Russian Journal of General Chemistry, Vol. 72, No. 4, 2002, pp. 632–641. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 4, 2002, pp. 678–687.

Surface Nanosegregation of Chemical Composition in Complex Oxides

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Received October 1, 2001

Abstract—A brief review of theoretical and experimental results in the field of surface nanosegregation of chemical composition of oxides (principal components), stimulated by temperature or other factors, is given. Experimental data, obtained exclusively for monocrystals *in situ* and *post situ* by Auger electron spectroscopy, X-ray electron spectroscopy, X-ray spectral microanalysis, and secondary-emission spectroscopy are considered. The model concepts assume a diffusion mechanism of segregation, and the theory parameters contain elastic constants and crystallochemical characteristics of substances. All the oxides investigated are divided into groups with different segregation degrees. The models allow prediction of the character of changes of the surface composition of oxides: segregate type and degree of nonstoichiometry.

1. INTRODUCTION

Many functional (catalytic, photo- and electrochromic, pyro- and ferroelectric, superconducting, etc.) properties of oxides are surface-sensitive. The character of surface electronic states and the parameters of surface electrical double layer [1] are essentially dependent on the chemical composition of surface nanolayers, which is an important factor influencing oxide properties. The segregation of chemical composition on the surface is induced both by external (temperature, pressure, radiation, the character of atmosphere, etc.) and internal factors (the concentration of components and admixtures, the type of chemical bonds, kinetic and diffusion processes, etc.).

The segregation of admixtures at metal grain boundaries and the segregation of components in dilute binary alloys have been studied in sufficient detail [2, 3]. The segregation processes of nanoscaled components themselves have received much less study. The model concept of dilute solid solutions and the monolayer approach seem to be problematic in this case. The works of Lo and Somorjai [4] (reversible change of surface composition in $SrTiO_3$ crystals) and Tomashpol'skii *et al.* [5, 6] (intermediate nanolayers and supporting films, consisting of titanium and titanium oxide in $BaTiO_3$ and $SrTiO_3$ films) seem to be the first to attach attention to thermally stimulated surface segregation of chemical composition of oxides. Later on, the great significance of segregation processes for surface chemistry and modern technologies has become evident. Surface chemical bonds and surface states in oxide catalysts, electrochemical anodes, chemical sensors, and functional elements for nanoelectronics are functions of the chemical composition of the surface, and optimal conditions of technological annealing of intermediates and of exploitation of products (made from monocrystals, ceramics, and films) at elevated temperatures, under radiation, and in various atmospheres, are evidently dependent on surface segregation phenomena. Moreover, oxides have wide possibilities for realizing different types of electronic structure (metallic, semiconductor, or dielectric) and of chemical bonds (from ionic to covalent) and can serve as model systems in studying surface segregation in multicomponent compounds.

This review is the first attempt of summarizing results on thermally stimulated surface nanosegregation on pure oxide surfaces. The review makes no pretence to the completeness of consideration and focuses mainly on general problems. Simple models of segregation in oxides are described, based on the concepts of crystallochemistry and electrostatics. The models explain some segregation mechanisms and experimental data and predict the character of segregation and the type of segregate. Experimental results obtained mostly at high and ultrahigh vacuum for monocrystals of complex oxides, whose surface was vacuum-cleaned, particularly by ion etching are presented. A classification with respect to the ability of complex oxides to segregation, to the segregation degree, and to the segregate type is given. Experimental estimates for the activation energy of diffusion as the main segregation mechanism are given. Examples of thermally stimulated surface nanosegrega-

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tion in a number of complex oxides, including those with technically important ferroelectric, piezoelectric, and pyroelectric properties are presented.

2. METHODOLOGICAL ASPECTS

The main experimental methods for studying segregation are Auger spectroscopy, X-ray photoelectron spectroscopy, X-ray spectral microanalysis, scanning electron microscopy, and secondary-emission spectroscopy. Two kinds of regimes are used, *in situ* and *post situ*, differing in measurement conditions. In the first case, the composition is measured in the course of stepwise heating, with keeping the system for 10–20 min at every temperature in a vacuum of 10^{-5}–10^{-8} Pa. In the second case, the composition is measured after cooling the surface from a given temperature after heating in a vacuum or in the atmosphere. The measurements are carried out on polished cuts, cleavage surfaces, and natural faces of oxide monocrystals. The sample surface is usually controlled using low-energy electron diffraction, which allows determination of the purification degree, the character of ordering, the phase composition, and some structural features of surface layers. The surface purification techniques include ion etching, controlled heating, and preparation of fresh cleavage surfaces.

