

# Surface Segregation in Ceramic Materials During Cooling or Under a Temperature Gradient

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## Abstract

*This paper concerns the dynamic segregation of impurities in ionic-covalent semiconducting compounds subject to large temperature changes. Simultaneously to the temperature gradient a chemical potential gradient takes place in these compounds. From the expression of the flux of mobile species (vacancies and cations in the considered materials) it has been shown that segregation (or precipitation) effects must be observed near surfaces. These effects are directly related to the mobilities of the different cations. The predicted effects are consistent with segregation layer thicknesses found experimentally in ceramic materials after cooling.*

*This analysis confirms the fact that in ceramic materials the dynamic segregation effects near surfaces during cooling must be taken into account in the interpretation of segregation results observed at room temperature. These changes in composition near surfaces can have important technological consequences, for example in ceramic powder preparation, and consequently in powder sintering or in the aging of ceramics subject to large temperature changes at high temperature.*

*Diese Arbeit befaßt sich mit der in-situ Konzentrationsverschiebung von Verunreinigungen in ionisch-kovalent gebundenen Halbleitermaterialien, die großen Temperaturschwankungen ausgesetzt sind. In diesen Verbindungen liegt neben dem Temperaturgradienten ein Gradient des chemischen Potentials vor. Ausgehend von der Flußgleichung beweglicher Teilchen (in den hier betrachteten Materialien: Leerstellen und Kationen) wird es bewiesen, daß Konzentrationsverschiebungen (oder Ausscheidungen) in der Nähe von Oberflächen beobachtbar sein müssen. Diese Effekte sind direkt mit den Beweglichkeiten der verschiedenen Kationen verbunden. Die theoretisch vorhergesagten*

*Effekte stimmen mit den an keramischen Teilen nach dem Abkühlen gemessenen Schichtdicken veränderter Zusammensetzung überein. Diese Untersuchung bestätigt, daß die bei keramischen Materialien nahe der Oberfläche während des Abkühlens auftretende in-situ Konzentrationsverschiebung bei der Auswertung von Konzentrationsverteilungen, die bei Raumtemperaturversuchen erhalten wurden, mit berücksichtigt werden muß. Die Änderung der oberflächennahen Zusammensetzung kann bei der Herstellung keramischer Pulver und dem zufolge beim Sintern bzw. beim Altern keramischer Bauteile, die bei hohen Temperaturen großen Temperaturschwankungen ausgesetzt sind, eine nicht zu vernachlässigende Rolle spielen.*

*On a étudié la ségrégation dynamique des impuretés dans des composés semi-conducteurs ionic-covalents soumis à d'importantes variations de température. On observe dans ces composés l'existence simultanée d'un gradient de température et d'un gradient de potentiel chimique. On montre à partir de l'expression du flux d'espèces mobiles (lacunes et cations dans le cas des matériaux considérés) que des effets de ségrégation (ou de précipitation) doivent être observés à proximité des surfaces. Ces effets sont directement reliés aux mobilités des différents cations. Les effets ainsi prévus sont en bon accord avec les valeurs de l'épaisseur de la couche de ségrégation déterminées expérimentalement dans des céramiques après refroidissement. Cette analyse montre que les effets de ségrégation dynamique se produisant à proximité des surfaces des céramiques lors de leur refroidissement doivent être pris en compte pour interpréter les résultats de ségrégation observés à température ambiante. Ces changements de composition près des surfaces peuvent avoir des conséquences technologiques importantes, notamment pour le qui est la*

*préparation des poudres de leur aptitude ou frittage, mais aussi du vieillissement de céramiques soumises à d'importantes variations de température lors de leur utilisation à haute température.*

## 1 Introduction

Segregation studies of cationic impurities on ceramic surfaces related to experimental and fundamental work have been the subject of increasing interest during the last decade. Indeed, the properties of ceramics depend to a large extent on the presence of impurities and on the structure and stability of surfaces and interfaces. The segregation effects can then severely alter the properties of materials and lead to their deterioration.

On the other hand, in ceramic elaboration, it is known that the powder preparation method can have a significant effect on the powder characteristics<sup>1</sup> and thus on the ceramic sintering. In particular, certain dopant layers which can be formed on powder surfaces may affect the diffusivity path for matter transport and have a profound influence on densification and microstructural developments.

