in Table 2. All the above metals in UOS in a phosphate matrix exhibit symmetrical EPR lines, the difference between the widths of the high-field and low-field signals being smaller than that in the case of borate, germanate, and silicate glasses.[37,38] This suggests that in phosphate glasses the ligand environment of the metal ions in UOS is more symmetrical than in other glasses.

Studies [32–36] of the optical characteristics of glasses irradiated at 77 and 300 K have shown that, in addition to the well known AB corresponding to the 'matrix' colour centres, additional AB are observed due to the introduction of various metal oxides. For example, it has been shown that on γ-irradiation of sodium borate glasses, the intensity of the absorption bands that appear after the introduction of metal oxides increases in parallel with the concentration of the oxides, whereas the intensities of the absorption bands with $\lambda = 350$ and 500 nm associated with BO_4^{4-} decrease correspondingly, until these bands disappear completely.[33] The spectra of borate glasses containing Zn, Cd, Ga, and Pb oxides and irradiated at 300 K, apart from the AB caused by BO_4^{4-}, contain broad absorption bands possessing a

Table 2. Characteristics of ions in unusual oxidation states in the glasses: 20% of $Li_2O(Na_2O, K_2O)$ – 70% of $B_2O_3(GeO_2, SiO_2, P_2O_5)$ – 10% of M_xO_y (M_xO_y — metal oxide).

Ion in UOS (J)[a]	Glass[b]	g-factor	$A_i/A_i^{(o)}$	λ_{max}/ nm	Ion in UOS (J)[a]	Glass[b]	g-factor	$A_i/A_i^{(o)}$	λ_{max}/ nm
Zn^{1+}	LBG	1.998	0.66		Sb^{4+}	LPG		0.028	
($\frac{5}{2}$)	SBG	1.998		310, 550	($\frac{7}{2}$)	SPG		0.023	
	SSG	1.988		320		PPG		0.038	
	BAPG			510		BAPG		0.025	
Ga^{2+}	LBG		0.36		Hg^{1+}	LBG	2.00	0.79	
($\frac{3}{2}$)	SBG		0.50	380, 470	($\frac{1}{2}$)	SBG	1.998	0.92	
	KBG					SGG			350
	SSG		0.22			BAPG		0.83	505
	LSG		0.29	256	Tl^{2+}	LBG	2.00	0.650	
	LPG		0.55	500	($\frac{1}{2}$)	SBG		0.653	420, 500
Ge^{3+}	LBG	1.996	0.31	300					640, 740
($\frac{9}{2}$)	SBG	1.997	0.33	300		PBG		0.60	
				(310)		LGG		0.52	
	LSG	1.996	0.78	275		SGG		0.54	413
	LPG		0.75	290		PGG		0.536	
Cd^{1+}	LBG	1.999	0.81			LSG		0.26	357, 610,
($\frac{1}{2}$)	SBG	1.998	0.86	330, 440					714
				(375, 480)		SSG		0.29	357, 633,
	PBG	1.996	0.88						730
	LGG	2.01	0.839			PSG		0.41	
	SGG	2.01	0.835	400		SPG		0.50	
	PGG	2.01	0.830			BAPG		0.56	340, 625,
	LSG	1.995	0.68						750, 1100
	SSG	1.993	0.59						
	PSG	1.989	0.54		Pb^{3+}	LBG	1.995	0.46	
	LPG		0.86	320, 420	($\frac{1}{2}$)	SBG		0.47	325, 500
	SPG		0.76						(340, 530)
	BAPG		0.80	520		PBG		0.44	
Sn^{3+}	LBG	1.995	0.56			LGG	1.996	0.36	
($\frac{1}{2}$)	PBG	1.989	0.58			SGG	1.992	0.41	465
	LGG	1.993	0.36			PGS	1.992	0.39	
	SGG	1.992	0.39			LSG	1.985	0.37	
	PGG	1.992	0.38			SSG	1.988	0.39	330, 440
	LSG	1.989		290		PSG	1.993	0.41	
Sb^{4+}	SBG		0.029	460, 500		LPG		0.49	330, 410,
($\frac{7}{2}$)				(380, 520)					730
	SGG	1.950	0.053	380		SPG		0.46	
	SSG	2.050		290		PPG		0.50	750, 900
						BAPG		0.41	760, 900

[a] The value of the nuclear spin of the odd isotope is given in parentheses. [b] Notation: LBG, SBG, and PBG — lithium, sodium, and potassium borate glasses, respectively; LSG, SSG, and PSG — lithium, sodium, and potassium silicate glasses; LGG, SGG, and PGG — lithium, sodium, and potassium germanate glasses; LPG, SPG, and PPG — lithium, sodium and potassium phosphate glasses; BAPG — barium aluminophosphate glasses.

low-intensity 'satellite' peak. These AB can be assigned to the Zn^{1+}, Cd^{1+}, Ga^{2+}, and Pb^{3+} ions as follows:

Ion	Zn^{1+}	Cd^{1+}	Ga^{2+}	Pb^{3+}
λ_{max} / nm	310	330	380	325
	550	440	470	500

The presence of the 'satellite' line indicates that the energy levels responsible for the optical transition are split due to the asymmetrical environment of the ions in sodium borate glasses. This is consistent with the EPR spectroscopic data, namely, with the anisotropy observed for the g-factor of the EPR signals corresponding to the ions in UOS in the region $g_e = 2.0023$.

The absorption spectra recorded at 77 K for ions in UOS in sodium borate glasses irradiated at 77 K are shifted to the long-wavelength region with respect to the spectra recorded at 300 K. For example, the following AB are observed for the Cd^{1+}, Pd^{3+}, Ge^{3+}, and Sb^{4+} ions at 77 K:

Ion	Cd^{1+}	Pb^{3+}	Ge^{3+}	Sb^{4+}
λ_{max}/ nm	375	340	310	380
	480	530	–	520

The EPR spectra exhibit additional signals due to these ions, the signals corresponding to BO_4^{4-} being virtually absent.[33, 34]

The absorption spectra of sodium borate glasses containing thallium oxide, measured after γ-irradiation at 300 K, exhibit AB with maxima at 420, 500, 640, and 740 nm. The intensity of the AB with a maximum at 420 nm varies in parallel with that of the 20 mT-wide EPR signal observed in the region of 580 mT and corresponding to Tl^{2+} ions.[33, 34] In addition, this is the only band that undergoes temperature displacement (at 77 K, the maximum absorption is observed at 430 nm); therefore it is assigned to the Tl^{2+} ion.

Of special note is the observation[36] that, in the $Tl_2O-Na_2O-SiO_2$ ($Tl_2O-Na_2O-B_2O_3-SiO_2$) and $PbO-Na_2O-SiO_2$ ($PbO-Na_2O-B_2O_3-SiO_2$) systems, there is no correlation between the increase in the intensity of some additional AB and the increase in the intensity of the EPR signals corresponding to Tl^{2+} and Pb^{3+} ions. This may be due to the fact that during the synthesis of these glasses under specific redox conditions, metallic clusters of the Pb_m^{n+} and Tl_m^{n+} type (where n, m = 1, 2, 3 ...) are formed. These clusters capture the electrons knocked out by γ-irradiation and thus give additional AB. Clusters of this type are also formed during the post-radiation annealing of glasses, when the following processes occur: $Tl^{1+} + Tl^{2+} \longrightarrow Tl_2^{3+}$; $Tl_2^{3+} + Tl^0 \longrightarrow Tl_3^{3+}$, etc. In place of thallium ions, these reactions can involve cadmium, lead, bismuth, and other ions. The cluster formation is induced by metal ions in UOS.

In the case of other kinds of glasses, it has also been found that the additional AB arise in parallel with the EPR signals corresponding to the UOS of metals. One intense bell-shaped AB is typical of glasses containing zinc, gallium, germanium, indium, tin, and antimony oxides, whereas in the case of glasses with cadmium, mercury, thallium, lead, and bismuth oxides, two or more optical absorption bands are recorded. The parameters of these bands are presented in Table 2.

It should be noted that for identical matrices with equal contents of oxides of Group IB–VB metals, the energy of the optical transitions $E_{\lambda_{max}}$ (the energy of the optical transition at the maximum λ_{max} of the optical absorption band corresponding to the metal in UOS was taken as $E_{\lambda_{max}}$) and the electron density in the ns-AO (which is characterised by the $A_i/A_i^{(o)}$ ratio) in the isoelectronic series $Cd^{1+}-In^{2+}-Sn^{3+}-Sb^{4+}$ and $Hg^{1+}-Tl^{2+}-Pb^{3+}-Bi^{4+}$ have been found to decrease with an increase in the formal oxidation number Z. An exception is provided by the $Zn^{1+}-Ga^{2+}-Ge^{3+}$ series, for which the reverse correlation has been established in lithium, sodium, and potassium phosphate glasses, i.e. the $E_{\lambda_{max}}$ and $A_i/A_i^{(o)}$ values increase with an increase in

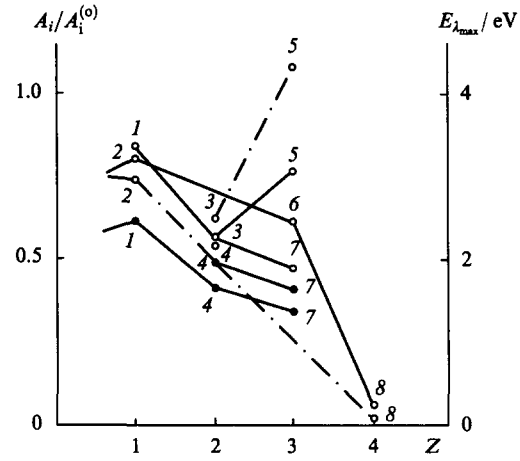


Figure 1. Dependence of the electron density in ns-AO (light circles) and of the energies of optical transitions at λ_{max} (dark circles) on Z for ions in UOS in barium aluminophosphate glasses (continuous line) and in lithium phosphate glasses (dot-and-dash line). (*1*) Hg^{1+}, (*2*) Cd^{1+}, (*3*) Ga^{2+}, (*4*) Tl^{2+}, (*5*) Ge^{3+}, (*6*) Sn^{3+}, (*7*) Pb^{3+}, (*8*) Sb^{4+}.

Z (Fig. 1). These results indicate both that the physicochemical properties of metals in UOS vary regularly as a function of their positions in the Periodic Table and that there is a possibility of controlling the course of the above dependences by changing the glass matrix, for example, by replacing one glass-forming oxide by another (SiO_2 by P_2O_5).[32–36]

The spectral characteristics of metal ions in UOS also depend on the alkali metal cation incorporated in the glass. In other words, for glasses of the same class with equal percentages of oxides, the parameters of metal ions in UOS change when the alkali metal oxide present is replaced by another one. It is seen from Table 2 that the $A_i/A_i^{(o)}$ ratios and other parameters for the same ions in UOS incorporated in glasses, containing equal proportions of oxides but different cations (Li^+, Na^+, K^+), are distinct. However, there is no general well-defined rule for the variation of the properties of metals in UOS in the series of alkali metal cations (Li^+, Na^+, and K^+).

When the temperature of the irradiation changes from 77 to 300 K, the absorption bands corresponding to metal ions in UOS in all matrices undergo a hypsochromic shift, the magnitude of which depends on the alkali metal cation introduced into the glass. It has been found that the more stable the metal ion in UOS, the greater this shift. Thus, the framework of alkali metal cations participates in the stabilisation of UOS. It can be suggested that the alkali metal cations participate in the rearrangement of the ligand environment of the metal during stabilisation of its UOS. This conclusion has also been confirmed by EPR data. The magnitude of the shift of the high-field component of the EPR spectrum, occurring when the irradiation temperature changes from 77 to 300 K, depends on the nature of the alkali metal cation. The nature of the alkali metal cation also influences the magnitude of the g-factor and the width of lines in high and low fields (the corresponding g_e).