For the sake of interpretation of experimental concentrations, practically all segregation models make use of the diffusion mechanism of motion of segregate to surface [2, 7]. Confining ourselves with several surface nanolayers and applying the steady-state diffusion equation, we obtain the following expression:

$$(C - C_0)/C_0 = \Delta C/C_0 = -\rho L^2/\tau C_0 D,$$

where C, C_0, and ΔC are the surface component concentration (in atomic fractions) after and before diffusion and their difference, respectively, ρ is the bulk component concentration, L is the diffusion length, τ is the diffusion time, and D is the diffusion coefficient. Assuming D to be exponentially related to temperature as

$$D = D_0 \exp(-E/RT),$$

where D_0 is a pre-exponential factor and E is the diffusion activation energy, the dependence logarithmically becomes

$$\ln(\Delta C/C_0) = \ln(\rho L^2/\tau C_0 D_0) + E/RT.$$

If there are rectilinear parts in the experimental dependence of $\ln(\Delta C/C_0)$ on $1/T$, the experimental value E^{exp} of diffusion activation energy can be determined from the slope.

3. MODEL CONCEPTS

In [7], we considered in detail a crystallochemical model in which the diffusion activation energy of a segregate is assumed to be equal to the work of overcoming the resistance of neighboring ions plus the difference in the bond energies of the segregate in different positions. Elementary diffusion jumps of the segregate from one lattice position to another determine the activation energy. Ion transport can proceed by either the vacancy or the interstitial mechanism. Segregation usually occurs under moderate heating, whereas anionic vacancies require activation energies of up to 480 kJ/mol at 1200 K [8]. Therefore, the most probable is the interstitial mechanism when

$$E^{\mathrm{calc}} = A + \Delta U, \qquad (1)$$

where A is the work of strain of neighboring ions and ΔU is the difference in the bond energies.

Since the crystallochemical radii of segregate ions are usually larger than cavities, segregate diffusion is accompanied by elastic strain of neighboring ions. This follows both from the segregation reversibility up to a certain temperature and from the analogy with the segregation model for binary alloys [2]. The elastic strain work is

$$A = 3\pi M R_{\mathrm{O}}(R_{\mathrm{seg}} - h/2)^2/4\rho s_{ij} a^3, \qquad (2)$$

where M is the molecular weight, s_{ij} is the elastic compliance tensor, R_{O}, R_{seg}, and h are the crystallochemical dimensions of oxygen ions, segregate, and cavities, and a is the lattice period.

The expression for electrostatic energy with no account for repulsion forces (whose contribution usually does not exceed several per cent) is

$$U = -\sum_k (\alpha^2 Z_1 Z_2 e^2 N)/r_{1k}, \qquad (3)$$

where α is the ionicity degree for compounds with an intermediate bond type (the fraction of the total charge of the ion), z_1 and z_k are the total charges of the segregate ion and of the kth ion of the surrounding, respectively, and N is Avogadro number.

Finally,

$$E^{\mathrm{calc}} = [3\pi M R_{\mathrm{O}}(R_{\mathrm{seg}} - h/2)^2/4\rho s_{ij} a^3] \pm \Delta \left| -[\sum_k \alpha^2 Z_1 Z_k e^2]/r_{1k} \right|. \qquad (4)$$

Table 1. Characteristics of oxide crystals and parameters of the method of elemental analysis with use of relative sensitivity factors P

Compound and properties	Method of growing	Surface type	Orientation	Element	Energy of Auger transition, eV	P factor
$BaTiO_3$, ferroelectric	From solution in melt	Natural face	{001}	Ba	584	Ba/Ti = 0.46
				Ti	380	Ba/O = 0.50
				O	510	O/Ti = 0.91
$SrTiO_3$, ferroelectric	Chokhralsky	Polished cut	{011}	Sr	104	Sr/Ti = 0.42
				Ti	380	Sr/O = 0.46
				O	510	
$PbTiO_3$, Ferro-, piezo-, pyroelectric	From solution in melt	″	{001}	Pb	90.94	Pb/Ti = 0.44
				Ti	380	Pb/O = 0.48
				O	510	

Table 2. Temperature ranges and degrees of reversible thermally stimulated surface nanosegregation in oxide crystals

Compound	T_1–T_2, K	Segregate	Segregation degree[a]
$SrTiO_3$	600–900	Ti	0.21
$BaTiO_3$	520–735	Ti	0.30
$PbTiO_3$	360–550	Ti	0.72

[a] $[(I_A/I_B)_{T_1} - (I_A/I_B)_{T_2}]/(I_A/I_B)_{T_1}$, where A and B are cations and I is the amplitude of Auger signal.

Table 3. Characteristics of irreversible thermally stimulated surface nanosegregation for some oxide crystals

Compound	Maximum heating, K	T_2, K	Segregate	Segregation degree[a] at room temperature
$SrTiO_3$	1500	900	Sr	0.19
$BaTiO_3$	1400	735	Ti	0.32
$PbTiO_3$	1150	550	Ti, Pb	1.0 3.7[b]

[a] $|(I_A/I_B)_{init} - (I_A/I_B)_{fin}|/(I_A/I_B)_{init}$. [b] At 1050 K.

