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Kinetic demixing of (Co, Mg)O and ZrO₂, Y₂O₃ solid solutions in an electrical field

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Abstract

In this work we have analyzed the conditions leading to a kinetic demixing of species in ceramics exposed to an electrical field. Time dependent cation redistribution profiles have been estimated for (Co,Mg)O and (ZrO₂,Y₂O₃) solid solutions. The computed data are compared to the experimental results.

INTRODUCTION

It is now well known that a generalized thermodynamic potential gradient can provide in ceramics, such as oxide solid solutions or compounds, a driving force leading to a kinetic demixing of the species⁽¹⁻³⁾. In the present paper a quantitative formulation of the kinetic demixing problem due to an electrical field will be emphasized for semiconducting oxides and ionic conductors such as the (Co,Mg)O and (ZrO₂,Y₂O₃) solid solutions, respectively.

STATEMENT OF THE PROBLEM

Let us consider for simplicity a compound (A,B)O placed in an uniform electrical field $(d\Phi/dz=-E)$. The total current density (I) which passes through the sample of uniform cross section and of conductivity σ , is due to the ionic (J_{ion}) and electronic (J_{el}) fluxes and is given by the following relation :

$$I = I = \sigma \left(-d\Phi/dz\right) = I_{el} + I_{ion} = f \Sigma Z_i \quad j_i$$
(1)

If one assumes that the current does not disturb the local chemical equilibrium between neutral and charged species and that the sample is placed between identical reversible electrodes $(d\mu_{h^*} = 0)$, we have shown that the flux of the cationic species can be expressed as a function of the concentration gradient of the neutral species (dx_i/dz) and of the reduced driving force of diffusion F_i ($F_i = q_i E/kT = -q_i U/kTL$):

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$$j_i = c_M D_i (-\frac{dx_i}{dz} + x_i F_i), \qquad (2)$$

where f is the Faraday constant, $q_i = Z_i$ e the charge of the ions A or B, Z_i the valence of the particle, D_i its diffusion coefficient, k the Bolzmann's constant, c_M the overall concentration (in mol cm⁻³) of cationic sites in the lattice, U the applied voltage.

According to Eqs. 1 and 2, the cationic current density $(I_{cat} = f \Sigma Z_{ij})$, can be written :

$$I_{cat} = f \{ c_M (z_B D_B - z_A D_A) \frac{dxA}{dz} - c_M (\Sigma x_i q_i^2 D_i) \frac{d\Phi/dz}{e kT} \}$$
(3)

This equation shows that the cationic current density reaches a constant value under a constant electrical field only when the concentration profile of the cations does not change with time i.e. at the steady state⁽¹⁻³⁾ when the velocities of the cationic species are equal at any point :

$$dx_B/dz = x_A x_B (D_B F_B - D_A F_A) / (D_A x_B + D_B x_A)$$
(4)

The matter transport is accompanied by a shift of the end surfaces of the sample in the same direction of the cationic fluxes. This displacement will be more or less important depending of the mobility of the cations. Two different cases have been treated. The solid-solution (Co,Mg)O in which the prevailing defects are cationic vacancies and the yttrium-doped zirconia solid electrolyte in which the matter transport is controlled by the minority point defects.

KINETIC DEMIXING IN (Co,Mg)O

The prevailing defects⁽²⁾ in this material are cationic vacancies α times ionized(V α ') and the thermodynamical equilibrium of the solid solution with the surrounding atmosphere can be described by the relation :

$$1/2 O_2 \leftrightarrow V^{\alpha'} + \alpha h^\circ + O_0$$
 (5)

Under an electrical field, a flux of cations occurs towards the cathode and new lattice sites are formed, in accordance with Eq.5. This flux is accompanied by an opposite flux of vacancies. At the anode, the reverse reaction occurs (Eq.5). Oxygen leaves the sublattice and lattice sites are destroyed. As a result, a shift of the end surfaces of the oxide occurs in the direction of the cathode. Because the concentration of vacancies is small in the (Co,Mg)O solid solutions ($[V^{\alpha}]$ <<1), the shift velocity of the end surfaces is given by :

$$v = (J_A + J_B) / C_M \approx - V_M J_V$$
(6)

Results and discussion

Kinetic demixing profiles have been calculated following the same procedure we previously used for calculating demixing under a chemical potential $gradient^{(2-3)}$, with the condition of a constant driving force for matter transport. As an example, we have reported Fig.1 the results obtained with a polycrystalline sample. The experimental and calculated results are in good agreement near the anode but a departure is observed near the cathode. This is due to short circuit effects created by platinum wires around which the crystal has been re-builted at the cathode level.



Figure 1 Demixing of an initially homogeneous polycrystal of (Co,Mg)O in an electrical field. Comparison of the experimental and calculated results.

KINETIC DEMIXING IN Y2O3 (9,5 mol.%) -DOPED ZIRCONIA

This material is a solid electrolyte. The cation diffusivities are several orders of magnitude lower than the anion diffusivities⁽⁴⁾ and the electronic conductivity is negligible. Entire molecular groups are then

transferred during the transport processes under an electrical field at a rate controlled by the cationic point defect concentration.

Results and discussion

In Figure 2, we have reported the experimental results obtained with a single crystal of zirconia doped with 9,5 mol% Y_2O_3 . They show that the cation redistributions concern a layer of 100µm. The calculations performed using diffusion coefficient values from the literature⁽⁴⁾ predict a concentration gradient close to 100ppm, for a depth of less than one micron. Such demixing would be undetectable. The difference between the experimental and calculated results may be due to the calculation approximations but also to the error in the diffusion coefficient values.



Figure 2 Demixing of an initially homogeneous single crystal of yttrium-doped zirconia in an electrical field.

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