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ScienceDirect
Surface Science 601 (2007) 4793–4800
SURFACE SCIENCE
www.elsevier.com/locate/susc

Dopant control over the crystal morphology of ceramic materials

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Received 19 February 2007; accepted for publication 20 July 2007
Available online 23 August 2007

Abstract

Doping is a common way to activate the behavior of ceramics. Its effect is not limited to the bulk: segregation of dopants to the surfaces also yields a way to modify, and ultimately control the crystal morphology. We propose a model that allows us to calculate the surface energy beyond the Langmuir isotherm for doped and defective surfaces from atomic-level simulations. The model also allows us to account for different compositions between the bulk and surface. Computational materials design can thus be applied to optimize simultaneously the crystal behavior at the atomic (surface structure and composition) and mesoscopic (crystal size and shape) length scales. We exemplify the model with orthorhombic $CaTiO_3$ perovskite doped with Mg^{2+}, Fe^{2+}, Ni^{2+}, Sr^{2+}, Ba^{2+} and Cd^{2+} ions, by predicting the effect that different dopants and dopant concentrations have on the crystal morphology. We find that a higher proportion of reactive {0 2 1} and {1 1 1} surfaces are exposed with the presence of divalent Mg^{2+}, Fe^{2+} and Ni^{2+} ions than in the undoped material and in perovskite doped with Ba^{2+} and Sr^{2+}. Cd^{2+} has only minor effects on crystal morphologies. These findings have important implications for predicting the reactivity of crystals doped with different ions and we show how this can be related to a simple parameter such as the ionic radius. We have tested our newly derived model by comparison with laboratory flux grown single crystals of $CaTiO_3$, $(Ni,Ca)TiO_3$ and $(Ba,Ca)TiO_3$ and find excellent agreement between theory and experiment.
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Keywords: Surface energy; Crystal morphology; Catalysis; Microelectronics; Biomaterial; Inter-atomic potentials; Single crystal

1. Introduction

Transition metal oxides and other ceramic materials are the key component in a range of advanced technologies, from microelectronics (for example dielectric resonators and piezoceramics) to heterogeneous catalysis [1]. These materials are easily processed as aggregates of microcrystalline particles. When the active phase is in this physical form, the relevant materials and device properties are often controlled by the size and shape of the constituent particles as much as by their chemical composition. Developing the ability to engineer crystal morphologies with desirable properties for optimal processing and end-use, is therefore a high priority area in current materials science [1,2]. The surface behavior of a crystal is completely described by its morphology, as it characterizes the type and relative area of the surfaces exposed. Here we examine how atomic-level computational techniques can contribute to the design of novel materials with controlled surface properties and morphological features.

Different theories have been formulated to relate the stable morphology of a crystalline solid to atomic-level information, such as crystal structure, surface orientation relative to the crystallographic axes, and relative surface energies, in both equilibrium and growth-controlled conditions (see e.g. Ref. [3] and references therein). At

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0039-6028/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2007.07.025

equilibrium, faces with the largest inter-planar distances (d_{hkl}-values) and lowest surface energies are exposed preferentially. These surfaces are usually the least reactive, and often require activation to enable a technologically useful application. One possibility is to modify the crystalline morphology so that it exposes more active faces. An alternative way to activate surfaces is by the use of dopant ions, which provide chemically active surface sites. The presence of the dopants can also modify the relative energy of the different crystal faces, thus yielding a way to control the crystal morphology, and ultimately the type and number of surface sites exposed. Experimentally it is well established that different dopants can alter both crystal shape and size, but little is known about the atomistic details of this effect [4–6]. Computer modeling is an obvious candidate to fill this gap, and being able to predict the stable morphology of crystals modified by different types and quantities of dopant ions would open up a new field of research in computational materials science, in which the crystal properties can be designed simultaneously at the atomic (surface structure and composition) and mesoscopic (morphology, i.e. crystal size and shape) length scales.

At present, while theories of crystal morphology are available, a general realistic model that incorporates the effect of dopant ions beyond the Langmuir isotherm is missing. Here we present a simple, but attractive, model to achieve this goal, which allows us to determine not only the surface energies as function of dopant concentration, but also the equilibrium surface structures and crystal morphologies.