The sign ± means that the segregate, moving through interstices, attains a position identical to the initial one (say, octahedral cavity), so that the bond energy will differ only in sign but not in magnitude.

4. EXPERIMENTAL RESULTS. COMPARISON WITH MODEL CONCEPTS

Main quantitative results on thermally stimulated surface nanosegregation were obtained for monocrystals of $SrTiO_3$, $BaTiO_3$, and $PbTiO_3$ by means of Auger electron spectroscopy *in situ* and *post situ* [7]. Some characteristics of the crystals and of the methods of their analysis are given in Table 1.

Heating of crystals causes thermally stimulated surface nanosegregation starting from temperature T_1. However, thermally stimulated surface nanosegregation is reversible up to temperature T_2, and the composition is completely restored after the temperature is lowered to T_1 (Table 2).

Table 3 lists the parameters of irreversible segregation for the same crystals.

With $PbTiO_3$, the thickness of the layer of changed composition varies from several nanometers to several tenths of micron; the chemical composition of the surface layer can be rather complex. In particular, accumulation of a segregate leads to transformation of the surface and to formation of surface phases. For example, the formation of a TiO_{2-x} surface phase on $BaTiO_3$ and $PbTiO_3$ has been established [9–11].

To obtain E^{exp} values for $SrTiO_3$, $BaTiO_3$, and $PbTiO_3$, we plotted $\ln(|C - C_0|/C_0)$, where C_0 and C are the initial and final surface concentrations of titanium, against inverse temperature (Fig. 1) [7].

For each of the three compounds (possessing the same perovskite structure), the linear dependences involve characteristic inflections, indicating that there are two diffusion activation energies, E_1 at low temperatures and E_2 at high temperatures (Table 4).

For comparing experimental data with calculations, Eqs. (1)–(4) were used with putting parameters for the above compounds. The elastic constants were taken from [12] or calculated by the authors [7]. The

Table 4. Experimental diffusion activation energies of Ti, kJ/mol

Compound	E_1^{exp}	E_2^{exp}
$SrTiO_3$	173 ± 30	33 ± 7
$BaTiO_3$	90 ± 20	25 ± 5
$PbTiO_3$	67 ± 10	17 ± 4

Table 5. Calculated works of overcoming elastic forces A, bond energies ΔU, ionicity degrees β^{a}, and diffusion activation energies for oxide crystals (E, kJ/mol)

Compound	A_1	A_2	$\lvert \Delta U \rvert$	β	$E_1^{\mathrm{calc\,b}}$	$E_2^{\mathrm{calc\,c}}$
$SrTiO_3$	85.4	42.2	76	0.75	161.4	33.8
$BaTiO_3$	23.1	21.9	52	0.62	75.1	30.1
$PbTiO_3$	19.0	20.8	41	0.55	60.0	20.2

[a] Effective ionic charges characterizing intermediate bond types. [b] $E_1^{\mathrm{calc}} = A_1 + \lvert \Delta U \rvert$. [c] $E_2^{\mathrm{calc}} = \lvert \Delta U \rvert - A_2$.

Table 6. Values of s_{11} in the directions <001> and <00.1> and the experimental data on the degree of thermally stimulated surface nanosegregation for various complex oxides

Compound and main properties	$1/s_{11}$[a]	Segregation degree[b]
$SrTiO_3$ (ferroelectric)	0.267	0.19
$LiNbO_3$ (pyro- and piezoelectric)	0.169	0.20
$LiTaO_3$ (pyro- and piezoelectric)	0.195	0.22
$BaTiO_3$ (ferroelectric)	0.120	0.32
$Gd_2(MoO_4)_3$ (ferroelectric)	0.067	0.40
$PbTiO_3$ (ferro-, pyro- and piezoelectric)	0.08	1.00
$Pb_5Ge_3O_{11}$ (ferro- and pyroelectric)	0.053	1.00

[a] $1/s_{11} = E \times 10^{12}$ m^2/H. [b] $[(I_A/I_B)_{\mathrm{init}} - (I_A/I_B)_{\mathrm{fin}}/(I_A/I_B)_{\mathrm{init}}$.

ionicity degree (the fraction of the total ionic charge averaged over separate bonds), as a characteristic of the intermediate type of bonds in these compounds [13], was chosen within 0.75–0.55, which agrees, for example, with the reported effective charge of $BaTiO_3$ (0.6) [14]. Such approach is consistent with the notion of bonds in these compounds as mostly ionic, with increased ionicity on the surface [15]. The calculation results are summarized in Table 5.

The fact that the experimental and calculated diffusion activation energies fairly fit each other for the three "model" crystals of complex oxides not only gave evidence for the validity of the interstitial diffusion model which is capable of explaining the mechanism of thermally stimulated surface nanosegregation, but also allowed us [7] to establish some regularities of predictive importance. It was shown that, in the first approximation (with no account for the bond energy), the degree of segregation of oxide compounds decreases with elastic compliance or with increasing Young modulus E (Table 6).