It has been noted [32–38] that by choosing appropriately the composition of glasses, one can achieve stabilisation of metal ions in UOS at 300 K for a period of a month or even longer; in other words, stable compounds of metals in UOS can be obtained in glasses. By varying the elemental composition of a glass or by creating particular redox conditions during its synthesis, one can enhance or reduce the ability of the glass to stabilise or destabilise UOS of metals, colour centres (CC), and paramagnetic centres (PMC).

The kinetic curves for the thermal annealing of ions in UOS have a stepped shape for all types of glasses and are linearised in the coordinates n/n_0 against $\lg(t/t_0)$ at a fixed temperature [here n and n_0 are the concentrations of ions in UOS at current (t) and

initial (t_0) instants of time, respectively]. The kinetic curves for photoannealing can also be linearised in the coordinates n/n_0 against $\lg(t/t_0)$ and depend both on the intensity and on the spectral composition of the incident light.[37, 38] The above characteristic features imply that there is a discrete set of activation energy values for these processes and that there exist sites for the stabilisation of metals in UOS, which are nonequivalent in their energy and structural parameters.

For glasses of the same composition synthesised under identical conditions but containing various metal oxides, the rates of the thermal annealing or photoannealing of PMC and CC (carried out at the same temperature or with light of the same spectral composition) are different. This refers both to the matrix PMC and CC (PO_4^{2-}, PO_3^{2-}, BO_4^{4-}, >SiO', >GeO', SiO_3^{2-}) and to metals in UOS in all the glasses considered above. If we assume that the rate (the efficiency) of the photodestruction of metals in UOS is proportional to the tangent of the slope ξ of the curve describing the kinetics of the destruction in the coordinates mentioned above, then the following rule is fulfilled: in the isoelectronic series of ions $Cd^{1+}-Sn^{3+}-Sb^{4+}$ and $Hg^{1+}-Tl^{2+}-Pb^{3+}-Bi^{4+}$, the efficiency of the thermo- (ξ_t) and photo- (ξ_{ph}) destruction decreases as the oxidation number of ions increases (Figs 2 and 3). In the case of the $Zn^{1+}-Ga^{2+}$ series of ions, the order of this correlation differs depending of the type of glass. For example, the efficiency of photodestruction of these ions in phosphate glasses varies in the reverse order.

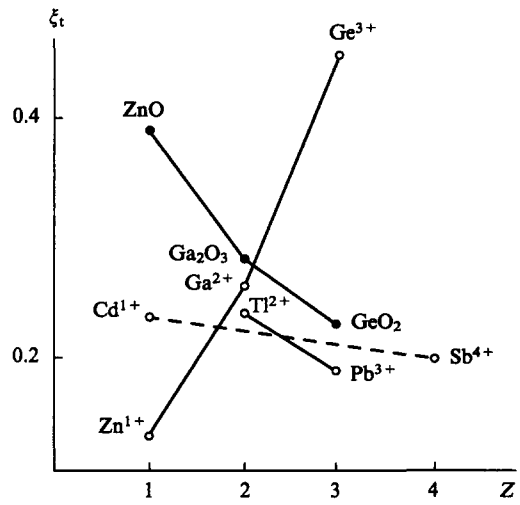


Figure 2. Dependence of ξ_t on Z in lithium borate glasses for ions in UOS (light circles) and for BO_4^{4-} ions (dark circles). All the glasses contain 10 mol % of the metal oxide, which gives rise to the ions in UOS.

The efficiency of the destruction of matrix PMC and CC in glasses with various oxides in the presence of various metals in UOS also depends linearly on Z. However, the course of these dependences can be opposite to the analogous dependence for the UOS. It is seen from Fig. 2 that in the $Zn^{1+}-Ga^{2+}-Ge^{3+}$ series, the ξ_t value for the cations in UOS increases with an increase in Z, while this value for the matrix BO_4^{4-} centre decreases. Thus, the ξ_t and ξ_{ph} values for the matrix centres PO_4^{2-}, PO_3^{2-}, BO_4^{4-}, >SiO', and >GeO' are influenced by the nature of the modifying metal introduced into the glass. The strength of this influence depends both on the position of this metal in the periodic system of elements and on its state in the glass, namely, whether the metal exists as a modifying cation or is incorporated into the glass-forming network.

Certainly, the structural features of the glass matrix have an influence on the course of the A_i-Z and $E_{\lambda_{max}}-Z$ dependences and determine the photo and thermal stability of ion ensembles.

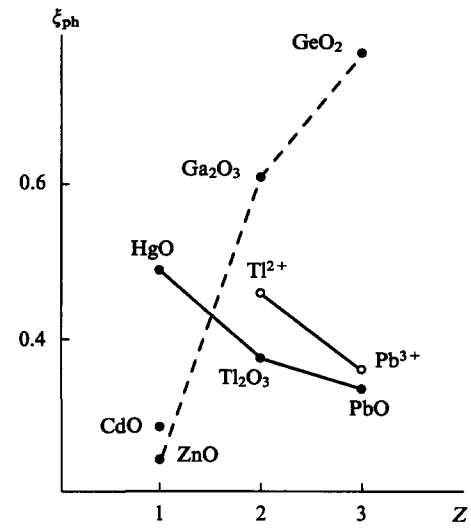


Figure 3. Dependence of ξ_{ph} on Z for ions in UOS (light circles) and for PO_4^{2-} ions (dark circles) in barium aluminophosphate glasses, containing 10 mol % of the metal oxide, which gives rise to the ions in UOS.

In fact, ions in UOS can be formed both in reactions with thermalised electrons (2) or in reactions with hole sites (3)

$$M^{(Z-1)+} + D^+ \longrightarrow M^{Z+}. \qquad (3)$$

The Zn^{1+}, Cd^{1+}, Hg^{1+}, Ga^{2+}, In^{2+}, Tl^{2+}, Ge^{3+}, Sn^{3+}, Pb^{3+}, Sb^{4+}, and Bi^{4+} ions are formed via reaction (2), and only the Tl^{2+}, Sn^{3+}, Pb^{3+}, Sb^{4+}, and Bi^{4+} ions are formed via reaction (3). Both reactions can occur simultaneously in the same glass if it contains pairs of ions, for example, $Sn^{2+}-Sn^{4+}$, $Tl^{1+}-Tl^{3+}$, $Pb^{2+}-Pb^{4+}$, $Sb^{3+}-Sb^{5+}$, or $Bi^{3+}-Bi^{5+}$.

These suggestions have been confirmed in a study of the kinetic behaviour of ions in UOS at various stages of formation and destruction, carried out by pulse radiolysis with optical recording. Such studies were reported for the first time by Aleksandrov et al.[45-47] The measurements were carried out using a setup with optical recording, designed based on a 'U-12F' accelerator and operating on the microsecond time scale ($t = 2.3$ μs, $E = 5$ MeV, $I = 0.2$ A).[7, 8] The radiation colour centres (RCC) arising due to a pulse of accelerated electrons were annealed in the light beam of a DKSSh-150 xenon lamp focused to a diameter of 3 mm. The absorption spectra were recorded within intervals from 2 μs to several minutes. The amount of metal oxides added ranged from 1 to 10 mol %. Simultaneously, optical characteristics of glasses of the same composition exposed to γ-irradiation at 77 and 300 K were measured.

In the case of pulse irradiation of sodium borate glasses with various metal oxides added, rapidly diminishing absorption was detected, the λ_{max} of which lay at 360 and 520 nm (without metal oxides), 350 nm (with ZnO added), 380 and 440 nm (CdO), 390 and 440 nm (Ga_2O_3), 430, 500, 550, 620, and 750 nm (Tl_2O_3), 360 and 430 nm (PbO), and 460 and 500 nm (Sb_2O_3). The λ_{max} values of the absorption bands corresponding to ions in a $^2S_{1/2}$ electronic state observed immediately after a pulse of fast electrons differ only slightly from those obtained in the case of γ-radiolysis at 77 K (see Table 2 and the data given in the text). However, 140–200 μs after the pulse, the absorption maxima start to shift toward the position at which they are observed in the case where the irradiation is carried out at 300 K. Since the EPR parameters (g-factors, A_i, intensities of EPR lines) of ions in a $^2S_{1/2}$ electronic state at 77 K and at 300 K are different,[33, 34] it is obvious that the changes in the optical spectra following the temperature rise or the photoannealing are due not only to the variation of the geometry of the nearest atom environment but also to the disappearance of some of the least photo- and thermostable ions in UOS. In fact, at

77 K the overall spectrum is recorded, whereas the spectrum obtained at 300 K corresponds only to those ions which are stable at this temperature.

The diminution of the absorption in glasses of the same composition corresponds to a linear dependence of D/D_0 on $\lg(t/t_0)$ (D and D_0 are optical densities at times t and t_0, respectively, $t_0 = 1$ μs). The kinetics of the destruction of an individual ion in a glass of a particular composition depend on the intensity of the light acting on the sample. When ions in a $^2S_{1/2}$ electronic state are photoannealed with unfiltered light within a broad time interval (from microseconds to minutes), the slope of the straight lines depends on the nature of the metal ion. The tangent of the slope ξ_{ph} characterises the efficiency of the photoannealing of a particular ion in an UOS. The higher the intensity of light, the more efficient the photoannealing. This follows from the dependences obtained with the light beam attenuated by 55% with a reticulated filter. Experiments on the photoannealing also confirm the fact that only ions in a $^2S_{1/2}$ electronic state, rather than cluster groups incorporating these ions, are formed in the glasses under consideration containing zinc, cadmium, gallium, germanium, and antimony oxides, because under various conditions of light treatment, all the optical absorption bands assigned to these ions disappear in parallel.

In glasses containing lead oxide, two types of species with dissimilar kinetic parameters exist, which account for the AB with $\lambda_{max} = 360$ and 430 nm, whereas glasses with thallium oxide contain at least three types of species, which absorb light at 430, 500 and 550, and 620 and 750 nm, respectively. Evidently, all the CC in these glasses belong to ions and clusters of thallium and are destroyed in parallel by the influence of light.

The energies of optical transitions at the maxima of the AB ($E_{\lambda_{max}}$) for the ions in a $^2S_{1/2}$ electronic state (Ag^0, Cd^{1+}, Ga^{2+}, Tl^{2+}, Ge^{3+}, Pb^{3+}, and Sb^{4+}), obtained on exposure to pulse radiation, depend on both the oxidation number Z of the metal and its position in the Periodic Table. In the isoelectronic series $Zn^{1+}-Ga^{2+}$, $Cd^{1+}-Sb^{4+}$, and $Tl^{2+}-Pb^{3+}$, the $E_{\lambda_{max}}$ values decrease as Z increases. A similar correlation has also been observed for the efficiency of the photoannealing of the above ions with unfiltered light. This is in agreement with the dependences found previously for the optical parameters and for the density of the unpaired electron in the outer *ns*-AO for ions in UOS in isoelectronic series.[33,34]

The method of pulse radiolysis has also been used to study the fast processes occurring in sodium silicate glasses (SSG), containing 10 mol% of Zn, Cd, In, Ga, Ge, Sn, Pb, and Sb oxides, exposed to ionising radiation.[47] It was found that in these glasses, apart from the known AB (with maxima at 460, 580, and 620 nm) typical of glasses containing no metal oxides,[48] additional AB corresponding to the long-lived products of radiolysis arise after irradiation. Simultaneously, the absorption bands associated with the sodium silicate matrix disappear. For example, for glasses with zinc, cadmium, gallium, germanium, tin, indium, and antimony oxides irradiated with a pulse of accelerated electrons at 300 K, the following absorption bands were observed:

Oxides	Zn	Cd	Ga	Ge	In	Sn	Sb
λ_{max}/nm	370	390	375	430	360	470	480
	–	460	435	–	490	–	–

The intensity of these bands depends on the concentration of the metal oxide added. The positions of the AB maxima corresponding to the products of the pulse radiolysis are in good agreement with the λ_{max} values of the AB obtained by γ-radiolysis at 77 K of the SSG containing the same compounds.[36] The absorption spectra of glasses containing cadmium, gallium, indium, and lead oxides recorded immediately after a pulse of accelerated electrons are broad AB accompanied by satellite lines of low intensity. Since no other AB arise upon irradiation of glasses with the above metal oxides, and the intensities of the main and the satellite lines vary in parallel, these AB can be attributed to the Zn^{1+}, Cd^{1+}, Ga^{2+}, In^{2+}, Pb^{3+}, Sn^{3+}, and Sb^{4+} ions in the $^2S_{1/2}$ electronic state. The presence of the satellite line indicates that the energy levels responsible for the optical transition are split due to the asymmetrical environment of the ions in UOS.