It would then seem important to know the reasons for the propensity for some impurities to congregate near surfaces in ceramic materials. Unfortunately, few observations have been available until now in the literature and the spread in data is large. Indeed, experimental studies on surfaces present significant difficulties. Sensitive analytical techniques such as Auger spectroscopy or SIMS are now available and have led to much of the existing data, but the main difficulties arise from the preparation of samples. High purity crystals, with controlled amounts of dopants, are quite often not available and coupled effects cannot be avoided in segregation experiments. Indeed, the impurity concentration is  $\gg 10^{-5}$  ion/lattice site in most ceramics, while the intrinsic vacancy concentration is very small (typically  $10^{-8}$  vacancy/lattice site) even close to the melting temperature of most ceramics, due to the high energy of defect formation in these materials. Furthermore, the segregation observations have been performed at room temperatures. Changes in solute distribution can then occur during the quench as has been shown by Kingery and coworkers<sup>2,3</sup> in MgO. In general, and in agreement with the analysis by Matzke,<sup>4</sup> the depth of segregation near surfaces higher than 100 Å cannot be attributed to a high temperature equilibrium segregation. Such segregation depths may be due to cooling effects, as shall be seen later.

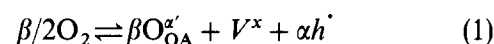
The present paper is concerned with the dynamic segregation of impurities during cooling in iono-covalent compounds. The approach is similar to that used elsewhere to describe changes in composition near surfaces in multicomponent oxides under chemical potential gradients.<sup>5,6,19</sup> It shows the difficulty in comparing theoretical results of equilibrium segregation at high temperatures with existing experimental data. The purpose of this paper is then to contribute to an understanding of the available segregation results and to provide an analysis of segregation and precipitation phenomena of certain dopants on ceramic surfaces.

## 2 Statement of the Problem

### 2.1 General approach

In the following section attention will be restricted to those iono-covalent compounds, such as certain of the oxides, in which the prevailing defects are cationic vacancies. These compounds form an important class of ceramic materials. In most of them, the energy for defect formation is very high and the amount of intrinsic defects is typically a thousand times lower than the extrinsic defect concentration due to the impurity concentration or to the influence of the oxygen partial pressure. *In these materials, the concentration of cationic vacancies is a function of  $T$  and  $P_{O_2}$  due either to variations in the departure from stoichiometry or to mixed valence effects.*

As an example, the formation of cationic vacancies in a non-stoichiometric compound  $AO_\beta$  may be described by the following equation:



According to the mass action law applied to eqn (1) and to the electroneutrality condition  $\alpha[V_A^{\alpha'}] = [h^{\cdot}]$ , one obtains:

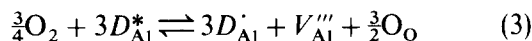
$$[V_A^{\alpha'}] = \alpha^{-\alpha/(1+\alpha)} K^{1/(1+\alpha)} P_{O_2}^{\beta/2(1+\alpha)} \quad (2a)$$

where  $O_O$ ,  $V_A^{\alpha'}$  and  $h^{\cdot}$  denote a neutral anion on an anion site, an ' $\alpha'$ '-fold ionized cationic vacancy and an electron hole. The square brackets denote the concentration of defects per mole of  $AO_\beta$ .  $K$  is the equilibrium constant related to the standard free enthalpy of formation of the defects ( $\Delta G_f$ ):

$$-RT \ln K = +\Delta G_f = \Delta H_f - T\Delta S_f \quad (2b)$$

It follows from eqns (2a) and (2b) that the concentration of vacancies increases or decreases with temperature in the material according to the sign of  $\Delta H_f$ .<sup>7</sup>

In the case of a stoichiometric compound, such as alumina, the impurity amount being well above the intrinsic defect concentration, impurities always dominate the properties. In a donor-dominated material the formation of cationic vacancies may be written as:<sup>8</sup>



In accordance with the mass action law and the electroneutrality condition<sup>8</sup> ( $D_{\text{Al}}' = 3[V_{\text{Al}}''']$ ):

$$[V_{\text{Al}}'''] = k_1 D_{\text{Al}}^{*3/4} P_{\text{O}_2}^{3/16} \quad (4)$$

where  $V_{\text{Al}}'''$  denotes three-fold ionized cationic vacancy,  $D_{\text{Al}}^*$  and  $D_{\text{Al}}'$  a cationic impurity on an aluminum site ionized three- and four-fold, respectively.