The exception for lithium tantalate and lithium niobate at close degrees of thermally stimulated surface nanosegregation is explained by the inaccuracy in the elastic constants.

This model relates to initial stages of thermally stimulated surface nanosegregation in the range of relatively low temperatures. The nature of segregation can change at higher temperatures. With $SrTiO_3$ or $PbTiO_3$, for example, the segregate type changes: Sr or Pb, respectively, are accumulated on the surface, instead of Ti. The high-temperature segregation is explained in terms of a model [3] assuming formation of a quasiliquid layer on the surface, where the solubility of a given component differs from its solubility in bulk crystal. The possibility of existence of such a layer in oxides was shown in [16] by the example of $BaTiO_3$. In this case, the nature of thermally stimulated surface nanosegregation for oxides like $A_mB_nO_p$ at high temperatures can be qualitatively explained on the basis of the phase diagrams A_mO_x–B_nO_y. To determine the segregate type and to estimate T_1, one should examine the homogeneity region with accounting for the following criteria. (1) The onset and degree of low-temperature segregation are determined by the temperature of formation of the liquid phase: The lower this temperature, the earlier is the onset of thermally stimulated surface nano-

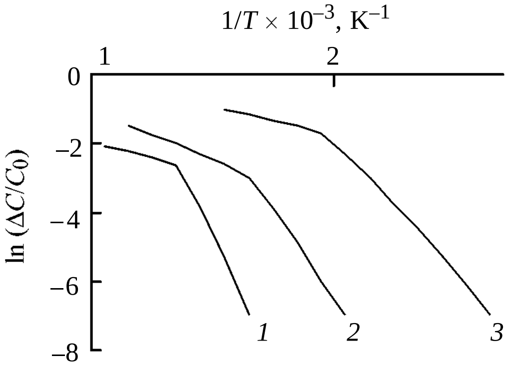

Fig. 1. Temperature dependence of $\ln(\Delta C/C_0)$ for thermally stimulated surface nanosegregation of titanium in oxides: (*1*) $SrTiO_3$, (*2*) $BaTiO_3$, and (*3*) $PbTiO_3$.

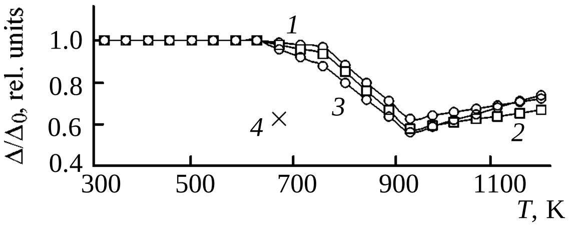

Fig. 2. Dependence of the secondary emission output from the surface of monocrystals of $PbTiO_3$ on the temperature of annealing (*1*–*3*) in air and (*4*) in a vacuum at the annealing temperature 600 K and at the probe energy 9 keV (three series of measurements). Raster dimensions, μm^2: (*1*) 24×18, (*2*) 120×90, and (*3*) 480×360.

segregation and the higher is its degree. (2) The segregate is a component (ion) which is better soluble in the liquid phase than in the solid phase and which forms better meltable compounds, eutectics, peritectics, etc. If there are liquid phases to the left and to the right of the homogeneity region of the oxide compound, that segregate will be accumulated on the surface whose solubility in one liquid phase is higher that the solubility of another segregate in the other liquid phase. For example, in the state diagrams of BaO–TiO_2 and SrO–TiO_2, a liquid phase enriched with titanium forms to the right of the 1/1 compound at a temperature much lower than liquid phases enriched with barium or strontium. Therefore, the titanium ion will be a segregate for both the oxides at the initial stage of thermally stimulated surface nanosegregation, and the segregation will first start in $BaTiO_3$, since its temperature of liquid phase formation of more than 100 K lower. At high temperatures, liquid phases exist both to the right and to the left of the 1/1 compound. In the case of $BaTiO_3$, the solubility of titanium in the right-hand liquid phase is higher than the solubility of barium in the left-hand liquid phase. The reverse situation occurs with $SrTiO_3$. Therefore, the surface segregation of Ti proceeds in $BaTiO_3$, whereas the segregation of Sr proceeds in $SrTiO_3$ at high temperatures, as is confirmed by experiment.

5. FORMATION OF SURFACE COMPOUNDS BY THERMALLY STIMULATED SURFACE NANOSEGREGATION

Thermally stimulated surface nanosegregation results in accumulation of certain components of an oxide compound on the surface. As a result, a new surface compound can form, stable within a certain temperature range. For example, a monocrystalline TiO_{2-x} layer 5 nm or more in thickness and stable at room temperature, forms at a temperature above 550 K in lead titanate [face (100)] subjected to heating up to 1100 K in air and in ultrahigh vacuum both *in situ* and *post situ* [17]. The surface of the resulting titanium dioxide film is faceted, and the density of defects in the layer is higher than in the mother crystal. The temperature range of formation of this surface phase is about 250 K, while above 900 K lead segregation is observed.