The kinetic curves for the photodestruction of the Zn^{1+}, Cd^{1+}, and Pb^{3+} ions are similar in appearance: they have no inflection points. The kinetic curves for the SSG with gallium, germanium, tin, and antimony oxides contain two sections, namely, a section where the absorption falls quickly (up to 100 μs) and a section where it diminishes slowly (up to several minutes). This implies that there are two pathways to the disappearance of the Ga^{2+}, Ge^{3+}, Sn^{3+}, and Sb^{4+} ions. In the case of indium, the kinetic curve for the diminution of the absorption in the coordinates mentioned above has a flat section (up to 0.1 s), which is followed by a steeper section. Thus, in terms of destruction kinetics, metal ions can be divided into three main groups: the first group includes Cd^{1+}, Zn^{1+}, and Pb^{3+} ions, the second group consists of Ga^{2+}, Ge^{3+}, Sn^{3+}, and Sb^{4+} ions, and In^{2+} belongs to the third group. Evidently, the difference between the kinetic behaviour of the ions is due to the specific structural features of the glass matrix that arise during the synthesis of glasses containing the corresponding metal oxides.

In fact, cadmium, zinc, and lead oxides are capable of being incorporated into the glass network formed by the main oxide, which constitutes the glass structure. Gallium, germanium, tin, and antimony oxides exhibit dual properties: they can act both as modifying compounds and as glass-forming compounds. A part of the ensemble corresponding to the modifying ions is responsible for the fast-diminution section on the kinetic curves. Indium oxides act as modifying ions existing both as free ions and as ions linked to bridging and nonbridging oxygen atoms. Under certain conditions the modifiers of the former type are fairly free to move in the matrix and react with the electrons knocked out of the glass matrix, similarly to ions in solution. This accounts for the fact that the kinetic curve for the photodestruction of In^{2+} ions consists of two components, one of which (for the free modifying ions) obeys formally second-order kinetics, i.e. it is linearised in the $1/D-t$ coordinates, and is most clear-cut for periods of time of the order of seconds. The other component follows the normal disappearance kinetics typical of solids, which has been observed for other ions (the initial more gently sloping section of the curve). Thus it is obvious that in the initial stage, the In^{2+} ions connected to the glass network through oxygen atoms predominantly disappear, and then the free modifying In^{2+} ions are destroyed. These ions vanish completely, i.e. the glass is completely 'photobleached' over a period of several seconds. This has also been observed for Zn^{1+} and Tl^{2+} ions in sodium borate glasses.[46]

The pulse radiolysis studies also permitted the following characteristic features to be elucidated. The course of the dependences of $E_{\lambda_{max}}$ and ξ_{ph} on Z coincides with the course of the kinetic curves for the destruction of the Zn^{1+}, Cd^{1+}, Ga^{2+}, In^{2+}, Ge^{3+}, Sn^{3+}, Pb^{3+}, and Sb^{4+} ions, plotted as $D/D_0-\lg(t/t_0)$ coordinates and obtained for the 'steady-state' variant in the analysis of the gently sloping sections. In contrast, the initial (steep) sections of the curves for the destruction of the Ga^{2+}, Ge^{3+}, Sn^{3+}, and Sb^{4+} ions show an inverted profile (Fig. 4). This fact is of fundamental importance, since it thus becomes obvious that there are several structurally different sites for the stabilisation of the same ion in an unusual oxidation state. However, despite the above distinctions, the general rule of the regular variation of physicochemical properties of ions in UOS as functions of the positions of these elements in the Periodic Table is retained.

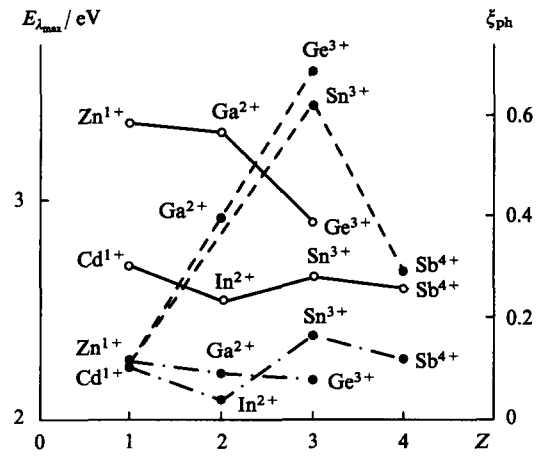


Figure 4. Dependence of $E_{\lambda_{max}}$ (continuous line) and of ξ_{ph} on the steep (dashed line) and gently sloping (dot-and-dash line) sections of the kinetic curves for the destruction of metal ions in UOS on the oxidation number Z in sodium silicate glasses.

3. Formation of unusual oxidation states of transition metals Ti, Ni, Mo, W, and Nb

When glasses containing transition metal oxides are exposed to radiation, ions in UOS are also formed. For example, Ni^{1+} ions have been detected in BAPG with nickel oxide. The EPR parameters of these ions depend substantially on the composition of the glass. When 10 mol % of nickel oxide is added, an EPR signal with triaxial anisotropy is observed, $g_1 = 2.355$, $g_2 = 2.229$, and $g_3 = 2.074$, and when the oxide concentration is increased to 30 mol %, a broad singlet with $g_{aver} = 2.327$ arises.

In alkali glasses and in BAPG, Ti^{3+}, Nb^{4+}, Mo^{5+}, and W^{5+} ions exhibiting characteristic EPR spectra have been detected following γ-irradiation at 77 K. For example, the Ti^{3+} ion in SPG is characterised by a line with biaxial anisotropy with $g_\perp = 1.876$ and $g_\parallel = 1.991$. In alkali phosphate glasses with high concentrations of tungsten oxide (more than 35 mol %), an EPR signal with $g_{aver} = 2.018$ and a line width ΔH of 2.25 mT arises. This signal differs from the known signals typical of W^{5+} ($g_\perp = 1.81$ and $g_\parallel = 1.66$).

In the case of LPG, SPG, and PPG (lithium, sodium, and potassium phosphate glasses) containing niobium oxide (Nb_2O_5 concentration not exceeding 20 mol %), the formation of niobium ions in UOS has been observed after γ-irradiation at 77 and 300 K. In fact, in addition to the doublet signals corresponding to the PO_4^{2-} radical anion, the EPR spectrum exhibited ten main lines extending by 252 mT, the distance between them being 28 mT. Since only Nb possesses a nuclear spin of $\frac{9}{2}$, this spectrum consisting of ten lines is unambiguously associated with the Nb^{4+} ion, for which $g_\perp = 1.91$, $g_\parallel = 1.88$, $A_\perp = 28.0$, $A_\parallel = 13.0$ mT, and $A_i/A_i^{(o)} = 0.12$. Apart from the signal due to Nb^{4+}, a 19.0 mT-wide singlet with $g_{aver} = 2.017$ arises in these glasses, when the concentration of Nb_2O_5 exceeds 20 mol %. As this signal appears, the signal due to Nb^{4+} disappears. The new signal has been attributed to a hole site.[32]

In view of the fact that the spectra of glasses with large amounts of WO_3, MoO_3, and Nb_2O_5 contain broad singlets, one may assume that an increase in the concentration of the oxides and, consequently, in the intensity of the EPR signals associated with the corresponding ions leads to the appearance of isotropic exchange interaction. Blurring of the HFS resulting in the appearance of broad lines (100.0 and 140.0 mT, respectively) has also been observed in glasses containing manganese oxides with an increase in the oxide concentration. In the EPR spectra of glasses with iron oxide a set of lines is recorded, the intensities of which depend on the redox conditions of the synthesis.

Short-lived radiation-induced defects have been studied by pulse radiolysis in the $M_2O-P_2O_5-Nb_2O_5$ glass systems (M = Na, K, Li) that exhibited no initial ('glass melting') absorption bands.[39] At low concentrations of Nb_2O_5, an AB with $\lambda_{max} = 500$ nm, typical of PO_4^{2-}, was observed. With an increase in the concentration of Nb_2O_5 the intensity of the absorption band corresponding to the PO_4^{2-} ion decreased, and an AB with $\lambda_{max} = 650$ nm appeared instead, its intensity increasing with increase in the concentration of Nb_2O_5. The lifetime of this AB, which was assigned to Nb^{4+}, is tens of microseconds at 300 K.

The $Na_2O-SiO_2-CeO_2$ (Eu_2O_3) glasses have been studied.[40] The spectra of these glasses exhibit at least two broad AB in the region of 500–700 nm. The kinetic parameters of the species responsible for these AB are influenced by the Na_2O/SiO_2 ratio and by the amount of the oxides CeO_2 and Eu_2O_3 added.

* * *

Thus, the studies of alkali glasses of four main classes described above permit the following conclusions to be made:

– the properties of ions in UOS vary regularly with the position of the element in the Periodic Table;

– the order of these dependences can be controlled by varying the ligand environment;

– formation of metal clusters in glasses is possible and is initiated by metal ions in UOS;

– the UOS of metals influence regularly the photo- and thermal stability of the matrix CC and PMC in glasses, the kinetic curves for the photoannealing and thermoannealing being linearised in the $n/n_0 - \lg(t/t_0)$ coordinates;

– the possibility of the long-term stabilisation of UOS of metals in alkali glasses was established, and the influence on it of the cationic framework was found.

All the above properties depend on the elemental composition of glasses and on the redox conditions of their synthesis. Evidently, it is these factors that are favourable for the stabilisation of the UOS and for the appearance of certain integral properties against the background of the topological disordering of the spatial structure of glass. Thus, the following causal relationship arises: composition–synthesis–structure–stabilisation or destabilisation of the UOS of a metal. From this it follows that by choosing the composition of a glass and the method for its synthesis under appropriate redox conditions one may impart desired properties to the glass by means of ions in UOS or by means of other species that arise with their participation.

4. Oxide glasses containing no alkali metals

We have considered above the processes of stabilisation of ions in UOS in glasses of four main classes (borate, silicate, germanate, and phosphate glasses) containing alkali metal cations. The role of alkali metal cations in the stabilisation of transition metal ions in UOS has been repeatedly emphasised. However, the role of the ligand environment, i.e. of the oxygen-containing network formed in the glass during its synthesis, has not been considered separately. The structure of the glass network is known to depend on the redox conditions under which it has been formed. These conditions account for a wide range of various matrix defects in a glass and ensure the formation of various types of coordination of ions in the glass network. These effects are most clear-cut in borate glasses in which boron can exist both in tricoordinated and tetracoordinated states.[23]

Studies carried out with $CdO-B_2O_3$, $CdO-SiO_2$, and $CdO-B_2O_3-SiO_2$ glasses[42,49,50] have shown that, if the synthesis is carried out under reducing conditions, the proportion of tricoordinated boron increases. This was found by comparison of the intensities of IR absorption bands at 1500–1150 cm^{-1} and at 1100–800 cm^{-1} corresponding to BO_3^{2-} and BO_4^{4-}, respectively.