The surface is an important discontinuity in the crystal. The environment of the species, ions and defects, is different from that of the bulk in terms of electrostatic and elastic forces. To a given species (defects or impurities) corresponds a free energy difference  $\Delta g$  between the free energies in the bulk and on the surface.<sup>9</sup> This leads to an equilibrium segregation which is generally assumed to be of the Langmuir or Arrhenius type. If one neglects the coverage effects the difference of impurities concentration between the bulk and the surface may be written:

$$x/y \propto \exp(-\Delta h/kT) \quad (5)$$

in which  $x$  and  $y$  are the impurity concentrations at the surface and in the bulk, respectively and  $\Delta h$  is the heat of segregation assumed to be independent of coverage.

It now seems to be known that the boundary thickness of ceramic materials diverging from the normal crystal structure extends over only a few monolayers.<sup>4</sup> The region of the crystal concerned by the equilibrium segregation must then be a layer of few tens of angström near the surface as has been shown by Matzke<sup>4</sup> in MgO, UO<sub>2</sub> and KBr or by Nowotny<sup>10</sup> in NiO, for example.

## 2.2 Experimental results

While extensive data with different materials are not available, some observations reported in the literature indicate that the segregation layer thickness near surfaces in ceramic materials can be significantly greater than that which corresponds to the equilibrium segregation. As segregation is a thermodynamic phenomenon, this apparent discrepancy may be attributed to cooling effects as will be seen later with some examples.<sup>2,3,11-13</sup>

### 2.2.1 Impurity segregation near surfaces in magnesium oxide<sup>2,3</sup>

The work of Kingery and coworkers<sup>2,3</sup> on MgO single crystals shows particularly well that most of the segregation observed at room temperature below the surface develops during cooling. In particular, marked effects of cooling rates have been observed by these authors on the extent of segregation and on the impurity concentration adjacent to the surface. In Fig. 1 results obtained by these authors for iron and aluminum are reported. They show that the amount and thickness of segregation seem to decrease as the quench rate increases. For the higher aluminum-doped sample (0.187 wt%), the formation of spinel precipitates has even been observed when

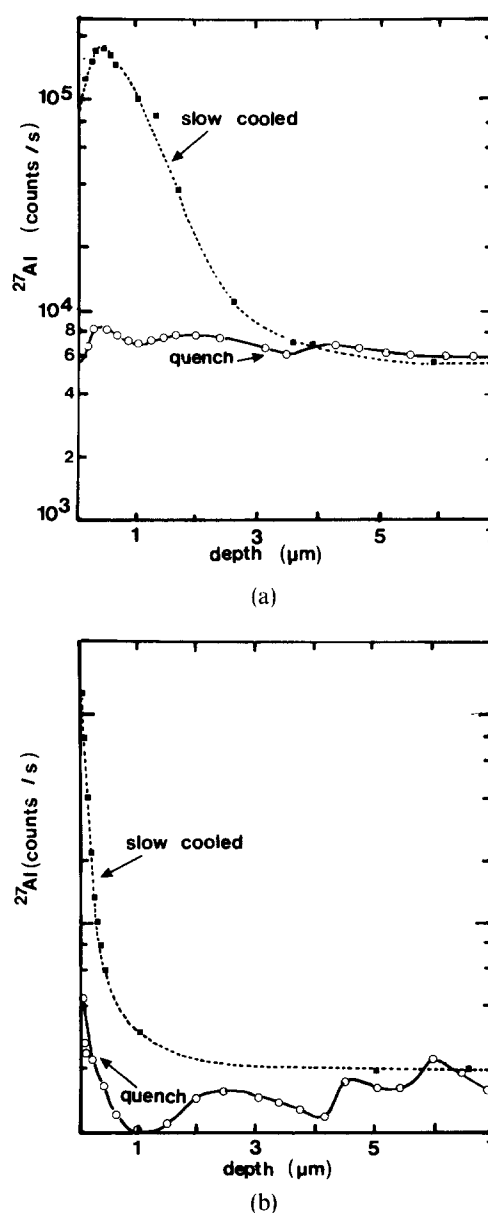


Fig. 1. Near-surface aluminum distribution in quenched and slow-cooled MgO samples containing (a) 0.187 wt% and (b) 0.006 wt% Al.<sup>2,3</sup>

