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NANO STRUCTURATION OF ZIRCONIA UNDER IRRADIATION: A WAY TO ENHANCE THE MECHANICAL STABILITY OF ZIRCONIA LAYER

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Abstract. Zirconia is one of the most important ceramic materials because of the large range of industrial applications (catalysis, coatings, spacecraft shielding, paint additives, oxygen sensors, fuel cells, nuclear fuel matrix, alternative high permitivity material to replace silicon oxide as gate dielectric in MOS devices…). It is now well established that a monoclinic to tetragonal phase transition occurs in this material. This transition can for instance be trigged by the grain size. The mechanism of this phase transition is now clearly understood. Zirconia can be considered a textbook example for describing these effects. In this paper, we will discuss the mechanism of the tetragonal to monoclinic martensitic phase transition induced by irradiation within the Landau theory framework, pointing out the peculiar effects related to nanostructuration of this material by irradiation. Such a work is an illustrative example of structural modification of solids induced by irradiation.

1. INTRODUCTION

Nanocrystalline ceramics are finding applications in several fields because of their excellent mechanical, electronic and thermodynamic properties. Indeed, these properties are very sensitive to the particle size. However, the elaboration of dense nanometric samples is a quite difficult task. The sintering of nanometric powders, by hydrostatic high pressure or by spark plasma leads to the increase of the grain size (by about 100 nm). Moreover, new properties can stem from materials kept in thermodynamical metastable states by irradiation or ball milling. Sometimes, the observed metastable phases of these driven systems are even more interesting from a technological point of view than the equilibrium ones. These considerations are at the origin of the large interest of the scientific community for modeling the behavior of these solids.

It is well known that micrometric grains of zirconia are monoclinic at room temperature and under normal pressure. A reversible first order phase transition is observed at about 1200K towards a tetragonal phase [1] that cannot be quenched at room temperature [2,3]. Aliovalent substitutions for Zr atoms can suppress all phase transitions stabilizing the high temperature cubic form but it is also well known that the best mechanical properties are obtained in partially stabilized zirconia which is a fine-scale mixture of monoclinic and tetragonal phases. It is also well known that this tetragonal phase can

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be observed at room temperature in zirconia nanoparticles [4] of less than 30 nm diameter. Several authors [5,6] confirm these observations and others report observations of metastable phases in various materials such as alumina [7] and graphite [8]. The existence of stabilized phases in very fine powders is generally explained in terms of a surface free energy in the nanocrystalline tetragonal phase lower than in the normal phase [9]. Nevertheless, this explanation is not generally accepted [10] and some authors report either the appearance of 6 nm diameter monoclinic zirconia nanoparticles [11] or they do not relate the decreasing of the tetragonal phase to the increase in the grain size of zirconia nanoparticles [5]. The main reasons for these controversial opinions seem to be related to extrinsic factors like the presence of impurities [12,13] and to the existence of residual stresses in the nanoparticle agglomerates [14].

In this paper, we investigate radiation effects on ZrO_2 micrometric samples and we propose a new mechanism to explain the unusual pattern observed on irradiated samples. To this purpose, we have studied the microstructure of pure ZrO_2 irradiated by different ions at room temperature using grazing X-ray diffraction. Rietveld refinements allow to extract the behavior of the structural and microstructural parameters and to describe their evolution versus the number of incident particles per surface unit, called fluence. By this analysis, it is then possible to establish a detailed description of the evolution of the tetragonal phase versus the fluence. These results are analyzed within the Landau theory and they can be understood by the mechanism of a size-induced phase transition.

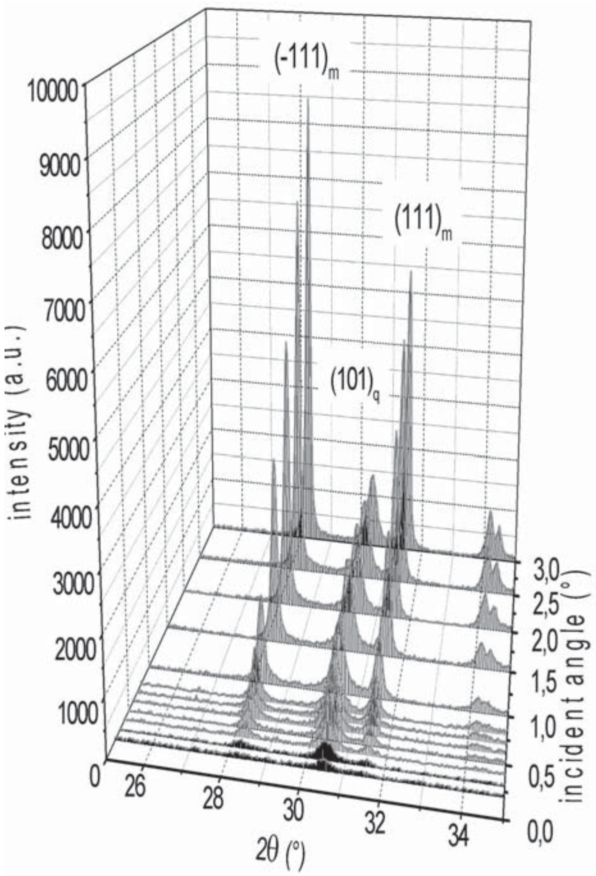

Fig. 1. Zoom of X-ray diffraction diagrams collected on irradiated zirconia samples at different incidence angles (i.e depths). Between two monoclinic Bragg peaks, a new peak associated to the tetragonal phase appears on irradiated samples. The saturation of the intensity of this peak suggests that the tetragonal phase is localized in the damaged area.