In addition, glasses obtained under these conditions exhibit a photochromic effect, which becomes more pronounced as the proportion of tricoordinated boron atoms increases.[49,50]

It has been shown by EPR[42] that following the photo- and γ-irradiation of cadmium-containing glasses, Cd^{1+} ions are formed, and it is these ions that account for the colour of the glasses. The maximum optical absorption of the Cd^{1+} ion is observed at 400–420 nm for both types of treatment, but the concentration of the Cd^{1+} ions arising upon γ-irradiation is higher than that arising upon UV irradiation by 1–2 orders of magnitude.[42] It is therefore obvious that any ion in an UOS can also be stabilised in the absence of alkali metal cations. Fig. 5 shows the plots for the accumulation of the hole (BO_4^{4-}) and electron (Cd^{1+}) sites in glasses exposed to equal doses of γ-radiation but synthesised under different conditions, namely, under normal and reducing conditions. The accumulation of hole sites in these glasses occurs similarly, whereas the accumulation of the electron sites depends essentially on the conditions of the synthesis. The amount of Cd^{1+} formed in the glasses synthesised under reducing conditions is several times greater than that formed in glasses synthesised under normal conditions. Apparently, the synthesis of glasses under oxygen-deficient conditions leads to greater instability of the system, to the rupture of chemical bonds, and to the displacement of the Cd^{1+} ions to the cationic part of the glass network.

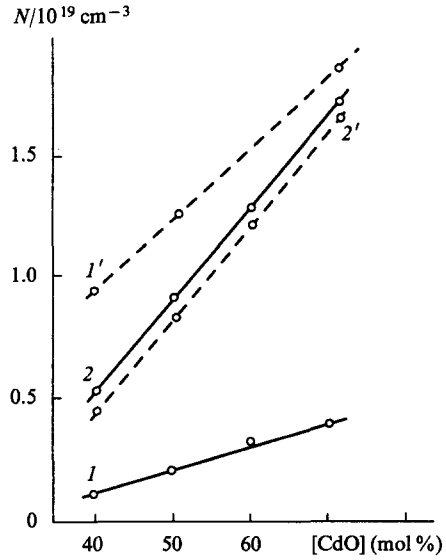


Figure 5. Accumulation of paramagnetic centres in cadmium borate glasses synthesised under normal (*1*, *2*) and reducing (*1'*, *2'*) conditions: (*1*, *1'*) Cd^{1+}; (*2*, *2'*) BO_4^{4-}.

Bismuth-containing glasses are also fairly sensitive to the conditions of the synthesis and are readily reduced as far as the liberation of metallic bismuth. By introducing transition metal oxides into these glasses, one may influence the occurrence of redox processes even during glass melting. This effect of added compounds is due to their influence on the glass structure. Data on the structure of bismuth borate glasses as well as on the influence of transition metal oxides on their structure are scarce, whereas data on the stabilisation of ions in UOS in these glasses are totally lacking. This problem has been investigated in relation to glasses melted on the basis of the $ZnO-Bi_2O_3-B_2O_3$ system and to the same glasses containing added tungsten oxide.[51]

An IR-spectroscopic study of bismuth-containing glasses showed that the initial glass exhibits AB in the region of 1300–1400 cm^{-1} and a band at 1250 cm^{-1} corresponding to the stretching vibrations in the $B^{3+}-O-B^{3+}$ and $B^{3+}-O-B^{4+}$ groups, respectively, and a weak band in the range 900–1000 cm^{-1} associated with the vibrations in the $B^{4+}-O-B^{4+}$ group. The EPR spectrum of the initial glass, containing no additives, recorded after γ-irradiation is a broad singlet with a *g*-factor of 2.022 (ΔH = 3.3 mT) due to Bi^{4+} ions, which can result both from localisation of electrons by Bi^{5+} ions and from capture of holes by Bi^{3+} ions. The strong broadening of the signal and the absence of a hyperfine structure in Bi (the nuclear spin *J* of Bi is $\frac{9}{2}$) suggest that bismuth exists in the glass as clusters, because under oxygen deficiency, a Bi–Bi bond is formed.

The introduction of tungsten oxide into bismuth-containing glasses leads to the appearance of an AB at 870 cm^{-1} in its IR spectrum, corresponding to the stretching vibrations of tungsten in the WO_6 octahedra. The intensity of this band increases with an increase in the content of tungsten oxide in the glass. The EPR spectra of these glasses contain an additional anisotropic line with g_{aver} = 1.607 (ΔH = 46 mT) corresponding to the W^{5+} ions and caused by the localisation of electrons at W^{6+} ions. The intensity of the signal due to Bi^{4+} simultaneously decreases. The relationship between the intensities of lines of Bi^{4+} and W^{5+} suggests that the tungsten ions are incorporated into the bismuth network of the glass. When bismuth and tungsten ions are located close to each other, the localisation of the free electrons during γ-irradiation occurs mainly at the W^{6+} ions, which possess stronger acceptor properties.[7] This conclusion has been supported by the results of X-ray phase analysis of thermally treated glasses: bismuth tungstates were detected as one of the phases in the products of crystallisation.[51] Thus, in bismuth-containing glasses modified by tungsten oxides, bismuth tungstate complexes are formed; they bind the bismuth ions strongly and prevent them from liberation as metallic macroparticles during the glass melting. This change in the glass structure favours the occurrence of single-electron processes accompanied by the formation of W^{5+} and Bi^{4+} ions under the influence of ionising radiation.

* * *

Thus, ions in UOS can also arise under the action of radiation in glasses containing no alkali metal cations. The fact that these ions are stabilised in the matrices of the glasses considered above implies that the set of various oxidation states of ions forming the glass network (for borate glasses, these are B^{3+} and B^{4+} ions) permit the processes of stabilisation to be accomplished also in the absence of alkali metal cations.

5. Sulfate-containing glasses

The studies described above have shown unambiguously that the stabilisation of UOS of metal ions is related to the structure of a glass. Since the stabilisation of UOS of metals is caused in some cases by mobile cations, the stabilisation of these cations, in its turn, can be due to the formation of ions in UOS. The latter, being present in the glass as modifying ions or being incorporated into the glass-forming network, can stabilise the cationic framework to different extents, since the Na^+, K^+, Li^+, and Cs^+ cations are incorporated into the 'ligand' environment of ions in UOS in different ways.

These considerations are related directly to the problem of neutralisation of radioactive wastes with medium activity level.[52] In fact, a glass matrix consisting of a continuous irregular network of coordination polyhedra of glass-forming units accumulates various radionuclides, which can either enter into the composition of the crystalline framework (Na_2O, Cs_2O, SrO, etc.) or be accumulated in the cavities of the structural network as discrete species (RuO_2, UO_2, PuO_2, etc.); a glass matrix can also accumulate inactive salts often containing sulfur. Therefore, the solution of the problem of stabilisation of radionuclide ions and sulfur-containing ions accompanying them can be linked to the stabilisation of ion metals in UOS, for example, Pb^{3+} and VO^{2+}, in sulfate-containing glasses of three main classes, namely, borate, phosphate, and silicate glasses.

Any information on the structure and the nature of radiation-induced defects, on the mechanism of damage arising under the action of radionuclide radiation, and on the radiation resistance of glasses during prolonged storage is of scientific and practical interest. For example, the possibility of stabilising ions of different natures in glasses of various compositions in the $Na_2O(PbO,V_2O_5)-EO_x(SiO_2,B_2O_3,P_2O_5)-SO_3$ systems has been studied by EPR.[53-60] It was found [53,56-59] that the regions of glass formation in the $Na_2O(PbO)-EO_x(SiO_2,B_2O_3,P_2O_5)-SO_3$ systems are broadened on passing from silicate glasses to borate and phosphate glasses and also on passing from sodium to lead glasses (Fig. 6 *a,b*). The largest region of glass formation was observed in the $PbO-P_2O_5-SO_3$ system (the maximum content of SO_3 being 33 mol %).

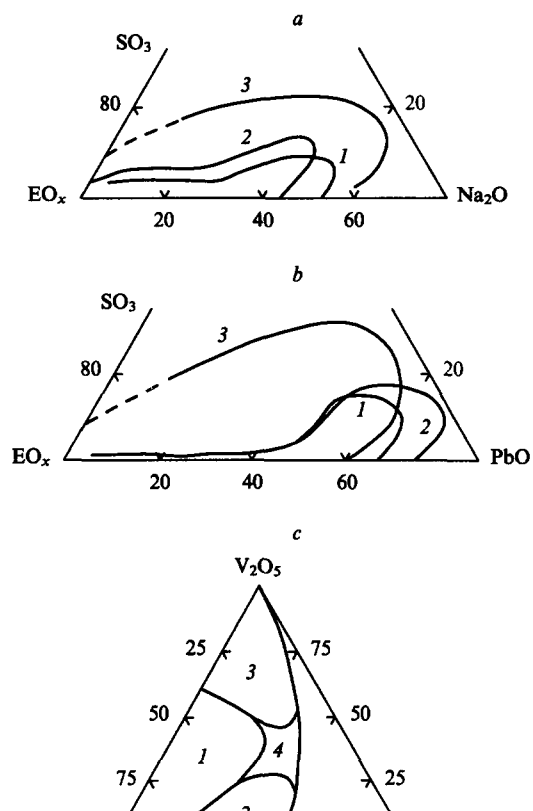


Figure 6. Regions of glass formation in the $Na_2O-EO_x-SO_3$ (*a*), $PbO-EO_x-SO_3$ (*b*), and $Na_2P_2O_6-V_2O_5-Na_2SO_4$ (*c*) systems. $EO_x = SiO_2$ (*1*), B_2O_3 (*2*), and P_2O_4 (*3*).

In order to study the structure in each system, two series of glasses were chosen, with the following concentrations of the initial components: $[SO_3]/([SO_3] + [EO_x]) = \text{const}$. in the first series and $[M_yO]/([SO_3] + [EO_x]) = \text{const}$. in the second series, where EO_x and M_yO are glass-forming oxides and modifying oxides, respectively.

Glasses based on the $Na_2O-SiO_2-SO_3$ system, in which the region of glass formation is the smallest among the glasses studied and the content of SO_3 does not exceed 7 mol %, give no EPR signals due to sulfur-and-oxygen-containing PMC; only signals corresponding to the silicon-and-oxygen PMC are observed.[58] The EPR spectra of sulfate-containing borate and sulfate-containing phosphate glasses, in addition to the signals corresponding to boron-and-oxygen and phosphorus-and-oxygen PMC, exhibit signals due to the sulfate constituent of the anionic character of the glass.[54,55,58]

The EPR spectra of binary alkali borate and sulfate-containing alkali borate glasses,[55] the compositions of which fall in the centre of the glass-formation region, exhibit signals characteristic of irradiated alkali borate glasses: BO_3^{2-} ($g_1 = 2.002$; $g_2 = 2.011$; $g_3 = 2.034$) and BO_4^{4-} ($g_{aver} = 2.012$ for glasses containing more than 20 mol % of Na_2O). In the spectra of sulfate-containing borate glasses (the compositions of which are at the boundary of the glass-formation region), in addition to the signals mentioned above, a signal due to the (SO_4^-) PMC has also been detected (a similar signal has been observed in irradiated solutions of H_2SO_4).[3] The formation of the (SO_4^-) PMC in this composition region can be associated with the processes of chemical differentiation leading to the formation of microregions enriched in sodium sulfate. This inference has been confirmed in a study of thermally treated glasses by electron microscopy.[55]

In the magnetic field region corresponding to $g < g_e$, for sulfate-containing borate glasses [57] with compositions lying at the centre of the glass-formation region, an electron site signal has been detected, the thermal behaviour of which differs from that of (BO_4^{4-}) or (SO_4^{2-}) PMC. This PMC was assigned to a sulfur-containing ion in UOS, namely, to the S^{5+} ion. This may arise when an electron is trapped by an SO_4 tetrahedron incorporated into the glass-forming chains (trapping of an electron is not typical of isolated SO_4^{2-} ions). Apparently, in this case, redistribution of the electron density occurs among mixed boron-sulfur-and-oxygen chains between the boron- and sulfur-and-oxygen fragments in the following way:

$$BO_4^{5-} + SO_4^{2-} \longrightarrow BO_4^{4-} + SO_4^{3-}.$$

This process accounts for the increase in the concentration of the S^{5+} ion. This assumption is supported by the fact that the (SO_4^{3-}) PMC is not found in the irradiated glasses, the compositions of which lie near the boundary of the glass-formation region, because chemical differentiation in these glasses leads to the destruction of the chains containing SO_4 polyhedra.