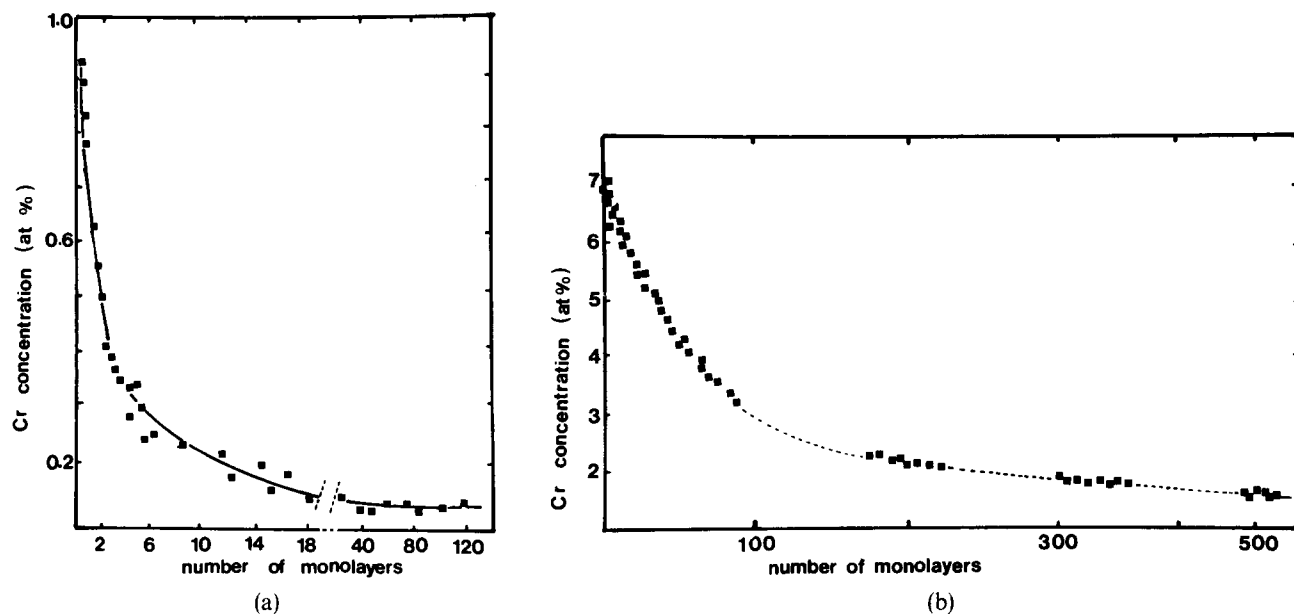


Fig. 2. Near-surface chromium distribution in chromium-doped (a) NiO and (b) CoO samples<sup>11-13</sup> (1 monolayer  $\approx 4 \text{ \AA}$ ).

the sample is cooled slowly. No precipitates were observed by these authors in the quenched samples, in which the concentration varies only in the hundred angstrom region adjacent to the surface, and in the less doped sample (0.006 wt%).

### 2.2.2 Impurity segregation near surfaces in transition metal oxides<sup>11-13</sup>

A segregation width below the surface has also been observed by Hirschwald and coworkers<sup>11-13</sup> for chromium in NiO and CoO. As an example, in Fig. 2, results obtained at room temperature from samples previously annealed in argon at 1353 K and quenched at a rate close to  $100^\circ\text{C min}^{-1}$  have been reported. The thickness of the layer exhibiting a chromium concentration enhancement is close to 80 monolayers (1 monolayer  $\approx 4 \text{ \AA}$ ) in NiO. For CoO, the chromium gradient extends over a considerably larger distance (higher than 500 monolayers). For these two oxides, the authors conclude that the chromium segregation near the surface may lead, for the higher doped samples (when the chromium concentration in the bulk exceeds 0.4 at.%), to the formation of a spinel phase ( $\text{M Cr}_2\text{O}_4$  with  $\text{M} = \text{Ni}$  or  $\text{Co}$ ).