The character of surface chemical reactions does not depend qualitatively on pressure. The difference is in quantitative parameters, specifically in the segregation degree and in the partial reduction of oxygen in titanium dioxide.

Special investigation on the character of the reduction and on the pressure effect on the formation of surface titanium dioxide by secondary-emission spectroscopy [18]. The problem was in relating the secondary-emission output to the change in the surface phase composition, produced by thermally stimulated surface nanosegregation. The emission measurements were carried out mainly in $PbTiO_3$ crystals annealed in air, as well as in a crystal annealed in ultrahigh vacuum at 600 K. The dependences of the emission output on the annealing temperature in air and in a vacuum are shown in Fig. 2. The emission output as a whole varies in the same direction as the cationic chemical composition. The single point *4* in Fig. 2 relates to the emission output value Δ of 0.63, corresponding to annealing in a vacuum at 600 K in the process of thermally stimulated surface nanosegregation of a crystal of $PbTiO_3$ with the layer of TiO_x on its surface. In this case, the Pb/Ti ratio is 0.93 (Fig. 2.). It is seen that the emission output from TiO_x is considerably lower as compared with that in close conditions of annealing in air. This corresponds to the difference in the emission outputs from a semiconductor and from a dielectric (the latter should be much higher). The above Pb/Ti ratio is attained, when the crystal is annealed in air, only at 800 K. The emission output would be 0.77 at that temperature. The difference in the emission outputs from TiO_2 and TiO_x films (0.63 and 0.77) is about 18%, which corresponds to a deficit of oxygen of about 0.6 mol. This value agrees with our earlier estimates from data of Auger spectroscopy [19] (20–30% deficit).

Structural models of the surface compound were also considered in [19]. A structural mosaic of fragments of the $PbTiO_3$ and TiO_2 phases (Fig. 3) is the most reliable model of the surface phase resulting from thermally stimulated surface nanosegregation. The degree of development of the mosaic structure depends on the depth of the vacuum on annealing. Complete covering of the support by the surface phase is possible in ultrahigh vacuum.

6. PECULIARITIES OF THERMALLY STIMULATED SURFACE NANOSEGREGATION IN VARIOUS OXIDE COMPOUNDS

There is abundant evidence showing that the degree of surface segregation in complex oxides can vary over a wide range. For example, many oxides can be arbitrarily divided into three groups. The first group includes compounds whose surface is only slightly influenced by temperature, specifically $LiNbO_3$ and $LiTaO_3$. The second groups of oxide compounds contains $SrTiO_3$, $BaTiO_3$, $Gd_2(MoO_4)_3$, and $Bi_4Ti_3O_{12}$. These compounds feature higher degrees of thermally stimulated surface nanosegregation than first-group oxides, but their chemical composition and surface structure are still determined by the mother phase. The third group include oxide compounds ($PbTiO_3$, $Pb_5Ge_3O_{11}$, $KNbO_3$, etc.) which undergo profound surface transformations and changes in chemical composition to give new surface phases. Change of segregate at changing temperature is also typical of this group. Let us consider the above groups in more detail.

Group I ($LiNbO_3$, $LiTaO_3$). The thermally stimulated surface nanosegregation in lithium niobate was investigated in [20]. Crystals of $LiNbO_3$ were annealed in a vacuum of 10^{-7} Pa in the stepwise heating mode with a dwell time of 10 min. The elemental composition was determined by Auger spectroscopy. Figure 4 depicts the *in situ* temperature dependences of the Li/Nb ratio which is proportional to the concentration ratio. As seen from the figure, the surface composition of layers about several nanometers in thickness changes irreversibly after annealing at about 1100 K, due to niobium segregation; the segregation degree is 0.20, implying that the surface of lithium niobate is relatively stable with respect to thermally stimulated surface nanosegregation. According to [21], the mechanism of the irreversible segregation of niobium in a micron surface layer consists in preferential diffusion of lithium to the bulk, so that the Li_2O/Nb_2O_5 ratio becomes less than unity. In this case, decreased, compared with stoichiometric, Li/Nb and O/Nb ratios and increased O/Li ratio on the surface. Comparison with the data of Auger spectroscopy shows that the mechanism of initial stages of thermally stimulated surface nanosegregation is similar to that under consideration. Thus, the process of thermally stimulated surface nanosegregation in lithium niobate begins in layers about several nanometers thick on annealing at about 1100 K and leads to decreased Li/Nb ratios. At the same time, the surface of lithium niobate is one of the most stable thermally, other conditions being equal.