2. EXPERIMENTAL

Zirconia pellets (purity of 99.97%, grain size of about 10 μm) were irradiated by low energetic ions (Xe 400 keV and Bi 800 keV). As the kinetic energy of these ions is low, their penetration depths are small (0.1 μm for Bi and 0.4 μm for Xe). The grazing incidence is the sole technic able to analyse with X-ray diffraction the area damaged by ions. Fig. 1 presents the evolution of diffraction diagrams collected on post irradiated samples versus the incidence angle (*i.e* the depth of the probed area). The existence of a new Bragg peak near 30° is the signature of a new phase produced by irradiation in pure monoclinic zirconia. The analysis of diffraction diagrams as well as Raman spectra has clearly shown that the phase produced by irradiation is the tetragonal one. Then, a monoclinic to tetragonal phase transitions occurs under irradiation in pure micrometric zirconia samples.

Transmission Electron Microscopy pictures (cf Fig. 2) permit to follow the microstructural evolutions produced on zirconia by irradiation. Dark field observations clearly show that tetragonal nanodomains of about 10 nm are produced along the ions paths.

In order to follow the microscopic evolution of this material under irradiation, optical measurements (diffuse reflectance spectroscopy) were used to reveal the existence of point defects (colour centers) in irradiated samples. The analysis of the Kubelka-Munk function clearly shows that oxygen vacancies, the so called F^+ centre, are produced in this material under irradiation.

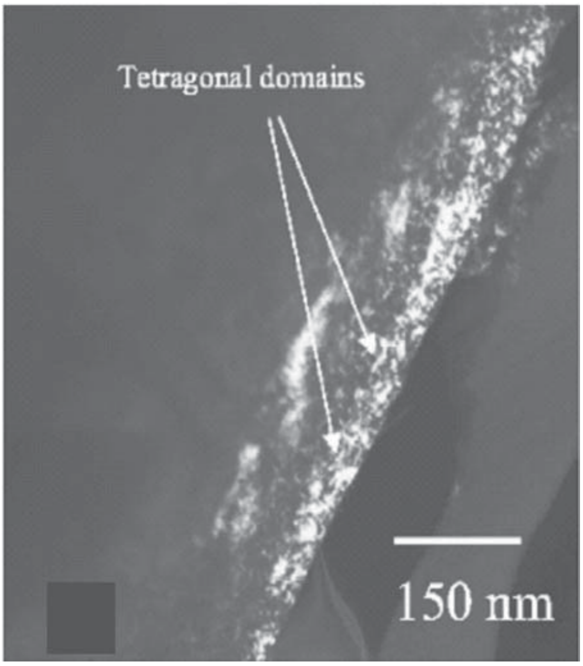

Fig. 2. Dark field image on the most irradiated zirconia samples. The dark field exhibits nanometric tetragonal domains. The size of these domains is similar to the one extracted from X-ray diffraction and is about 10 nm.

The comparison of diffraction diagrams and optical spectra collected after different isochronal annealings exhibits the vanishing of point defect as well as the tetragonal nano domains at the same temperature (520K).

All these experimental facts lead us to propose a mechanism to explain the nanostructuration of micrometric zirconia under irradiation.