### 2.2.3 Discussion

It follows from these two sets of results that more extensive data with a wider range of materials, of solute concentrations, of annealing conditions and cooling rates are necessary for a detailed interpretation of the quenching effects. Nevertheless, it is clear after the work of Kingery and coworkers<sup>2,3</sup> that an interpretation of segregation phenomena

experiments near surfaces without consideration of the possibility of matter transport occurring during cooling is inadequate to characterize the material.

In the following section the influence of a driving force for impurity segregation due to thermal and chemical potential gradients has been considered. As shall be seen, such gradients occur simultaneously in the material during cooling, due to the temperature differences between the bulk and the surface of the crystal.

## 3 Solute Segregation Near Surfaces During Cooling

### 3.1 General equations

As has previously been shown, the defect concentration of oxides at high temperatures is generally controlled by the thermodynamic equilibrium conditions, temperature and oxygen partial pressure (eqns (1)–(4)). When a sample previously annealed at high temperatures is cooled, it can be assumed that the surface of the crystal is in thermodynamic equilibrium with the surrounding atmosphere. Consequently, the decrease of temperature can lead (if  $\Delta H_f > 0$ ) to a decrease of the vacancy concentration at the surface of the crystal (eqns (2)–(4)). An electrochemical potential gradient then occurs simultaneously to the temperature gradient in the material; this leads to a redistribution of the mobile species—cations and vacancies. Under these conditions, the flux of matter which appears in ionic-covalent compounds can be assumed to be proportional to a linear combination of the electrochemical driving force ( $\nabla\eta_i$ )<sup>5,6,19</sup> and of the thermal driving force

$(\nabla \ln T)$ .<sup>14,15</sup> If the correlation effects are neglected this equation can be written:

$$J_i = -c_i(D_i/RT)(\delta\eta_i/\delta x + Q_i^* \delta \ln T/\delta x) \quad (6)$$

In the electronic conductor materials as considered in the present work (eqns (1) and (2)):<sup>5,6,19</sup>

$$\delta\eta_i = \delta\mu_i$$

where  $\mu_i$  is the chemical potential of the electrically neutral species related to the thermodynamic activity ( $a_i$ ) by the relation:<sup>5,6,9</sup>

$$\delta\mu_i/\delta x = RT \delta \ln a_i/\delta x$$

where  $D_i$  is the diffusion coefficient of the species  $i$ ,  $c_i$  their concentration and  $Q_i^*$  the reduced heat of transport related to the enthalpy of motion  $\Delta H_m$ . From theoretical models and in agreement with experimental data it follows that<sup>16</sup>

$$Q_i^* \leq \Delta H_m$$

In the following section the influence of these two driving forces will be considered successively in connection to the diffusion processes which occur in the materials in order to try to understand the response of the compound.

### 3.2 Dynamic segregation of impurities under chemical potential gradients

A solid solution (AO, BO<sub>γ</sub>) in which the prevailing defects in the host material, AO, are formed according to eqn (1) will now be considered. In these materials the cationic vacancies are responsible for the matter transport, while the oxygen ions are closely packed and practically immobile. According to eqns (2a) and (2b) the cationic vacancy concentration decreases with decreasing temperature, at constant oxygen partial pressure, if the enthalpy of formation of vacancies is positive ( $\Delta H_f > 0$ ). Consequently, if a local chemical equilibrium at the surface of the crystal during cooling is assumed, this involves an annihilation of the cationic vacancies at the surface, which corresponds to a reduction process. A vacancy concentration gradient is set up in the sample, which leads to a diffusion of these defects in the direction of the surface. This flux is of course accompanied by a flux of cations in the opposite direction. A reduction front then moves in the crystal with a velocity  $v$ , given by the relation:

$$v = -J_v V_M \quad (7)$$

where  $J_v$  is the flux of vacancies and  $V_M$  the molar volume of the oxide.

The flux of vacancies under the vacancy concentration gradient is related to the chemical diffusion coefficient  $\tilde{D}$  by Fick's law:<sup>5,6,17</sup>

$$J_v = -c_M \tilde{D} (d[V_A^{\alpha}]/dx) \quad (8)$$

where  $c_M$  is the overall concentration (in mol/cm<sup>3</sup>) of cation sites in the host lattice AO.