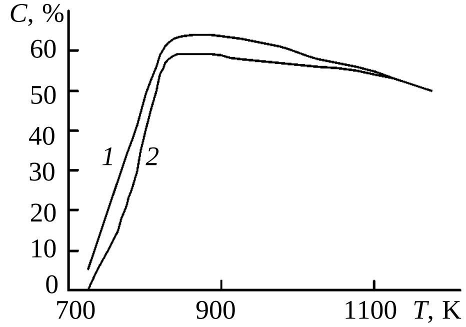

Fig. 3. Dependence of the content of the TiO_2 phase on the surface of monocrystals of $PbTiO_3$ on the temperature of annealing in air by (*1*) secondary-emission and (*2*) Auger electron spectroscopy.

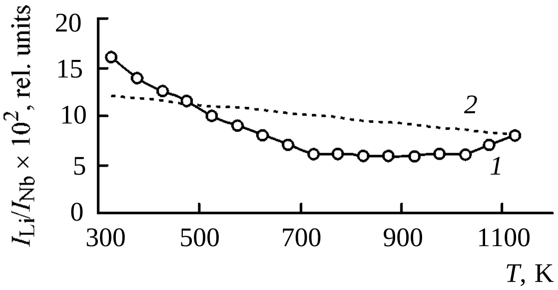

Fig. 4. *In situ* temperature dependence of the (*1*) Li/Nb Auger signal and (*2*) I_{Li}/I_{Nb} value at room temperature after annealing at 1120 K.

Group II [$SrTiO_3$, $BaTiO_3$, $Gd_2(MoO_4)_3$, $Bi_4Ti_3O_{12}$]. The thermally stimulated surface nanosegregation in the first two compounds was considered above. The thermally stimulated surface nanosegregation in the complex oxides $Gd_2(MoO_4)_3$ and $Bi_4Ti_3O_{12}$ was investigated in [22]. On early stages of segregation the surface is enriched with molybdenum, up to 24% in place of 18% by stoichiometry (Fig. 5). The surface segregation of gadolinium proceeds at higher temperatures. After annealing at 1270 K and cooling to room temperature, the surface molybdenum concentration is 17 at. %, and the concentration of gadolinium is 13 at. % (instead of 6 at. % of gadolinium at early stages of segregation). T_2 = 600 K and $\Delta C/C_0$ = 0.40 for irreversible thermally stimulated surface nanosegregation. Thus, a slight deficiency of molybdenum arises on the surface of gadolinium molibdate after high-temperature annealing and cooling.

For the oxide $Bi_4Ti_3O_{12}$, the temperature dependences of the Bi/Ti and O/Ti ratios point to invariable

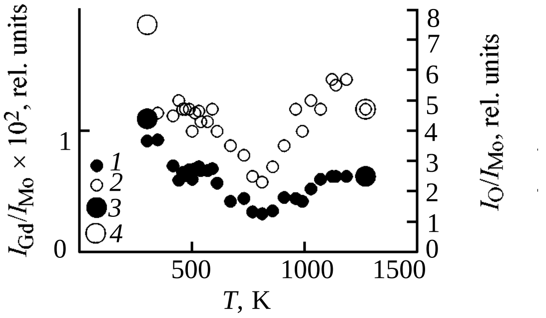

Fig. 5. *In situ* temperature dependence of the (*1*) Gd/Mo and (*2*) O/Mo Auger signals for the {001} surface of $Gd_2(MoO_4)_3$ and the (*3*) I_{Gd}/I_{Mo} and (*4*) I_O/I_{Mo} values at room temperature after annealing at 1170 K.

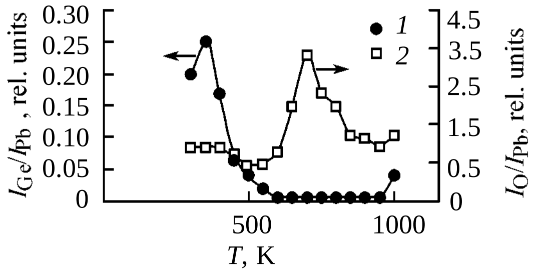

Fig. 6. Temperature dependence of the amplitude ratios of the (*1*) Ge/Pb and (*2*) O/Pb Auger signals for the (00.1) natural face of lead germanate.

surface composition within the temperature ranges from room temperature to 500 K, from 600 to 900 K, and from 950 to 1070 K. This corresponds to a number of surface phases: with an excess of titanium (**I**), $Bi_4Ti_3O_{12}$ (**II**), and $Bi_2Ti_2O_7$ (**III**). In addition, there are islands of the TiO_x surface phase at temperatures below 1100 K. The segregate cation is titanium, T_2 = 580 K and $\Delta C/C_0$ = 0.60 for irreversible thermally stimulated surface nanosegregation.

Group III ($PbTiO_3$, $Pb_5Ge_3O_{12}$, $KNbO_3$, $PbFe_{0.5} \cdot Nb_{0.5}O_3$). The thermally stimulated surface nanosegregation in lead titanate is described above. The thermally stimulated surface nanosegregation of crystals of lead germanate obtained from its solution in a melt, was studied *in situ* by Auger spectroscopy [23]. The crystals were purified with a solvent of chemically pure gradw and also with argon ion etching in a high-vacuum chamber.

