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1989 J. Phys.: Condens. Matter 1 SB237

(http://iopscience.iop.org/0953-8984/1/SB/057)

J. Phys.: Condens. Matter **1** (1989) SB237–SB238. Printed in the UK

Sr segregation in doped MgO

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Received 23 March 1989

Abstract. The surface coverage of Sr on doped MgO ceramics has been measured by XPS for bulk doping levels in the range 3 to 30 ppm. The experimental data are compared with results derived from ionic model simulations of the doped surface.

Electrical and mechanical properties of ceramic oxides are governed to a large extent by segregation of dopants to surfaces and grain boundaries. We report here a parallel experimental and theoretical study of Sr segregation in MgO, a prototype isovalent dopant system.

Sr-doped MgO ceramics were fired at 1360 °C for 48 h to equilibrate the surface Sr coverage. A well defined strontium signal was observed in the XPS of all samples with a

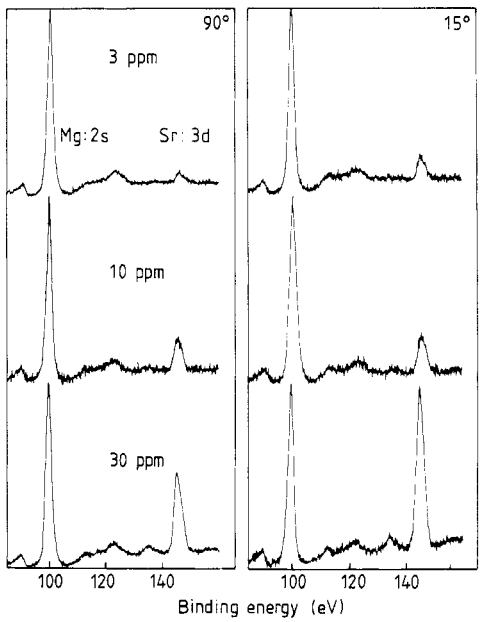

Figure 1. Al Kα-excited XPS of Sr-doped MgO at the bulk doping levels indicated after equilibration of the Sr at 1360 °C for 48 h. Normal and 15° emission data are shown.

bulk dopant level in the range 3–30 ppm (figure 1), with increased intensity at shallow offtake angle as expected for segregated dopant species sitting in the topmost ionic layers of the ceramic.

In our atomistic ionic model simulations of Sr-doped MgO it is assumed that Sr ions segregate to cation sites in the topmost ionic layer only. The heat of segregation $\Delta h(x_s)$ is first calculated as a function of the surface cation ratio x_s between Sr and Mg. The equilibrium surface ratio is then obtained from the bulk ratio x_b by solving the non-linear equation

$$x_s = x_b \exp\{-[\Delta h(x_s) + x_s(1+x_s)\mathrm{d}\Delta h(x_s)/\mathrm{d}x_s]/RT\}.$$

With a variation of Δh with x_s of the form found by us previously [1] we calculate surface enrichment ratios x_s/x_b of 6.25×10^4, 2.2×10^4 and 0.856×10^4 at bulk doping levels of 3, 10 and 30 ppm respectively. These have the same order of magnitude as experimental ratios of 2.1×10^4, 2.8×10^4 and 4.5×10^4 to be inferred from the data of figure 1. To improve agreement between theory and experiment we believe it will be necessary to take account of accommodation of Sr at inter-grain boundaries at low doping levels and to allow the build up of SrO multilayers on top of the MgO at high doping levels (i.e. BET-type behaviour).

Reference

[1] Tasker P W, Colbourn E A and Mackrodt W C 1985 *J. Am. Ceram. Soc.* **66** 111