Knowing  $\tilde{D}$  allows the mean penetration ( $\Delta x$ ) of the reduction front after a time  $t$  to be found:

$$\Delta x \simeq \sqrt{\tilde{D}t} \quad (9)$$

Now consider the oxide AO, BO<sub>γ</sub> in the form of a plate of thickness  $x$  whose main surfaces are exposed to different chemical potentials (different temperatures at constant  $P_{O_2}$  or different  $P_{O_2}$  at constant temperature, eqns (1)–(4)). If a local equilibrium on each surface is assumed, a lower concentration of vacancies appears then on the side exposed to the lower oxygen partial pressures at constant temperature<sup>5</sup> or on the side exposed to the lower temperature at constant  $P_{O_2}$ , if  $\Delta H_f > 0$ . As has been indicated previously, this leads to a cationic vacancy flux in the direction of the lower concentration of vacancies accompanied by a flux of cations in the opposite direction. Far from vacancy sources and sinks, lattice sites are conserved. These fluxes are then coupled through the condition:

$$J_v + \sum J_C = 0 \quad (10)$$

A demixing tendency takes place in the material when the transport rate of A is different from that of B. This situation occurs when the diffusivities of A and B are unequal ( $D_A \neq D_B$ ). The exchange frequency between vacancies and neighboring cations is lower for the less mobile cations. Consequently (if the correlation effects are neglected), this leads to an enrichment of the less mobile cations at the side of the lower concentration of vacancies, i.e. on the surface of the compound during cooling, if  $\Delta H_f > 0$ . This demixing tendency is sometimes accompanied by the formation of new phases, as has been observed by Wolfenstine *et al.*<sup>18</sup> in NiCr<sub>2</sub>O<sub>4</sub> or by Schmalzried<sup>19</sup> in Fe<sub>2</sub>SiO<sub>4</sub> and in NiTiO<sub>3</sub>, in experiments performed under an oxygen potential gradient, at constant temperature.

Therefore, in order to have a quantitative formulation of the problem, it is advisable to express the transport equations of the mobile species (A and B) in the system under consideration (AO, BO<sub>γ</sub>). If the reference frame is fixed on the oxygen plumes, it has previously been shown<sup>5,6</sup> that the fluxes of the A and B cations can be written as a function of the

chemical potential gradient ( $\delta \ln a_{\text{O}}/\delta x$ ) across the sample, by the formula:

$$J_{\text{A}}^{2+} = c_{\text{M}}D_{\text{A}}(\delta m/\delta x + (1 - m)\delta \ln a_{\text{O}}/\delta x) \quad (11a)$$

$$J_{\text{B}}^{2+} = -c_{\text{M}}D_{\text{B}}(\delta m/\delta x - m\gamma\delta \ln a_{\text{O}}/\delta x) \quad (11b)$$

with, according to eqn (2a), when  $\beta = 1$ :

$$\delta \ln a_{\text{O}}/\delta x = (1 + \alpha)\delta \ln [V_{\text{A}}^{\alpha}]/\delta x \quad (12)$$

where,  $\delta \ln [V_{\text{A}}^{\alpha}]/\delta x$  is the concentration gradient of vacancies in the host material AO (eqns (1), (2a) and (2b)) and  $\delta m/\delta x$  the impurity (B in the present case) concentration gradient.

Inserting eqns (11) into eqn (10) yields:

$$\begin{aligned} c_{\text{M}}(D_{\text{B}} - D_{\text{A}})\delta m/\delta x \\ = J_{\text{V}} + c_{\text{M}}(D_{\text{A}} + m(\gamma D_{\text{B}} - D_{\text{A}}))\delta \ln a_{\text{O}}/\delta x \end{aligned} \quad (13)$$

Equations (12) and (13) show that the impurity concentration gradient which appears in the compound AO,  $\text{BO}_{\gamma}$ , if  $D_{\text{B}} \neq D_{\text{A}}$ , is related to the concentration gradient of vacancies and to the flux of vacancies, i.e. to a drift term. The above impurity concentration gradient is then related to the shift velocity of the reduction front in the material (eqn (7)), i.e. to the shift of the oxide/gas interface with respect to the laboratory reference frame (due to the annihilation of the cationic vacancies on the surface and to the departure of oxygen: eqns (1) and (3)).