The temperature dependences of the Ge/Pb and O/Pb ratios, shown in Fig. 6, can be divided into three regions: 293–570, 570–870, and above 870 K. In the first region, the Ge/Pb and O/Pb ratios show that the lead germanate surface is enriched with lead. At 570 K, there occur complete segregation of lead on the surface and formation of an oxide layer, probably, of variable composition PbO_x. In the second region, the oxygen content grows due to increasing concentration of adsorbed oxygen (CO and CO_2 molecules), which is further descreased to a constant level by carbon desorption. In the third region (until 920 K), the composition of the surface phase of lead oxide changes only slightly. Melting and lead loss start above this temperature, so that only germanium and oxygen lines remain in the Auger spectrum. Comparing the lead-enrichment processes in lead germanate in the bulk and on the surface, one can note that composition changes in the bulk occur above 870 K, whereas the temperature of thermally stimulated surface nanosegregation decreases to 400 K. Only lead oxide is present on the surface at 570 K. Enrichment with lead starts on the surface and develops into the bulk. Therefore, the surface of lead germanate changes chemical composition already at temperatures below 450 K, which is especially noticeable in thin films. For the {00.1} face of $Pb_5Ge_3O_{11}$, T_2 = 350 K and $\Delta C/C_0$ = 1.00 for irreversible thermally stimulated surface nanosegregation.

In the compound $PbFe_{0.5}Nb_{0.5}O_3$, where the Ti cation has been replaced by Fe and Nb, thermally stimulated surface nanosegregation is similar to that observed in $PbTiO_3$ [22] (Fig. 7). Hence, the mechanism of thermally stimulated surface nanosegregation in this compound is the same as in lead titanate. At 650–900 K and above 1150 K, lead is absent on the (100) surface, whereas the Fe/Nb ratio is stable enough. For the (100) surface of $PbFe_{0.5}Nb_{0.5}O_3$, T_2 = 330 K and $\Delta C/C_0$ is equal to 1.00 (Fe, Nb) or 1.26 (Pb) at 970 K.

Figure 8 [24] represents a typical dependence of the K/Nb ratio on annealing temperature for the natural monocrystal face {100}. The K/Nb curves have a minimum, like those for barium titanate and some other complex oxides [7]. Below 700 K, the surface concentration of Nb increases and that of K decreases (analogously to Ti and Ba, respectively, in barium titanate). The peculiarity of the temperature dependences of K/Nb and Nb is the presence of anomalies at 500 and 700 K, which are observable irrespective of the energy of Auger transitions in different monocrystals of potassium niobate. At the same time, there is no anomaly in the temperature curves for potassium. The anomalies are assumed to occur because of phase transitions in potassium niobate at 498 and 708 K. In the region of phase transitions, the elastic constants are high values, the diffusion activation energy grows, which, in its turn,

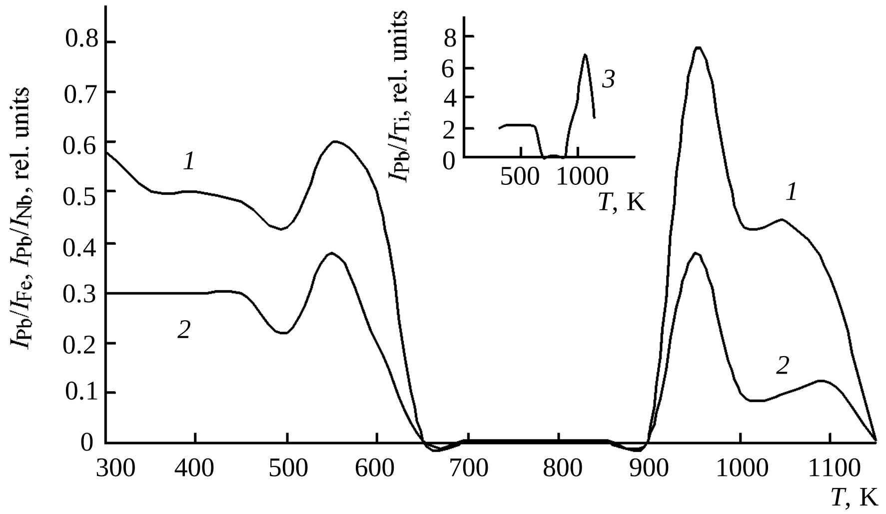

Fig. 7. *In situ* temperature dependence of the Auger signal from the {001} surface of $PbFe_{0.5}Nb_{0.5}O_3$: (*1*) Pb/Fe and (*2*) Pb/Nb. (*3*) Temperature dependence of the I_{Pb}/I_{Ti} ratio for $PbTiO_3$.

enhances niobium diffusion to the surface. The second important peculiarity of the thermally stimulated surface nanosegregation in potassium niobate is the fact that T_2 is lower than room temperature, whereas $\Delta C/C_0$ = 0.36 for irreversible thermally stimulated surface nanosegregation.

