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Solute Segregations at the Space-Charge Layers of Stabilized Zirconia: an Opportunity for Ameliorating Conductivity

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Abstract

According to a space-charge theory analysis, the space-charge potential of YSZ is negative, which corresponds to a $V_o^{\cdot\cdot}$ *depletion in the space-charge layer. An extremely low grain-boundary conductivity of the high-purity YSZ is thus explained. Under the condition that the bulk property is ensured by the optimal dopant additions, an idea of increasing the grain-boundary conductivity by the segregations of solutes with positive effective charge is put forward. The most likely driving force for the segregations is the elastic strain energy. And the feasibility of this idea has been proved by some experimental and theoretical results.*

1 Introduction

In thermodynamic equilibrium the grain boundaries of an ionic crystal may carry an electric potential resulting from the presence of excess ions of one sign, this potential is compensated by space-charge layers of the opposite sign adjacent to the boundaries. The nature of the space charge is dependent on the formation energies of point defects (vacancies and interstitials) in pure ionic crystals, it is more likely, as in almost all practical cases, that it is dictated by the effective charge of the aliovalent dopants and/or impurities.[1–3] A number of studies on the space-charge layers have appeared,[3–15] however, most of them are centered on the alkali halides.

The segregations of aliovalent solutes to the grain boundaries can be substantially affected by the presence of the space-charge layers, the space-charge segregations of Mg, Fe and Ti in Al_2O_3,[8,11] Al and Si in AgCl,[9] Sr in KCl[10] and Al in $CuCl_2$[12] have been discovered, and the segregations usually cause enhancement or diminution of some types of lattice-defect concentrations in the space-charge layers. According to Maier,[13] the grain-boundary conduction consists of the contribution from the grain-boundary interfaces and that from the space-charge layers. A space-charge layer can be treated as a normal resistor element, and its conduction mechanism is bulk-like. The variation of defect concentrations in the space-charge layers will surely change the grain-boundary conductivity, which thus suggests an opportunity for ameliorating the conductivity of ionic crystals: to increase the concentration of charge carrier in the space-charge layers by the solute segregations there. However, the bulk property can be ensured by optimal dopant additions. In the present work, an application of this idea in Y_2O_3-stabilized ZrO_2 (YSZ) is presented. Kröger–Vink notation is used throughout this paper.

2 Space-Charge Potential and Defect Distribution

In YSZ, the predominant defect is $V_o^{\cdot\cdot}$, it is produced from a defect reaction occurring as follows

$$Y_2O_3 \rightleftarrows 2Y_{Zr}' + V_o^{\cdot\cdot} + 3O_o^x \qquad (1)$$

If the effects of elastic field and solute-vacancy associates are not considered, and referencing the spatially varying electrostatic potential $\Phi(x)$ to zero at the grain boundaries ($\Phi(x)$ is a comprehensive value of space-charge potential and grain-boundary interface potential, x is the distance from the grain-boundary interfaces), it is readily shown[3,14,15] that the concentration of $V_o^{\cdot\cdot}$ as a function of distance from the interfaces is, if the dopant concentration meets the requirement of dilute solution, given by

$$[V_o^{\cdot\cdot}]\,(x) = 2\exp\left(\frac{-G_{V_o} - 2e\Phi(x)}{KT}\right) \qquad (2)$$

where G_{V_o} is the formation free energy of $V_o^{\cdot\cdot}$. In the bulk, the electrostatic potential is $e\Phi_\infty$, then eqn (2) becomes

$$[V_o^{\cdot\cdot}]_\infty = 2\exp\left(\frac{-G_{V_o} - 2e\Phi_\infty}{KT}\right) \tag{3}$$

The potential difference between the bulk and the grain boundaries (in this convention simply the bulk potential, $e\Phi_\infty$) is determined by applying the bulk electroneutrality condition, which in this case is