The EPR spectra of sulfate-containing borate glasses with compositions corresponding to the metaphosphate region, together with the known signals due to the (PO_4^{2-}) and (PO_3^{2-}) PMC, also exhibit a signal associated with SO_4^-.[55] As the proportion of the sulfur-and-oxygen-containing constituent in the anionic character of the glass increases, the concentration of phosphorus-and-oxygen PMC decreases, while that of SO_4^- increases. The irradiation of glasses with compositions lying in the ultraphosphate region [54] also results in the formation of PMC associated with branched units and ring structures like $P_4O_{12}^{3-}$. Simultaneously, the (SO_3^-) PMC with $g = 2.004$ are formed upon rupture of phosphorus-sulfur-oxygen chains under the action of γ-radiation ($-O-PO_2-O-SO_2-O \longrightarrow -O-PO_2-O + -SO_2-O$). On passing from the ultraphosphate region to the metaphosphate region of composition, the concentrations of SO_3^- and $P_4O_{12}^{3-}$ decrease, whereas those of SO_4^- and PO_4^{2-} increase. This is associated with the depolymerisation of the sulfate-phosphate network. Evidently, ultraphosphate glasses incorporate a common phosphorus-sulfur-oxygen network, while metaphosphate glasses contain phosphorus-oxygen chains and isolated sulfate ions. This interpretation of the EPR spectra is not inconsistent with the van Wazer rearrangement theory.[61]

The EPR spectra of irradiated sulfate-containing lead silicate, borate, and phosphate glasses with a PbO concentration of more than 30 mol % exhibit only one well-known singlet due to Pb^{3+} in the g_e region and at high fields.[53,56,58,59] Glasses containing $\leqslant 30$ mol % of PbO can be synthesised only in the sulfate-phosphate system. The EPR spectra of glasses containing not less than 20 mol % of SO_3 or Na_2SO_4 are complex in appearance, being a superposition of the singlets corresponding to Pb^{3+} and SO_4^-.

For glasses based on the $PbO-SiO_2(B_2O_3)-SO_3(Na_2SO_4)$ systems, no signals corresponding to sulfur-oxygen PMC have been recorded. However, with an increase in the content of sulfate

ions, the shape of the Pb^{3+} line changes; in particular, anisotropy of the g-factor increases ($g_\perp = 2.004$, $g_\parallel = 1.955$), which is associated with a change in the glass structure. This is also indicated by the presence of maxima in the curves of the dependence of the concentration (the width of the EPR line) of the Pb^{3+} ion on the composition of the glass (Fig. 7). However, the fact that only the signal for SO_4^- ions is recorded in the EPR spectra indicates that sulfate ions, responsible for their formation in the networks of lead glasses, are mainly isolated.

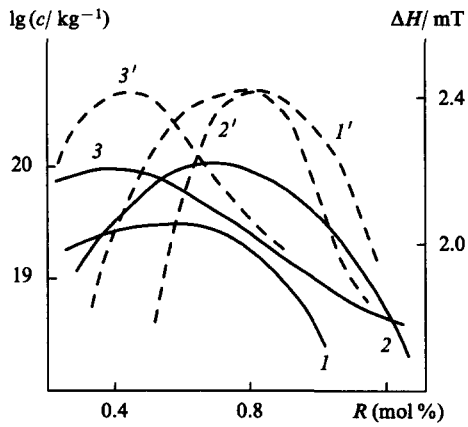


Figure 7. Dependences of the concentration of Pb^{3+} (curves *1*–*3*) and of the line width $\Delta H(Pb^{3+})$ (curves *1'*–*3'*) on the composition of the glass $PbO-P_2O_5-SO_3$ {$R = [PbO]/([P_2O_5]+[SO_3])$, mol %}. Content of SO_3, mol %: 0 (*1*), 10 (*2*), 20 (*3*).

The influence of sulfate ions on the radiation resistance of vanadate glasses has been studied in relation to the pseudoternary $Na_2P_2O_6-V_2O_5-Na_2SO_4$ system.[60] Fig. 6,*c* shows the region of glass formation in this system. It was found [60] that this region can be divided into four areas, according to the character and behaviour of the PMC formed in them. In the first area the HFS, due to VO^{2+} with $g_\perp = 1.994$, $g_\parallel = 1.932$; $A_\perp = 9.0$ and $A_\parallel = 21.2$ mT, is observed at 77 and 300 K. In the second area, the HFS due to VO^{2+} is also observed at 77 K; however, at 300 K in nonirradiated glasses and at 77 and 300 K in the case of γ-irradiated glasses, a symmetrical singlet with $g_{aver} = 1.957$ and $\Delta H = 2.5$ mT is recorded. The EPR spectra recorded for the third area at 77 K are characterised by poorly resolved HFS, while at 300 K, they exhibit a broad line with $\Delta H = 28$ mT and $g_{aver} = 1.970$, which narrows as the content of V_2O_5 increases from 50%–60% to 90%–100% and turns into a narrow asymmetrical line with $g_{eff} = 1.975$. For γ-irradiated glasses corresponding to this area, only an asymmetrical singlet is recorded at 77 and 300 K. In the fourth area, well resolved HFS corresponding to VO^{2+} is observed at 77 K, while at 300 K a low-intensity symmetrical singlet line with $g_{aver} = 1.960$ and $\Delta H = 2.0$ mT is recorded. The spectra of glasses γ-irradiated at 77 and 295 K contain no singlet with $g_{aver} = 1.960$; an anisotropic singlet with $g_{eff} = 1.975$ appears instead. All these changes were attributed to variations in the glass structure. The structure of the glass in the first area is based on the phosphorus–oxygen network, which may incorporate vanadium–oxygen tetrahedra, and the cavities in the network are occupied by Na^+, SO_4^{2-}, and VO^{2+} ions. The network consisting of vanadium–oxygen chains with tetrahedrally coordinated vanadium predominates in the third area. In the second area, the glass contains a fairly large amount of VO^{2+} ions present in an octahedral coordination with tetragonal constriction as well as VO^{2+} ions arranged in the cavities of the structural network as modifying ions. In the fourth area glasses have an intermediate structure: they consist of phosphorus–oxygen, vanadium–oxygen, and mixed chains as well as of sulfate ions.

The studies considered in this Section reflect most clearly the principle of construction of a glassy matrix based on the composition–structure dependence and the possibility of investigating the glass structure by EPR. When various glasses are compared, one can note that the course of the composition–property dependence for sulfate-containing phosphate glasses varies more smoothly than that for silicate or borate glasses. This difference may be attributed to the higher homogeneity of sulfate-containing phosphate glasses. Sulfate ions increase the radiation resistance of glasses. Some chemically inert and radiation-resistant lead-containing glasses may incorporate up to 25 mol % of sulfate-containing wastes.

III. Electron dynamics in oxide glasses

1. Reactions of reversible electron transfer occurring under the action of light

We have described above the processes of destruction of ions in UOS on exposure to light. It was noted that photoannealing with boundary filters leads to partial destruction of both CC and PMC. As the region of transmission of the boundary filter used moves to the UV region, energetically more stable CC and PMC (i.e. centres for which the activation energies for the photodestruction are higher) are annealed, the photoannealing curves being linearised in the $n/n_0 - \lg(t/t_0)$ coordinates. By now it has been established that if CC with nonoverlapping AB arise in a γ-irradiated glass, reversible phototransfer of an electron between the species responsible for these AB is possible. From this standpoint, lithium, sodium, potassium, and barium aluminophosphate glasses proved most promising, since γ-irradiation of these glasses leads to the appearance of $PO_4^{2-}-M^{Z+}$ pairs of species ($Z+$ is an unusual oxidation number), which are responsible for nonoverlapping AB. In fact, an AB with $\lambda_{max} = 500$ nm corresponds to the PO_4^{2-} ion, while, for example, Tl^{2+} and Nb^{4+} ions account for AB with $\lambda_{max} = 420$ and 650 nm, respectively.

It has been shown that these ions arising on irradiation can be involved in reversible photoprocesses of the type

$$PO_4^- + M^{Z+} \underset{h\nu_2}{\overset{h\nu_1}{\rightleftharpoons}} PO_4^{2-} + M^{(Z+1)+}, \qquad (4)$$

and the unpaired electron can thus be transferred from the ion in UOS to the PO_4^- ion by phototreatment (in the region of the AB corresponding to the ion in UOS). The reverse process is carried out by treating the PO_4^{2-} ion with light (in the region of the AB with $\lambda_{max} = 500$ nm). In this case, the kinetic curves are also linearised in the $n/n_0 - \lg(t/t_0)$ coordinates. The concentration of the PO_4^{2-} ions being destroyed decreases in parallel with an increase in the concentration of the ions in UOS being formed (for example, Tl^{2+} and Nb^{4+} ions); this can be written as $|\Delta[PO_4^{2-}]| = |\Delta[Tl^{2+}]|\{|\Delta[Nb^{4+}]|\}$. The paramagnetic species PO_4^{2-}, Tl^{2+}, and Nb^{4+} are especially convenient, because the reversible processes involving these species can be monitored both by optical spectroscopy and by EPR.

The number of cycles in such reversible processes is influenced by the structure of the glass as well as by the degree of overlap of an edge of the AB corresponding to the ion in UOS with an edge of the AB due to the phosphorus-containing radical ion resulting from the light treatment. The formation in the glass of cluster species of the M_m^{n+} type (where m and n are 1, 2, 3, ...), together with the ions in UOS, prevents the realisation of a large number of cycles; the clusters also participate in the electron dynamics thus creating additional reaction pathways and blurring the pattern of 'ideal' photoreversible transitions between the radiation-induced CC and PMC. In the case of phosphate glasses with added Nb_2O_5 the pattern of reversible photoreactions is also blurred because niobium oxide forms its own niobium–oxygen network, along which the electron, knocked out from PO_4^{2-} by the phototreatment, can migrate. Apparently, this electron no longer participates in the reverse reactions. This may be why the number of cycles for the $PO_4^{2-}-Nb^{4+}$ pair is much smaller than for the $PO_4^{2-}-Tl^{2+}$ pair.

2. Temperature-dependent reactions of reversible electron transfer

An attempt has been made [62] to obtain metal ions in UOS without the action of ionising radiation. For this purpose, lithium tungstate-, lithium niobate-, and lithium molybdate-phosphate glasses (LTPG, LNPG, and LMPG) with added tin, titanium, vanadium, molybdenum, tungsten, and nickel oxides have been synthesised under reducing conditions. The completed glasses were intensely coloured (the 'glass melting' colour). The following PMC were found in these glasses by EPR:[62] Nb^{4+}, Mo^{5+}, W^{5+}, Ti^{3+}, VO^{2+}, and Ni^0. The integral intensity of the EPR signals corresponding to the above PMC in these glasses increased by several orders of magnitude as the temperature decreased from 300 to 6 K. It was also found that as the temperature decreased, the EPR parameters of the PMC already present altered, which points to structural changes in the glass network, at least in the local environment of the ions in UOS. As the temperature decreased, the edge of the fundamental absorption for all the above glasses shifted to the UV region of the optical spectrum by 5–10 nm. For the matrix LNPG, the intensity of the AB with λ_{max} = 800 nm decreased, whereas the intensity of the AB with λ_{max} = 600 nm increased with a decrease in the temperature, i.e. a low-temperature thermochromic effect was observed. All the processes and parameters are temperature-reversible, i.e. the parameters return with time to the values corresponding to a given temperature.