It should be remembered that the flux of vacancies in the pure material is given by the formula:

$$J_{\text{V}} = -c_{\text{M}}D_{\text{A}}\delta \ln a_{\text{O}}/\delta x \quad (14)$$

Consequently eqn (13) can also be written:

$$\begin{aligned} c_{\text{M}}(D_{\text{B}} - D_{\text{A}})\delta m/\delta x \\ = \Delta J_{\text{V}} + c_{\text{M}}m(\gamma D_{\text{B}} - D_{\text{A}})\delta \ln a_{\text{O}}/\delta x \end{aligned} \quad (15)$$

where  $\Delta J_{\text{V}}$  is the difference of the vacancy fluxes in the doped and pure material.

The knowledge of the rate of displacement of the reduction front in the pure and doped material and of the diffusion coefficient is then necessary to estimate the behavior of the impurities under a chemical potential gradient.

Experimental results in literature<sup>18,19</sup> confirm these demixing effects under oxygen potential gradients. Calculations have even been performed by Schmalzried<sup>19</sup> when a steady state is reached, i.e. when the impurity concentration gradient in the specimen is constant while the sample grows toward the higher oxygen partial pressure side with a constant velocity.

### 3.3 Dynamic segregation of impurities due to the thermal driving force

Now consider a vacancy surrounded by cations. The

exchange frequency of the cations and the vacancy is proportional to the probability for the cation to jump to the vacancy site:

$$\omega = \nu \exp(-\Delta G_{\text{m}}/RT) \quad (16)$$

where  $\nu$  is the vibrational frequency of the cation in the direction of the vacancy and  $\Delta G_{\text{m}}$  the height of the saddle point which corresponds to the activation free energy of migration. The effect of temperature on atomic diffusion then appears through the enthalpy of motion  $\Delta H_{\text{m}}$ , with:

$$\Delta G_{\text{m}} = \Delta H_{\text{m}} - T\Delta S_{\text{m}}$$

The jump probability is then higher when the temperature increases (after eqn (16):  $\delta\omega/\delta T > 0$ ). The temperature gradient then has the effect of causing the cations to move from the higher to the lower temperature side. The magnitude of the heat of transport ( $Q^*$ ) in the present case is equal to the migration enthalpy.<sup>14</sup> (Few data for  $Q_i^*$  have been available until now in the literature and it follows from the review of Gillan<sup>14</sup> that the conclusion of this simple theory is generally satisfactory for a vacancy mechanism. However, in a macroscopic scale the hopping of a cation generally involves the cooperative motion of several atoms. Other mechanisms can also be considered. Nevertheless, after Yoo & Wuensch<sup>16</sup>  $Q_i^*$  seems to be at most the enthalpy of motion:  $Q_i^* \leq \Delta H_{\text{m}}$ .)

It should be noticed that the fluxes due to the temperature gradient and to the chemical potential gradient driving forces occur in the opposite direction in the case of the material considered (cf. Section 3.2,  $\Delta H_{\text{f}} > 0$ ), but in the same direction if  $\Delta H_{\text{f}} < 0$  (the concentration of defects increases when the temperature decreases eqn (2)). This last case corresponds to materials in which the concentration of defects gives rise to defect aggregates or clusters, as in MnO or FeO, for example.<sup>7,20</sup>

### 3.4 Relative magnitude of these two driving forces

Experiments reported by Petuskey & Bowen<sup>15</sup> with an iron aluminate spinel have allowed them to detect the vacancy flow which appears in the material when it is exposed to a temperature gradient under different boundary conditions. Firstly, the sample was exposed to a temperature gradient and the exchanges between the specimen and the surrounding atmosphere were possible. Markers attached to the end of the crystal exposed to the lower temperature have made it possible to detect the vacancy flow. In this experiment, the driving forces due to the temperature and to the chemical potential gradients coexist in the specimen. At the end of the

experiment, they observed an enrichment of aluminum near the side exposed to the higher temperature and a displacement of the markers, which confirms a net vacancy flow toward the higher temperature side. In the second type of experiments, the sample was encapsulated in a platinum foil. Exchange with the atmosphere was not possible. The sample was then exposed only to the driving force due to the temperature gradient. The segregation effects observed at the end of the experiment were negligible. Consequently, *when the sample is exposed to a temperature gradient and when exchange with the surrounding atmosphere is possible, the matter transport observed seems to be due essentially to the chemical potential driving force.*

### 3.5 Estimation of the thickness of the segregation layer due to cooling effects

In their work, Black & Kingery<sup>2,3</sup> have shown the influence of cooling rates (Fig. 1) both on the surface segregation impurity concentration and on the thickness of the enriched layers. These thicknesses are of the same order of magnitude as those found by Hirschwald and coworkers<sup>11-13</sup> for Cr in NiO or CoO (Fig. 2), i.e. larger than those expected for high-temperature equilibrium segregation.