$$2[V_o^{\cdot\cdot}]_\infty = [Y_{Zr}']_\infty \tag{4}$$

Equating eqns (3) and (4), the potential difference is given by

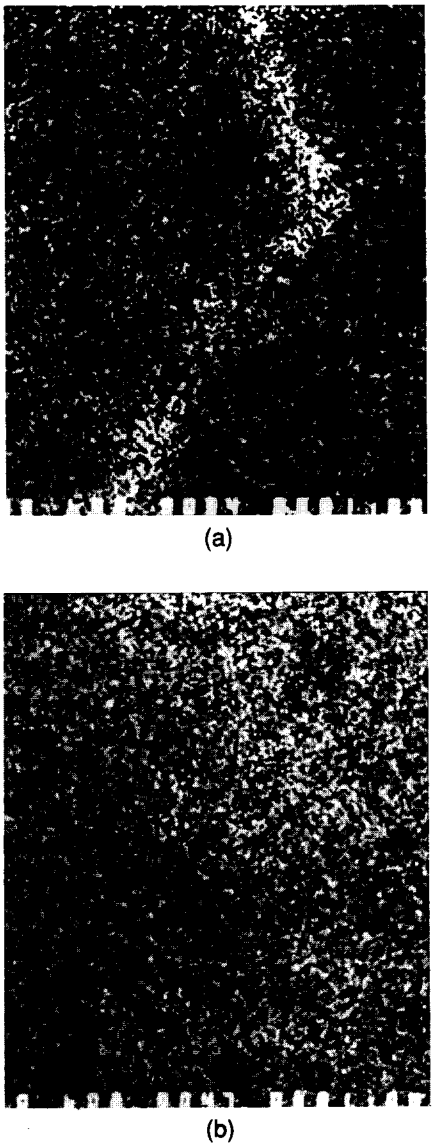
$$e\Phi_\infty = -\frac{1}{2}\left\{G_{V_o} + KT\ln\frac{[Y_{Zr}']_\infty}{4}\right\} \tag{5}$$

If the effect of Y_{Zr}' dominates over that of the intrinsic defects and there are no defect associates, we have $e\Phi_\infty < 0$, thus the space-charge potential in YSZ is negative, which corresponds to an Y_{Zr}' segregation and a $V_o^{\cdot\cdot}$ depletion in the space-charge layers at equilibrium. Whereas, the potential of the grain-boundary interfaces should be positive to compensate the negative space-charge potential, as a result, the electrostatic potential $\Phi(x)$ reaches zero at the grain boundaries, i.e. $\Phi(0) = 0$. The author has detected 17·47 mol% Y_2O_3 at the surface of a specimen with a composition of 9 mol% Y_2O_3–ZrO_2 by XPS. And the Y_2O_3 segregation at the grain boundaries has also been observed by Winnubst and co-workers.[16] These two factors together provide compelling proofs for the correctness of eqn (5). And it can be easily seen from the above analysis that the space-charge potential in Y_2O_3-stabilized CeO_2, MgO or CaO-stabilized ZrO_2 should also be negative. Usually 8–9 mol% Y_2O_3 is doped to ZrO_2, the dilute solution requirement is no longer met, but because of the negative effective charge of Y_{Zr}', the nature of the space-charge potential will not be altered. The specific conductivity of the grain boundaries for high-purity YSZ where the grain-boundary interface second phase is almost absent was found to be about 100 times smaller than that of the bulk,[17] this extremely low grain-boundary conductivity surely cannot be accounted for by the blocking effect of the second phase, it thus must be the result of the $V_o^{\cdot\cdot}$ depletion in the space-charge layers. In Y_2O_3-stabilized CeO_2,[18] the calculated thickness of the blocking layer was found to be larger than that of the second phase covering the grain boundaries. This finding further supports the idea of $V_o^{\cdot\cdot}$ depletion in the space-charge layers.

3 Experimental and Discussion

As mentioned earlier, the $V_o^{\cdot\cdot}$ depletion is related to Y_{Zr}' segregation, thus to ease or even prevent the Y_{Zr}' segregation at the grain boundaries there may be a method to increase $V_o^{\cdot\cdot}$ concentration in the space-charge layers. The feasibility of this idea is shown in Fig. 1. The grain-boundary solute segregation in a specimen with a nominal composition of 1·5 mol% Al_2O_3–9 mol% Y_2O_3–ZrO_2 was detected by an electron probe X-ray microanalyzer (JCXA-733). An obvious aluminium segregation (Fig. 1(a)) was observed, however, no yttrium segregation (Fig. 1(b)) was observed.