3. DISCUSSION

The mechanism of the tetragonal to monoclinic phase transition occurring in pure micrometric zirconia was recently analyzed within the Landau theory framework [15]. In micrometric zirconia crystals, accurate data, obtained by neutron diffraction, were used to monitor this first order reconstructive phase transition as a function of the temperature both during heating and cooling. The analysis of the static and thermal displacements of the O atoms, of the thermal displacements of Zr atoms and of the thermal expansion of the lattice in the tetragonal phase supports a displacive mechanism for this phase transition. Within a mean field approach, the thermal dependence of these displacements in the monoclinic phase is proportional to the square root of (T_C-T). These experimental facts can be fully explained within the two-phonon model proposed by Negita [16] that involves the condensation of two phonons (φ and η) belonging respectively to M_1 and M_2 irreducible representations at the M point of the tetragonal Brillouin zone, $\boldsymbol{k}_M$=(π/a_t π/a_t 0). The compatibility relations between the two phases imply a well defined order for these phonon condensations: φ must be the first one to freeze. This doubles the unit cell, leading to an unstable intermediate orthorhombic phase (Pbcn) before the second condensation takes place (actually this tetragonal M_2 mode is now a zone center B_{2g} mode for the Pbcn phase). A Landau free energy expression [15] can be built up to describe all the possible couplings between these modes (the primary order parameters) and the strain field (the secondary order parameter) induced during the phase transition by the volume difference between the two phases. This expression predicts the observed linear evolution of the monoclinic distortion versus temperature near the phase transition. In fact, the first order semi-reconstructive tetragonal to monoclinic phase transition is described as a two stages process. The condensation of the M_1 phonon in the tetragonal phase, φ, produces an orthorhombic phase (Pbcn). This phase, never experimentally observed, is unstable and therefore associated with a critical saddle point in the Landau free energy expression. Therefore, any instability related to the condensation of the second phonon belonging to M_2 irreducible representation, η, at this saddle point is amplified. This leads to the actual monoclinic phase, characterized by a drastic change in the Zr coordination from 8 to 7. This semi-reconstructive character of the phase transition also explains the observed strain and volume change. These features make zirconia a very interesting material to study precisely the effects of strain on the martensitic transformation since a strong coupling exists between elastic energy and unstable phonons in Landau free energy expansion. The existence of a strong coupling between secondary and primary order parameters leads to a pinning at a fixed value of the primary order parameters.

This coupling is then responsible for the stability of the tetragonal phase in nanocrystals [17].

Moreover, *ab initio* calculations [18] suggest that the more efficient defects occurring in the tetragonal phase stabilization are O vacancies forming color centers; these defects are actually quite common in several ionic compounds under irradiation. These particular defects generate a strong local strain field. A strong coupling between strain and atom displace-

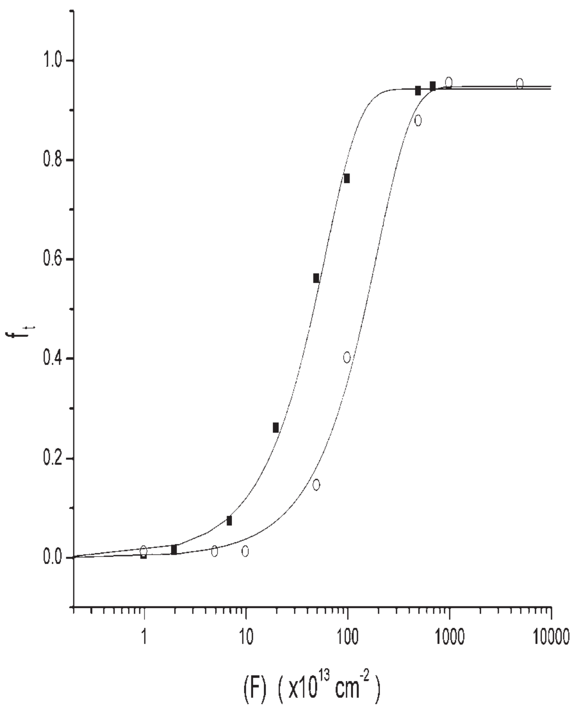

Fig. 3. Evolution of the tetragonal volume fraction of zirconia versus the fluence for different incident ions (black squares for 800 keV Bi and open dots for 400 keV Xe). Simple kinetic equations (full lines) fit experimental data.

ments lowers the temperature of the tetragonal to monoclinic transition and it quenches the tetragonal phase at room temperature in the irradiated samples. Because these defects also carry randomly oriented electric dipoles, a glass-like state is expected, preventing the coalescence of these tetragonal domains. These regions act almost independently and a simple kinetic equation for the defect concentration successfully explains the structural effects observed under irradiation [19].

Fig. 3 presents the evolution of the tetragonal volume fraction of zirconia versus the ion fluence. A simple kinetic equation captures all experimental features.

4. CONCLUSION

Based on the framework of the Landau theory of phase transition, it has been possible to describe the phase transition induced by irradiation in zirconia. The existence of a strong coupling between atomic movements and strain field is responsible for the appearance of the tetragonal phase under irradiation. Such a microscopic approach may be extended to describe martensitic, or in a more general way, displacive phase transitions in solids submitted to external perturbation like irradiation or ball milling. These findings may also have important consequences in modern microelectronic technologies that are increasingly endangered from energetic radiations from several sources. The effects of these high energy particles on microelectronic devices can significantly increase the soft error rates in these systems but also trigger structural modifications, damaging the crystal lattice in nanostructured high-k oxides like ZrO_2 and HfO_2 that are promising candidates for replacing SiO_2 in these devices.

On the other way, ion beam irradiation can be an useful tool to produce specific materials. Increasing the kinetic energy of incident ions, it could be possible to control the penetration depth of these particles and then their profiles of defects. Pure monoclinic layers of zirconia of micrometric thickness could then be uniformly nanostructured.

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