One can consider that the cooling of a sample can take only a few minutes in air quenched experiments. At room temperature, the ceramic material can be considered as structurally frozen. Consequently, *are these cooling lapses of time sufficient to allow for segregation effects? Furthermore, is the thickness of the layer involved in dynamic segregation larger than the few atom layers which seem to be concerned by the high temperature equilibrium segregation?*

The thickness of the layer altered by the transport processes under a temperature gradient and due to the chemical potential driving force has been estimated from the depth of penetration of the reduction (or oxidation) front (eqn (9)). The general problem is complex to solve. Thus, it has been assumed that the transport processes due to the chemical potential gradient which occurs during cooling, are equivalent to those which appear in the material at an average constant temperature ( $T_m$ ) for a lapse of time which decreases when the cooling rate increases. In Table 1, the depths estimated for CoO and NiO (eqn (9)) are reported. The calculated thicknesses at  $T_m = 300^\circ\text{C}$  and for times close to 1000 s are consistent with the results of Hirschwald and coworkers<sup>11,12</sup> reported in Fig. 2 (close to 2500 and 300 Å for CoO and NiO, respectively). Furthermore, the ratios of the segregation layer thicknesses found experimentally for CoO and NiO

**Table 1.** Depth of segregation in NiO and CoO for different times and temperatures

Time (s)	$\Delta x = \sqrt{\tilde{D}t}$ Å				Temperature (°C)
	100	200	500	1000	
CoO	748	1050	1700	2450	300
NiO	87	120	190	270	300
CoO	5190	7300	11400	14000	400
NiO	846	1200	1900	2700	400
CoO	21900	30900	49000	69000	500
NiO	4500	6400	10100	14300	500

$$\tilde{D}(\text{CoO}) = 0.13 \exp - 30 (\text{kcal})/\text{RT} (\text{cm}^2 \text{s}^{-1}),^{22}$$

$$\tilde{D}(\text{NiO}) = 0.14 \exp - 35 (\text{kcal})/\text{RT} (\text{cm}^2 \text{s}^{-1}).^{21}$$

(Fig. 2) are in good agreement with the calculated values (Table 1,  $5 < r < 10$ ). Unfortunately, the lack of data ( $\tilde{D}$ ) for MgO has not allowed similar estimations to be made.

Finally, this analysis (using the results available for NiO and CoO, for example) suggests that dynamic segregation effects during cooling must be taken into account in the interpretation of segregation results observed at room temperature in open systems (i.e. when the exchange with the gaseous environment is possible). Nevertheless, according to the results of Petuskey & Bowen,<sup>15</sup> it can be pointed out *that high temperature equilibrium segregation may be expected to be observed at room temperature on samples maintained during cooling in a closed system, i.e. in a system in which the exchange with the gaseous environment is not possible* (for example, the sample encapsulated in a platinum foil, as has been done by Petuskey & Bowen<sup>15</sup>).

## 4 Conclusion

In this work, the mechanism of dynamic segregation (and phase precipitation) near surface in iono-covalent semiconducting compounds subject to large temperature changes has been analyzed. According to available experimental results, the chemical potential driving force (which occurs simultaneously to the thermal driving force) seems to be the prevailing force of matter transport. From the expression of the flux of mobile species it has been shown that compositional changes must be generally observed in multicomponent compounds. These effects are directly related to the mobilities of the different cations. The importance of segregation phenomena in ceramics after cooling have been discussed on the basis of available results in doped materials (MgO, NiO and CoO). The segregation layer thicknesses have been estimated in NiO and CoO. The good agreement between the experimental and calculated values seems then to confirm that

dynamic segregation effects occurring during cooling must be taken into account in the interpretation of segregation results observed at room temperature. However, more extensive data on a wider range of materials are necessary for a better understanding of these phenomena, which show important technological consequences such as in ceramic powder sintering, or in the aging of ceramics subject to large temperature changes at high temperatures.

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