7. EXAMPLES OF OTHER FACTORS INITIATING THERMALLY STIMULATED SURFACE NANOSEGREGATION

As mentioned in the introduction, along with temperature, some other factors can induce surface segregation of chemical composition in oxides. One of such factors is irradiation of the surface. It was discovered [25] that irradiation of $BaTiO_3$ and $PbTiO_3$ surfaces with argon ions initiates vigorous segregation of titanium whose concentration increases with irradiation time. Herewith, the character of changes in the chemical composition conflicts with the generally accepted cascade theory [26] which predicts that barium titanate surface should be enriched with barium, while lead titanate surface, with lead. The degrees of thermally stimulated surface nanosegregation in these compounds are 0.32 and 1.0, respectively; these values correlate with the segregation degrees obtained by ionic irradiation of these crystals: 0.32 and 0.82. Herewith, the trends in composition with temperature and irradiation time are roughly similar. These results suggest that the segregation observed is caused by radiation-stimulated diffusion of titanium to the surface. Mechanistically, this process is similar to the thermally stimulated process, when titanium ions move to the surface through interstices with the diffusion activation energy $E = A \pm \Delta U$, where A is the work of overcoming continuum elastic forces by a segregate and ΔU is the difference in the segregate bond energy at the beginning and at the end of the diffusion jump. The irreversible segregation onset temperature T_2 is 620 and 550 K for $BaTiO_3$ and $PbTiO_3$, respectively. Such heating can be attained by bombarding dielectric oxides with ions with an energy of about 5 keV, taking into account that 75–95% of the energy of bombarding ions is converted into heat [27].

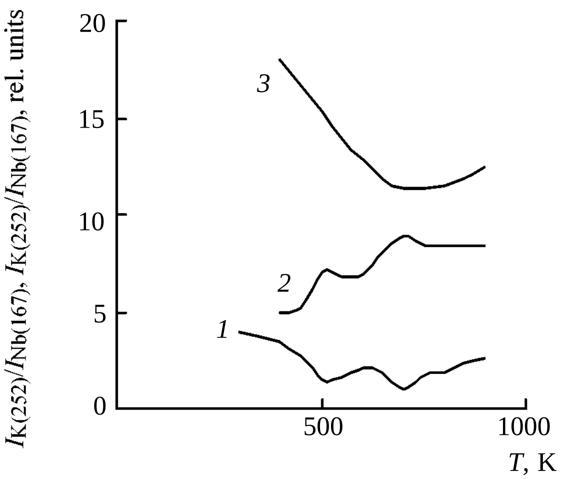

Fig. 8. Temperature dependences of the amplitudes of the Auger signals from the {100} surface of $KNbO_3$, proportional to element concentrations: (*1*) K(252)/Nb(167), (*2*) Nb(167), and (*3*) K(252). The curves were obtained for crystals purified by ionic sputtering. Parentheses show the energies of Auger transitions in eV.

8. CONCLUSION

Thus, the investigations on complex oxides led us to conclude that their capacity for surface nanosegregation can vary over a wide range: The surface composition of certain oxides remains almost invariable at high temperatures, while others undergo radical surface transformations not only on moderate heating, but also at room temperature (potassium niobate). Characteristic temperature ranges for thermally stimulated segregation are established, within which surface chemical composition can be recovered by cooling, whereas above the upper limit of these ranges segregation becomes irreversible. One of the manifestations of surface nanosegregation is formation of surface compounds (for example, titanium oxide on lead titanate) as either discontinuous structures or covering the surface completely. Surface segregation can be stimulated not only by temperature, but also, for example, by ionic radiation treatment (argon bombardment of barium titanate and lead titanate).

Although a comprehensive microscopic theory of surface nanosegregation has not yet been elaborated and the influence of the character of chemical bonds has been scarcely explored, the diffusion mechanism is one of the most probable. This is confirmed by the satisfactory agreement between the calculated diffusion activation energies of segregates and the experimental values obtained *in situ* for monocrystalline samples in ultrahigh vacuum.

The state of model concepts allows us, to a certain extent, to predict the type of segregate from phase diagrams and to predict the ability of a substance to segregation from values of elastic constants, although such predictions seem to be a first approximation.

Further investigations both on oxide compounds and on other types of multicomponent substances, as well as of samples as powders, ceramics, films, intermediates, and finished products, should essentially contribute to surface chemistry and favor development of high technologies.

ACKNOWLEDGMENTS

The author are grateful to N.V. Sadovskaya for assistance in selecting references related to segregation studies by secondary-emission spectroscopy.

The work is partly supported by the Russian Foundation for Basic Research (project no. 00-03-32614).

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