Aleksandrov et al.[62] believe that these variations are due to the stabilisation–destabilisation (localisation–delocalisation) of electron pairs caused by slight local variations of the structural network of the glass. A decrease or an increase in the temperature leads to the transfer of an electron pair and to disproportionation reactions of the type:

$$Nb^{3+} + Ni^{2+} \underset{+T}{\overset{-T}{\rightleftharpoons}} Nb^{5+} + Ni^0, \quad (5)$$

$$M^{Z+} + M^{(Z+2)+} \underset{+T}{\overset{-T}{\rightleftharpoons}} 2\,M^{(Z+1)+}, \quad (6)$$

where Z is the oxidation number; M^{Z+} are Nb^{3+}, Sn^{2+}, Ti^{2+}, V^{3+}, Mo^{4+}, and W^{4+} ions at which a pair of electrons with opposite spins is localised due to structural features of the glasses obtained. The existence of $M^{(Z+2)+}$ ions in the glasses synthesised is indicated unambiguously by the fact that the γ-irradiation of these glasses at 300 K leads to reduction reactions of the following type

$$M^{(Z+2)+} + e_t^- \xrightarrow{\gamma} M^{(Z+1)+}. \quad (7)$$

The continuous increase in the concentration of ions in UOS as the temperature decreases down to 6 K (Fig. 8) is evidence in favour of the disproportionation of electron pairs [according to reaction (6)].

Thus, Aleksandrov et al. [62] showed for the first time the possibility of temperature-dependent reversible transfer and disproportionation of a pair of electrons in oxide glasses, i.e. the so-called P_e-processes and D^2-disproportionation reactions, the existence of which in solids had already been suggested in theoretical papers.[63–65]

Aleksandrov et al. [66] have also proved unambiguously the possibility that during the synthesis of glasses, D^+ and D^- sites arise on transition metal ions, i.e. pairs of negatively and positively charged defective sites existing in charge equilibrium. The quantum level of the D^- site is occupied by two electrons, while that of the D^+ site contains no electrons. The reason why these sites are defective was considered by Street and Mott in their model of glassy media.[65] The quantum levels of the D^+ and D^- sites are located near the conduction band and near the valence band, respectively. According to Street and Mott, the metastable D^0 site, which is a level singly occupied by an unpaired electron, is located in the middle of the forbidden gap; this site results from an external action on the glassy medium during reduction or oxidation reactions involving D^+ and D^- sites. In the examples described above, ions in UOS act as D^0 sites. Aleksandrov et al. [62] were the first to find experimentally the D^+, D^-, and D^0 defects at transition metal ions in oxide glasses.

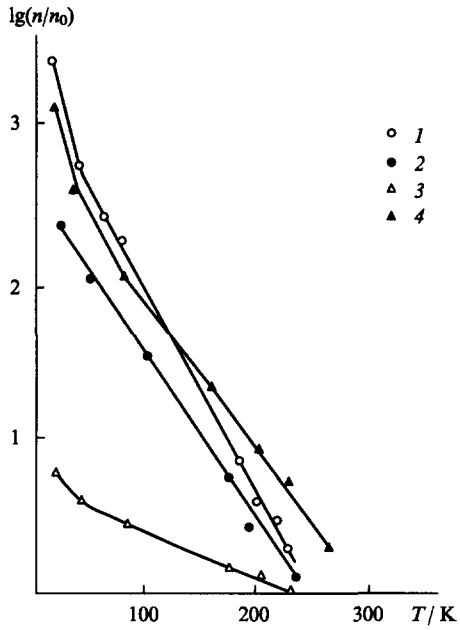


Figure 8. Dependences of the concentration of (Nb^{4+}) PMC on temperature in the 'matrix' LNPG (*1*) and in LNPG with added tin (*2*), vanadium (*3*), or titanium (*4*) oxide. Curve *4* shows the overall concentration $Nb^{4+} + Ti^{3+}$.

It is noteworthy that in the LNPG doped with tin oxide, additional PMC have been observed only on Nb^{4+}; when the glass is doped with titanium oxide, PMC can be detected either on both Nb^{4+} and Ti^{3+} or only on Ti^{3+}, depending on the composition of the glass and on the glass melting conditions; in the case where vanadium, molybdenum, and tungsten oxides act as dopants, only PMC caused by VO^{2+}, Mo^{5+}, and W^{5+} are observed. In the LMPG system doped with tungsten oxide, (Mo^{5+}) and (W^{5+}) PMC have been observed, the ratio between the concentrations of Mo^{5+} and W^{5+} depending on the composition of the glass and on the glass melting conditions. The yields of all ions on decreasing the temperature are strongly dependent on these conditions. Thus, it is obvious that under certain conditions the D^2-disproportionation reactions are preceded by the P_e-process involving the transfer of an electron pair from Nb^{3+} to V^{5+}, Mo^{6+}, W^{6+}, and Ti^{4+} yielding V^{3+}, Mo^{4+}, W^{4+}, and Ti^{2+} and then V^{4+}, Mo^{5+}, W^{5+}, and Ti^{3+}. The Nb^{4+} ion is not formed in these glasses, i.e. the separated electrons do not react with the dopant. Apparently, this is an example of accepting an electron pair and subsequent accepting of the separated electrons by a stronger acceptor.

If glasses contain dopants leading to the formation of metal ions with weaker accepting properties compared with those of the V^{5+}, Mo^{5+}, W^{5+}, and Ti^{4+} ions, only Nb^{4+} is formed. However, the influence of the compounds added on the trapping of the electrons resulting from the dissociation of electron pairs can be judged from the increase in the concentration of the Nb^{4+} ion with a decrease in the temperature. Fig. 9 shows the dependence of the concentration of the Nb^{4+} ions at 77 K in LNPG on the kind of dopant (silver, zinc, indium, tin, antimony, gallium, or germanium oxide), which can lead to the formation of ions in UOS with the corresponding oxidation number Z. The dopants were introduced during the glass melting in a concentration of 3 mol %. The pattern of the $\Delta[Nb^{4+}] - Z$ plot coincides with those

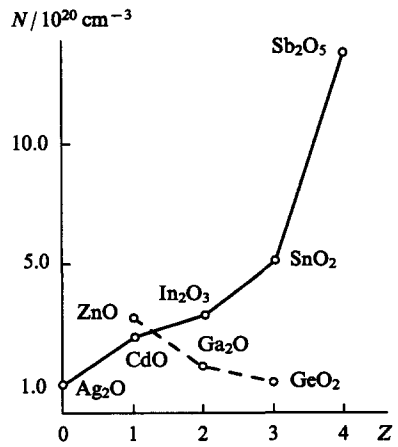


Figure 9. Dependence of the yield of Nb^{4+} ions at 77 K in LNPG containing metals, forming the corresponding ions in UOS, added as dopants (introduced as oxides in an amount of 3 mol %).

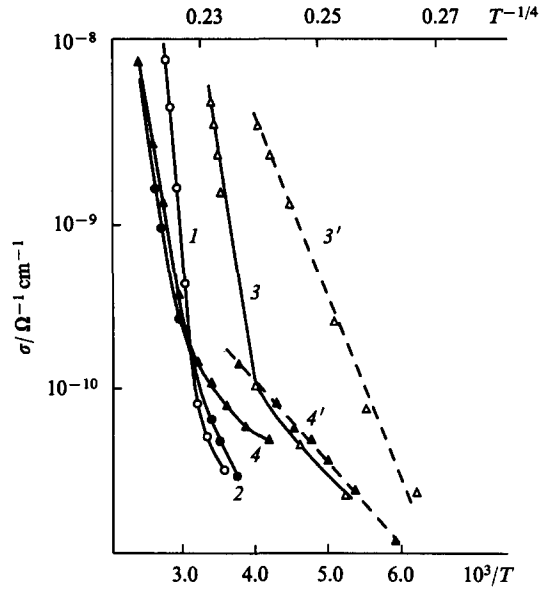


Figure 10. Temperature dependence of electrical conductivity in the $\sigma - 10^3/T$ coordinates (curves *1–4*) and in the $\sigma - T^{-1/4}$ coordinates (curves *3'–4'*) in the 'matrix' LNPG (*1*) and in LNPG with added tin (*2*), vanadium (*3*, *3'*), or titanium (*4*, *4'*) oxide.

of the $A_i/A_i^{(0)} - Z$ and $E_{\lambda_{max}} - Z$ plots obtained for γ-irradiated alkali phosphate glasses. Evidently, after the decomposition of species with paired electrons to single-electron species, doping metals enter into redox reactions with them yielding ions in UOS, as with the action of γ-radiation.

Since niobium oxide acts in LNPG as the glass-forming compound, forming a glass network possessing microcavities, channels, and pores peculiar to it, one can assume that surface disproportionation reactions occur, which are accompanied by surface transport of electron pairs to stronger acceptors affording ions in UOS. Naturally, the disproportionation reactions proceeding within the structural units of the glass also contribute to this process.

To elucidate the mechanism of the reversible low-temperature disproportionation (RLD) and the reasons for stabilisation of particular concentrations of elements in UOS at a fixed temperature, the following experiments have been carried out. LNPG (this glass is subsequently referred to as the 'matrix LNPG') with added titanium, tin, and vanadium oxides, containing Nb, Li, P, and M (Sn, Ti, V) atoms in concentrations of $(1-4)\times10^{21}$, $(4-8)\times10^{21}$, $(1-3)\times10^{22}$, and 2×10^{20} cm^{-3}, respectively, were taken as model objects. These glasses had an intense ('glass melting') colour, resulting from the reducing conditions used in their synthesis. The number of PMC was determined from the EPR spectra recorded in the integration regime.[66] In this case, up to 10^{21} PMC per cm^3 arise.

It is seen from Fig. 8 that the activation energy for the increase in the concentration of elements in UOS depends on temperature, $E = f(T)$. The increase in the concentration of ions in UOS (Nb^{4+}, Ti^{3+}, etc.) is caused by several processes for which a spread in energy parameters is possible due to the statistical distribution of the initial transition metal ions in the glass matrix. These processes include: decomposition of species with electron pairs (denoted formally by Nb^{3+}, Ti^{2+}, Mo^{4+}, W^{4+}, etc); and stabilisation of 'separate' electrons (subsequently, this term refers to 'exchange' electrons participating in exchange processes and to the free electrons in the glass matrix). These processes end with the formation of ions in UOS: Nb^{4+}, Ti^{3+}, etc., which are stable at a given temperature.

In order to evaluate the contributions of the stabilisation of 'separate' electrons, and of those electrons resulting from the decomposition of species with electron pairs, to the RLD effect (to the formation of the Nb^{4+}, Ti^{3+}, etc. UOS), the temperature dependences of the electrical conductivity at direct current have been recorded (by the four-electron method) for the matrix LNPG and for the LNPG doped with vanadium, titanium, and tin oxides (Fig. 10). In fact, since the electrical conductivity varies down to low temperatures (200 K), the hopping mechanism of conductivity is valid, as well as the thermostimulated conductivity of electrons and holes, described by the dependence $\sigma = \sigma_0 \exp(\Delta E/kT)$, where $\Delta E = E_c - E_F$ for electrons and $\Delta E = E_F - E_v$ for holes (E_c, E_v, and E_F are the energies of the edge of the conduction band, the edge of the valence band, and the Fermi level, respectively). The hopping conductivity involves tunnelling of thermoactivated charge carriers from one trap to another over the energy levels at the edges of the bands (in the energy ranges $E_c - E_a$ and $E_b - E_v$), occurring in accordance with the geometrical and energy distances between the individual traps (see Fig. 11).