This observation means that the yttrium segregation can be subdued by the preferential segregations of other elements. The preferential segregation of aluminium may be due to the substantial size misfit between Al^{3+} and Zr^{4+}, thus the substantial elastic strain energy. The space-charge potential can be greatly modified by the segregations induced by the elastic strain energy. A particular case of this type is that when a minority solute



(a)

(b)

Fig. 1. Solute distributions in a specimen with a composition of 1·5 mol% Al_2O_3–9 mol% Y_2O_3–ZrO_2 detected by an electron probe X-ray microanalyzer. (a) Aluminum distribution, (b) yttrim distribution (The bar is 1.0μm).

has a large elastic strain energy and segregates strongly to the boundaries. In this case the segregation of the majority solute will be significantly suppressed, even depleted. This phenomenon has been theoretically proved by Yan *et al.*[15] If Al_2O_3 is substitutionally dissolved in YSZ, the Al_{Zr}' segregation will not change the $V_o^{\cdot\cdot}$ depletion in the space-charge layers; if Al_2O_3 is interstitially dissolved in YSZ, $Al_i^{\cdot\cdot\cdot}$ segregation will change the sign of the space-charge potential, which corresponds to a $V_o^{\cdot\cdot}$ enrichment in the space-charge layers. The variation of the sign of the space-charge potential with doping has been observed in TiO_2.[19] It was reported that the conductivity of YSZ can be enhanced by the addition of Al_2O_3,[20,21] this enhancement was explained by the scavenging of SiO_2 located at the grain boundaries by Al_2O_3.[22] According to the above analysis, the possible influence of Al_2O_3 on the space-charge layers resulting from the Al_2O_3 segregation should also be considered. The enhanced space-charge conduction resulting from the segregations of aliovalent solutes has been found in AgCl[9] and $CuCl_2$.[12]

If pentavalent oxides M_2O_5, e.g. Nb_2O_5 and Ta_2O_5, are added to YSZ, supposing that they are substitutionally dissolved, and a defect reaction, e.g. eqn (6), occurs

$$2M_2O_5 \rightarrow 4M_{Zr}^{\cdot} + V_{Zr}'''' + 10 0_0^{x} \qquad (6)$$

The segregation of $M_{Zr}^{\cdot}$ will change the sign of the space-charge potential and cause a $V_o^{\cdot\cdot}$ enrichment in the space-charge layers. As the positively charged grain-boundary interfaces of YSZ will repulse $M_{Zr}^{\cdot}$, the only possible driving force for the segregation of $M_Z^{\cdot}$ is the elastic strain energy. Unfortunately, if the pentavalent cation solutes M^{5+} are compensated by electrons, electron conduction will be involved. However, if the amounts of the additions are very low, the electron conduction may not be a serious problem. It has been proved that pentavalent oxides, Nb_2O_5 and Ta_2O_5, do not segregate to the grain boundaries of Ce-TZP.[23] According to the study of Naik and Tien,[24] Nb^{5+} and Ta^{5+} are compensated by Ce^{3+} in CeO_2, and Ce^{3+} induces a positive charge on the grain boundaries,[22] the segregations of Nb^{5+} and Ta^{5+} are thus prevented. The addition of M_2O_5 in YSZ will not introduce Zr^{3+} in it, therefore, the M_2O_5 segregations at the grain boundaries of YSZ is possible provided that the elastic strain energy resulting from the size misfit between M^{5+} and Zr^{4+} is much larger than that resulting from the size misfit between Y^{3+} and Zr^{4+}. The solubility of Nb_2O_5 or Ta_2O_5 in ZrO_2 has been proved to be very high.[25]

4 Conclusion

According to a space-charge theory analysis, the space-charge potential of YSZ is negative, which corresponds to a $V_o^{\cdot\cdot}$ depletion in the space-charge layers and a very low grain-boundary conductivity. Under the condition that the bulk conductivity is ensured by the optimal dopant additions, e.g. 8–9 mol% Y_2O_3 or 13–14 mol% CaO, an idea of increasing the grain-boundary conductivity by the segregations of solutes with positive effective charge is thus put forward. The most likely driving force for the segregations is the elastic strain energy. However, because of the positive potential of the grain–boundary interfaces, the interfaces will repulse the positively charged solutes, then more pronounced enhancement of the grain-boundary conductivity will be obtained only if the interfaces are modified, e.g. by second phase precipitations at the same time. In the cases of dopants other than MgO, CaO and Y_2O_3, the charge compensation mechanisms are still uncertain, this makes more realistic analysis impossible.

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