In the present study we apply our model to orthorhombic $CaTiO_3$, as a representative system for the family of ABO_3 perovskites (see Fig. 1). Doped $CaTiO_3$ is studied for applications as varied as microwave dielectrics and heterogeneous catalysis [7–9], but it is also often used as a model system for the study of the deep Earth, in the place of high pressure experimental work on the analogue structure $MgSiO_3$, which is unstable under ambient conditions [10,11]. In addition $CaTiO_3$ was recently proposed as a suitable biocompatible material for coating of medical implants [12].

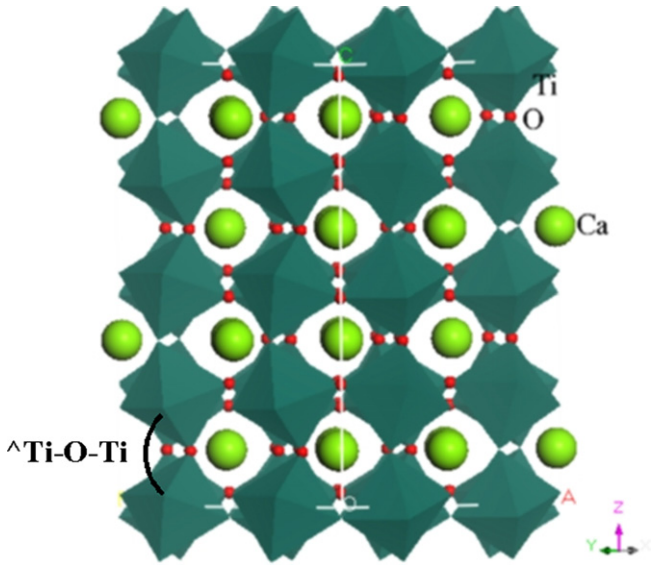

Fig. 1. Orthorhombic Pbnm structure of $CaTiO_3$ ($a = 5.380$; 5.442; $c = 7.640$ Å [28]); Ti^{4+} is in octahedral environment, forming a linked network of corner-sharing TiO_6 octahedra, while Ca^{2+} occupies 12-fold coordinated sites. TiO_6 is represented by green octahedra; Ca^{2+} and O^{2-} ions as light green and red balls, respectively. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

2. Surface energies of doped crystals

Surface energies are crucially important in determining the morphology of crystals, and they are therefore the focus of our discussion. The surface energy of undoped solids, E_S^0, is easily defined in atomic-level calculations as the energy difference, per unit of surface area (S), between equal and stoichiometric amounts of the compound at the surface and in the bulk:

$$E_S^0 = (E_{surf} - E_{bulk})/S. \quad (1)$$

Extension of this definition to doped surfaces is not straightforward, as the likely segregation of the dopants to the surface in real materials may make the surface composition non-stoichiometric and different from the bulk. Alternative approaches should therefore be formulated, and here we propose a working scheme for calculating the surface energy of doped and defective surfaces from atomic-level modeling, which can be applied to predict crystal morphologies as a function of dopant type and concentration, according to the "Equilibrium model" [13]. In the "Equilibrium model" the morphology is derived from the calculated surface energies, making the assumption that crystal faces with the lowest surface energies control the crystal morphology. To select the faces of highest importance we apply the law of Donnay and Harker [14]. Since the surface energies change in the presence of dopants, it is to be expected that the crystal morphology will also be modified in the presence of the dopants.

Let us consider the simplest case of doping, i.e. an isovalent ion X able to replace in 1:1 stoichiometry a host-crystal ion, M. We indicate as X_M the substitutional defect and M_M a host-crystal site. In order to define the surface energy of the doped material, we assume a chemical equilibrium of the dopant between bulk and surface, and call E_{seg} the segregation energy, i.e. the energy difference between one dopant located in bulk and surface [15]. This can be unambiguously calculated using the following reaction:

$$X_M : \text{bulk} + M_M : \text{surface} \rightarrow M_M : \text{bulk} + X_M : \text{surface}, \quad (2)$$

where the same simulation cells are employed to represent the undoped material (M_M) and the case with one dopant ion (X_M) in bulk and surface respectively. The process is energetically favorable if $E_{seg} < 0$. Both first-principles

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