Apparently, one more charge transfer mechanism occurs. It involves 'jumps' of various distances over localised states near the Fermi level. For this type of conductivity, Mott[67] has found the relation $\sigma = \sigma_1 \exp[-(T_0/T)^{1/4}]$. It is the Mott's temperature dependence of the conductivity that is obeyed at low temperatures in the glasses under consideration (Fig. 10). Tentative values for the number of conduction electrons (numerically equal to the

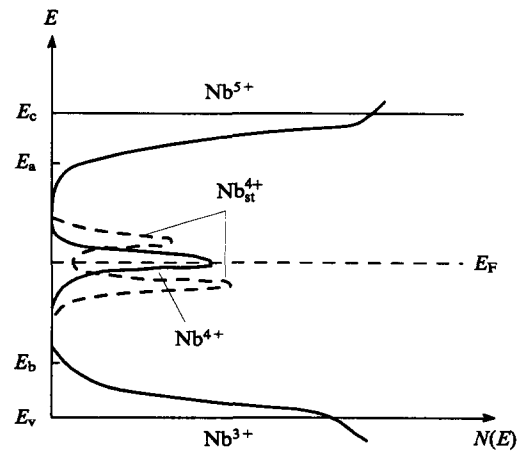


Figure 11. Scheme for the density of the electron states on ions in LNPG at low temperatures (the dashed line shows the possible energy spectrum of niobium ions intercalated with Li^+ cations).

concentration of 'separate' electrons) in these glasses are $10^6-10^{12}\,cm^{-3}$. This is less by many orders of magnitude than the number of Nb^{4+} and Ti^{3+} UOS arising by the RLD mechanism in the same glasses on decreasing the temperature. Thus, it is obvious that the contribution of the stabilisation processes of the exchange and free electrons to the formation of UOS is quite insignificant. The UOS observed arise largely via the type (6) disproportionation of species with paired electrons. In addition, the conductivity of the glasses increases by several orders of magnitude following the introduction of transition metal oxides (Fig. 10); and the conductivity determined for direct current is time-dependent. Hence, it can be claimed that there is a contribution of the cationic framework to the conductivity of this class of glasses; in other words, these glasses incorporate a mobile cationic framework.

It has been found [66] that the yields of Nb^{4+} and Ti^{3+} in LNPG with a constant Nb_2O_5/P_2O_5 ratio depend on the number of lithium cations, since the concentrations of Nb^{4+} and Ti^{3+} pass through a maximum at a particular Li^+ concentration and fall to undetectable values as the latter decreases. This suggests that the mobile cation ensemble has an influence on the dissociation of the electron pairs at Nb^{3+} and on the subsequent stabilisation of the UOS of niobium ion, Nb^{4+}. Evidently the cationic ensemble stimulates the reaction (6) and stabilises the resulting UOS by the following multistage mechanism.

In the first stage, the electron pair at Nb^{3+} dissociates, and Nb^{4+} is stabilised by a lithium cation.

$$Nb^{3+} + Li^+ \underset{+T}{\overset{-T}{\rightleftharpoons}} (Nb^{4+}\text{---}Li^+) + e^- . \qquad (8)$$

The unpaired electron thus liberated reacts with Nb^{5+}

$$e^- + Nb^{5+} \underset{+T}{\overset{-T}{\rightleftharpoons}} Nb^{4+}, \qquad (9)$$

and the resulting Nb^{4+}, in its turn, is stabilised by a lithium cation

$$Nb^{4+} + Li^+ \underset{+T}{\overset{-T}{\rightleftharpoons}} (Nb^{4+}\text{---}Li^+). \qquad (10)$$

Thus, if we refer the designations Nb^{3+}, Nb^{4+}, Nb^{5+}, Ti^{2+}, etc. to oxygen-containing cluster species incorporating a particular ion in the corresponding oxidation state and consider that the lithium ions are located within the sphere of this cluster and are probably bound to the metal (titanium, niobium, etc.) ions via oxygen bridges, then formally $Nb_{st}^{4+} = (Nb^{4+}...Li^+)$. The stable Nb_{st}^{4+} ion is now detectable by the EPR method (strictly speaking, only Nb_{st}^{4+} can be detected 'directly' by EPR). Thus, the temperature-dependent reversible liberation–capture of the cations from shallow to deep energy traps stabilises the forming UOS and promotes the disproportionation reaction (6). This is certainly accompanied by variations of the charge density in the local space in the vicinity of the ion in UOS.

Obviously, the cationic ensemble also influences the conductivity of glasses, since intercalation of a glass with lithium changes (splits, shifts, etc.; see Fig. 11) the energy levels of all the ions present. The transfer of electrons and holes at low temperatures occurs along the system of the lithium-intercalated glass, i.e. the glass in which energy levels and quantitative ratios of ions have changed.

Thus the RLD effect can be considered to be associated with the crucial role of the cationic framework in the stabilisation of UOS and, consequently, with the occurrence of the disproportionation processes (6). The cationic framework determines the $Nb^{3+}/Nb^{4+}/Nb^{5+}$ ratio of ion concentrations. However, at the concentrations found $[Nb^{4+}] = N = 10^{21}\,cm^{-3}$, the value $NZ_B < 0.25$ (Z_B is the Bohr radius of Nb), i.e. according to the Mott criterion,[67] metallisation of this glassy system has still not been achieved.

3. Formation of ions in UOS as a result of mechanochemical treatment

It follows from the above that the unpaired electrons arising due to various kinds of treatment of a solid (γ-radiation, phototreatment, heat treatment) are characterised by similar chemical behaviour: they give rise to ions in UOS in the glass matrix. It should be expected that mechanical treatment of the glasses described above will also lead to the appearance of ions in UOS. It has been noted [68] that when a LiF crystal is cracked, F atoms are liberated. One of the hypotheses put forward for the explanation of the emission of F atoms states that the following electron transfer reactions occur during the cracking: $F_v^- \longrightarrow F + e^-$, $Li^+ + e^- \longrightarrow Li$, where F_v^- is a vibrating F^- ion which has undergone vibrational excitation immediately after the cleavage of bonds in the mouth of the mechanical crack. If the amplitude of these vibrations reaches 0.75 of the magnitude of the lattice parameter, rupture of the chemical bond occurs according to the above scheme. The mechanisms of dislocation-induced excitation of the electron subsystem of a solid, according to which electron-hole pairs are formed upon collision of dislocations or upon their exposure at the surface of a pore (or a crack) in a solid, have also been reported.[69,70] The collision or surface exposure of dislocations is accompanied by intense acoustic emission, i.e. vibrational excitation of atoms. If the amplitude of vibrations of the atoms exceeds the limit mentioned above, an electron-hole pair is formed. Obviously, the subsequent scheme of elementary chemical steps following the mechanical destruction of a solid should include reaction (2) (formation of ions in UOS).

We carried out experiments on mechanical treatment in a ball mill of sodium silicate (SSG) and sodium borate (SBG) glasses at 77 K. It was found by EPR that in the SSG doped with cadmium, tin, thallium, and lead oxides, Cd^{1+}, Sn^{3+}, Tl^{2+}, and Pb^{3+} ions are formed. The $A_i/A_i^{(o)}$ ratios for these ions are 0.64, 0.35, 0.55, and 0.48, respectively. It is seen that the $A_i/A_i^{(o)} - Z$ dependences for the ions in UOS obtained by mechanical treatment and by γ-irradiation at 77 K are similar.

After the mechanical treatment of SBG in a ball mill at 77 K, only weak signals corresponding to BO_4^{4-} PMC were observed. Apparently, the number of ions in UOS in these glasses is so small that they cannot be detected by EPR.

These data are in good agreement with the views on the structure of inorganic glasses presented above and with the model of the vibrational formation of electron-hole pairs in a glass after mechanical treatment. In fact, boron oxide usually forms linear chains in glasses with low resistance to deformation, whereas silicate glasses consist of highly rigid three-dimensional networks.[71] Naturally, the stronger the glass, the higher is the mechanical stress needed for its destruction, and the more intense in amplitude and frequency are the vibrational processes arising in it. Hence, it is clear that the formation of electron-hole pairs and, consequently, of ions in UOS, should be more intense in silicate glasses. This is in good agreement with the above experimental results.

4. The role of metals in UOS in the nucleation in a glass

The formation of the crystalline phase from glasses and melts is an important problem in the theory and practice of the glassy state. This process plays a key role in the preparation of crystalline enamels and glazes, in the directed colloidal colouring of glasses, and in the production of glass ceramics, photo glass ceramics, and photochromic glasses existing in both the amorphous and crystalline states. The theoretical foundations for these processes have been formulated by Kolmogorov [72] and developed further by other researchers.[73–81] However, stage-by-stage molecular chemical investigation of the mechanism of the formation of the crystalline phase has hardly been developed. In all these studies, only the initial and final substances were examined. Nothing was said about the role of disproportionation reactions.

The formation of the colloidal and crystalline phases can be divided conventionally into three stages: (1) the formation of atomic centres; (2) the appearance of molecular aggregates; and (3) the formation of colloidal and crystalline inclusions. The first two stages are often combined into a single stage — nucleation, the growth of crystals and colloids being regarded as the second stage.

To obtain the nuclei, photosensitisers, thermosensitisers and photosensitive metals are introduced into photo glass ceramics and in photochromic glasses. Ce, Sm, and Pr compounds, i.e. compounds of elements that readily release electrons on exposure to light, for example, by the reaction

$$Ce^{3+} + h\nu \longrightarrow Ce^{4+} + e^- \qquad (11)$$

act as photosensitisers.

The wavelength of the active light depends on the nature and properties of both the photosensitiser and the matrix glass. The metals Sn, Sb, Pb, etc., small amounts of which (0.02% – 1.5%) increase the capability of a photosensitive metal to form nuclei during heat treatment of the glass and thus decrease the irradiation time, are referred to as thermoreducing sensitisers.

Photosensitive metals are mainly Cu, Ag, Au, and Pt. Thermosensitisers can reduce the ions of photosensitive metals even during glass melting. In this case, the following reactions occur on exposure to light:

$$Cu^{1+} + h\nu \longrightarrow Cu^{2+} + e^-,$$

$$Cu^{1+} + e^- \longrightarrow Cu^0.$$

The atomic copper, gold, silver, etc. form colloidal and crystalline phases when heated to a certain temperature. Cerium added to the glass permits the yields of Cu^0, Ag^0, and Au^0 to be increased, due to the occurrence of reactions of the type

$$Ce^{3+} + Cu^{1+} + h\nu \longrightarrow Ce^{4+} + Cu^0.$$

Photosensitive materials can act as self-sensitisers

$$2Cu^{1+} + h\nu \longrightarrow Cu^{2+} + Cu^0 + \Delta,$$

where Δ is the excess energy liberated. Hard radiation exerts a similar influence on these glasses, i.e. γ-irradiation also creates prerequisites for the nucleation.

Spontaneous (homogeneous) crystallisation can proceed in a glass melt. The process of nucleation in this case has been rationalised at the microquantitative level by Weyl,[77,78] who relates the nucleation to defects or asymmetric fragments. In his opinion, the 'asymmetry' is caused by disproportionation (not electronic) of the bonding forces, which lowers the energy barrier to the formation of crystallisation centres. Berezhnoi[79] believes that the 'appearance of the centres for spontaneous crystallisation in complex glasses is associated with the diffuse chemical differentiation of atoms and structural groups forming aggregates as zones, the composition of which is close to that of the segregating crystals.' Thermodynamic description of the homogeneous crystallisation has also been reported.[73]

An important role in the theory of heterogeneous (or catalytic) crystallisation is played by metastable zones, the necessity of wetting the catalyst with the crystalline phase, and the similarity of crystal structures and interatomic distances in the catalyst and in the crystalline phase. This process is greatly influenced by stirring or vibration of the supercooled melt or by the action of ultrasound, electrical and magnetic fields, and γ-irradiation. The oxides TiO_2, ZrO_2, P_2O, ZnO, Cr_2O_3, V_2O_5, NiO, Nb_2O_5, WO_3, and MoO_3 are used as catalysts. The choice of the catalyst in each particular case depends on the composition and properties of the glass melt.

Turnbull[80] has derived equations for calculating the rate of formation of crystallisation centres for heterogeneous crystallisation. After that, the rules for the selection of the catalyst have been established:[81] the catalyst should be readily soluble in the glass blend at the temperature of glass melting (and manufacture) and be sparingly soluble at low temperatures; the free activation energy for the formation of homogeneous crystallisation centres from the melt at low temperatures should be low, which is favoured by a low surface energy of the dissolved and crystalline phases and by a high degree of supersaturation on cooling; the free activation energy for the diffusion process should be low; the surface energy at the interface between the glass and the catalyst crystal should be low; the parameters of the crystal lattice of the catalyst should be close to those of the segregating crystalline phase. However, Weyl[77,78] has noted that the distribution of chemical bonds within the system is also important.

It is clear from the foregoing that the processes of nucleation and segregation of the crystalline and colloidal phases from glasses have mainly been described at a macroscopic level. The role of transition metal ions and ions in UOS as well as concepts at the molecular level, similar to those considered above in relation to the formation of metal clusters M_m^{n+} (M = Pb, Tl, Bi), was not mentioned in any of these studies. In none of the papers surveyed in relevant monographs[79,82,83] is mention made of the fact that only the presence of atoms capable of disproportionating, such as $Bi^{3+} - Bi^{5+}$, $Tl^{1+} - Tl^{3+}$, $Cu^{1+} - Cu^{3+}$, $Pt^{2+} - Pt^{4+}$, $Ti^{2+} - Ti^{4+}$, in combination with ions in UOS acting as sensitisers, is the crucial factor for the beginning of the nucleation process.

The above is confirmed by the reversible formation and decomposition of Cu_m^{n+} colloidal particles, induced by ions in UOS obtained by irradiation, such as Zn^{1+}, Cd^{1+}, Hg^{1+}, In^{2+}, Tl^{2+}, Sn^{3+}, Pb^{3+}, Sb^{4+}, and Bi^{4+}.[84] Let us consider a sodium aluminoborosilicate glass with added cadmium and copper oxides. It has been shown by EPR that irradiation of this glass leads to the formation of Cd^{1+} and BO_4^{4-} ions. On heating to 150 – 200 °C these ions virtually disappear. Further heating to 800 °C leads to the formation and destruction of particles of colloidal copper Cu_m^{n+}. This indicates that the Cd^{1+} and BO_4^{4-} ions are not merely annihilated, but enter into redox reactions with Cu^{2+}

$$Cd^{1+} + Cu^{2+} \longrightarrow Cd^{2+} + Cu^{1+},$$

$$BO_4^{4-} + Cu^{2+} \longrightarrow BO_4^{5-} + Cu^{3+},$$

which afford the D^-, D^+ defects, i.e. the Cu^{1+} and Cu^{3+} ions. It is pairs of these ions, identified based on the AB with λ_{max} = 570 nm, that act as the precursors of the nuclei of colloidal copper. In fact, the lattice around the D^+ defect should be substantially stressed, whereas the D^- defect interacts with the environment only weakly but possesses a higher mobility. This leads to the possible occurrence of the following reactions:

$$Cu^{3+} + Cu^{2+} \longrightarrow Cu_2^{5+}, \quad Cu^{3+} + Cu^{1+} \longrightarrow Cu_2^{4+},$$

$$Cu^{2+} + Cu^{1+} \longrightarrow Cu_2^{3+}, \quad Cu^{1+} + Cu^{1+} \longrightarrow Cu_2^{2+}, \text{ etc.}$$

The species Cu_2^{5+}, Cu_2^{4+}, Cu_2^{3+}, and Cu_2^{2+} can also be regarded formally as D^- and D^+ defects. Some of them are more mobile than others. Reactions then proceed in which the number of copper atoms in one nucleus increases to give Cu_m^{n+} particles.

The decomposition of the colloidal particles Cu_m^{n+} following further increase in the temperature occurs stepwise. This is indicated by the decrease in the intensity of the AB with λ_{max} = 570 nm and by the appearance of an AB with λ_{max} = 455 nm, which also disappears as the temperature is further increased. The latter AB corresponds apparently to species with lower numbers of copper atoms or to small colloidal particles of copper incorporating cadmium atoms. It can be assumed that the decomposition of Cu_m^{n+} is related to the high-temperature disproportionation reactions. The diagram for this process is shown in Fig. 12. This process can be repeated many times, beginning with the radiation-induced generation of the Cd^{1+} and BO_4^{4-} ions at 300 K.

Thus, the following sequence of transformations occurs: low-temperature defects ⟶ disproportionation reactions ⟶ high-temperature products ⟶ disproportionation reactions ⟶

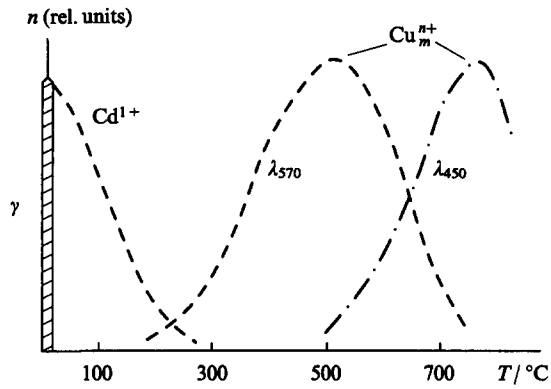


Figure 12. Processes in the accumulation and disappearance of Cd^{1+} ions and Cu_m^{n+} clusters after γ-irradiation followed by thermoannealing.

return to the initial state. To control the formation of the nuclei of crystalline and colloidal phases in glasses, in glass-like materials, and, possibly, in ceramics, one should elucidate the relationships in this sequence. The problem of elucidating these relationships can be solved only by detailed investigation of the whole set of ions present in the glass and of the electron dynamics of their interactions,[85] which, in the presence of disproportionation reactions, may be complex and involve in oxide glasses both the metal and oxygen. For example, the following disproportionation reactions of the D^2 type may occur

$$M^{4+} + 2O^{2-} \longrightarrow M^{2+} + O_2^{2-}.$$

Oxygen ions and clusters should promote the disproportionation reactions.[86-90] Obviously, studies along these lines will be continued.

IV. Conclusion

The data presented in our review imply that the stabilisation and reversible stabilisation–destabilisation of metal ions in UOS with the localisation of one or two electrons are complex processes involving the whole glass or the glass-like solid. These processes are associated with the electron-vibrational and conformational rearrangements, electron density transfer, shifts of atoms, and with variations (reversible or irreversible) of the local structure of the glass. The processes of electron disproportionation are accompanied by redox chemical reactions. Specific features of these processes are determined by the structure of the glass (the network geometry and the characteristic features of the electronic structure).

Currently the most common view on the structure of glasses is that the borate, germanate, silicate, and phosphate glasses are built of the main structural units $BO_{3/2}$, $BO_{4/2}$, $GeO_{4/2}$, $SiO_{4/2}$, and $OPO_{4/2}$ (the indices 3/2 and 4/2 point to the fact that the B, Ge, Si, and P atoms are linked to the glass network via three or four bridging oxygen atoms), which are transformed during the synthesis into progressively more complex structures,[91-98] i.e. mono-, di-, and oligomeric anions. The latter are converted, in their turn, into diverse macroanions (MA) of linear $(SiO_3^{2-})_n$, layered (philo) $[BO_{3/2}(O^-)]_{mn}^{2nn}$, or network (texto) $(Si_2O_5^{2-})_n$ type or into clusters with any number of atoms. Thus, glass can be treated as a solid, porous at the molecular level, with an immense inner surface, the channels and pores of which are occupied by modifying cations, and dangling bonds also emerge there.[38,84]

The dangling chemical bonds and modified structural groups give rise to a set of various defects of donor or acceptor character. The frequency of origination of these sites (defects) is determined by the free energy of formation of each of them. At the same time, if a glass contains no paramagnetic ions introduced during the synthesis, it is a diamagnetic material. If singly charged positive and negative defects could arise during the synthesis of glasses, they would correspond to high concentrations of unpaired electrons. However, EPR studies indicate unambiguously that their concentration is lower than $10^{15}\,cm^{-3}$ and can be brought to $10^{17}-10^{19}\,cm^{-3}$ in amorphous Si and Ge only by various external factors.[99,100] The presence of singly charged positive and negative defective sites would also cause substantial conductivity at low temperatures, but no contribution of this conductivity has been found so far.[83]

These contradictions have been resolved in terms of the theory of chemical bonding describing the characteristic features of the electronic structure of glass. A great contribution to the development of this theory has been made by Anderson.[101] He noted that in amorphous semiconductors and glasses, electrons tend to be combined in pairs thus forming stable states. The stability of the states with paired electrons is due to the fact that the energy of the Coulomb repulsion is lower than the energy of the electron-phonon interaction; the polarisability of the solid lattice surrounding the electrons should also be taken into account. Later Street and Mott[65] and Kastner, Adler, and Fritzche[102] developed (almost contemporaneously) the theory of localised states in a glass, which are positively and negatively charged defects (D^+ and D^-, respectively). These authors claim that a half of the defects remain unoccupied with electrons and acquire a positive charge (D^+ site), and the rest of the defects are occupied by electron pairs and have a negative charge (D^- site). These studies made it possible to explain the diamagnetism of glass and the linearity of the variation of the molecular heat capacity of glasses at low temperature.

Lucovsky[103] and Greaves[104] have developed these views in relation to glassy SiO_2. They proved that the abstraction of an electron from a D^- site or the addition of an excited electron from the valence band to a D^+ site result in the formation of a paramagnetic neutral D^0 site. Within the framework of quantum chemistry, all these models are based on the fact that the heterolytic rupture of chemical bonds yielding D^+ and D^- sites is energetically more favourable than the homolytic rupture of bonds leading to the formation of sites with unpaired spins. The antibonding state has an electronic configuration that is described by the D^+ state located in the forbidden gap below the conduction band, while the D^- state has a completely filled valence electronic shell, forms no additional bonds, and is located in the forbidden gap above the valence band. The smaller the polarisation of the lattice caused by the D^- site, the stronger the polarisation effect caused by the D^+ site.

All the models considered above describe the same effect; they go under the general name of the model of charged defective sites, which is valid only for fairly simple structures in the glass.[83] A more adequate model, namely, the model of quasimolecular defects, has been suggested by Popov.[105] This model involves the realisation of multicentre multielectron bonds in glasses. This model shares a number of traits with the Dembovskii model, which develops the theory of 'soft' three-centre bonds (arising due to the fact that the bonds are formed by antibonding electrons).[106] It is clear that the extension of the above concepts to the description of the geometric and electronic structure of glass has not yet been completed.

If we suggest, from general chemical knowledge, that an analogy between the processes of structural disordering in glass and dissociation reactions like $2H_2O \rightleftharpoons H_3O^+ + OH^-$ in aqueous media can be drawn legitimately,[55,101-105] then the acid–base concept applied to oxide melts and glasses correlates quite well with views on the redox disproportionation yielding D^+ and D^- sites. According to this concept, the heterolytic rupture of bonds leads to the formation of a D^+ hole site on the oxygen atom bound to three silicon atoms $[^+O(SiO_{3/2})_3]$ and of a D^- two-electron site on the oxygen atom bound to one silicon atom $[SiO_{3/2}O^-]$. In the presence of foreign metal oxides, the scheme by which the defective sites arise changes: metal cations act as the D^+ sites instead of $^+O(SiO_{3/2})_3$. This refers also to three other main types of oxide glasses: borate, germanate, and phosphate glasses.[83,107]

The modelling of the formation and stabilisation of ions in UOS at the level of local reactions, with allowance for the disproportionation of the electron density between the selected atomic centres, makes it possible to explain completely the processes of stabilisation of ions and switching of bonds both during the synthesis of glasses and following various kinds of physical treatment of them.[108] Moreover, it follows from the data presented in our review that a key role in the stabilisation of ions in UOS in low-temperature glasses is played by hydrogen bonds, due to which a glass-like network is formed. In this case, protons act as the mobile cationic framework; after the addition of an unpaired electron to a metal cation, protons occupy energetically favourable positions in its environment and lead to the redistribution of the electron density due to local disproportionation reactions.

Thus, allowance for the structural features of glass, the presence of dangling and multicentre bonds leading to the initial localisation of the electron pairs, and the presence of a mobile cationic ensemble determine the subsequent cooperative processes based on redox reactions, which are similar as regards the nature of the elementary step and lead to the formation and stabilisation of ions in UOS.

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