Complex Microstructures

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Can We Describe Phase Transition in Insulators within the Landau PT Theory Framework?

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ABSTRACT

Based on studies of simple oxides, this paper demonstrates that the specific energy deposition modes under irradiation induce modifications of materials over different length scales. On the other hand, we show the Landau phase transition theory, widely used to explain the structural stability of materials out of irradiation, can give a general framework to describe the behavior of these oxides under irradiation. The use of X-ray diffraction techniques coupled with the Raman spectroscopy allows defining in a quantitative way the phenomenological parameters leading to predictive results. This paper clearly shows that in two model systems, pure zirconia and spinels, no unexpected new phases are produced in these oxides irradiated at room temperature and with different fluxes. Such a phenomenological approach may be useful to study the radiation tolerance of many crystalline ceramics (e.g. the zirconium based americium ceramics).

INTRODUCTION

A significant growth in the utilization of nuclear power is expected to occur over the next several decades due to increasing demand for energy and environmental concerns related to emissions from fossil fuel plants. This has focused increasing attention on issues related to the permanent disposal of nuclear waste and the improvement of nuclear plants technologies. The achievement of such a goal requires continued improvements in safety and efficiency particularly related to the performance of materials [1]. The related research challenges represent some of the most demanding tests of our fundamental understanding of materials science and chemistry, and they provide significant opportunities for advancing basic science with broad impacts in the material science community. The fundamental challenge is to understand and control chemical and physical phenomena in multi-component systems from femto-seconds to millennia, at temperatures up to 1000°C, and for radiation doses up to hundreds of displacements per atom (dpa). New understanding is required for the microstructural evolution of the materials. Their phase stability under irradiation is an active field of debate.

In this context, ceramics appear to be incontrovertible materials. Crystalline oxide waste forms such as zircon [2] or spinel [3] have been proposed to accommodate a limited range of active species such as plutonium and multiphase systems such as Synroc [4] to accommodate a broader range of active species. On the other hand, carbides are promising candidates for claddings or diffusion barriers in the next generation of nuclear plants. The predictive understanding of microstructural evolutions and property changes of these ceramics under high temperature and elevated dpa is essential for the rational design of materials for structural, fuels, and waste-form applications. A clear relationship between energy depositions by impinging particles, phase stability and mechanical behavior has to be achieved.

The Phase Transition Landau framework remains a powerful tool to describe the evolution of solids submitted to various conditions (temperature, pressure) [6]. Variation of order parameters, concentration waves and strain field can be analyzed with the same formalism in term of minimization of an "effective Hamiltonian" within the mean field approximation [6,7,8]. Numerous authors try to analyze the behavior of alloys under irradiation within this framework [9,10]. A question naturally arises: can we apply this formalism to describe and to capture the main features of radiation induced phase transition in ceramics and in a more general way structural evolution of ceramics under irradiation?. The answer to such a question is not simple. In condensed matter, the control parameter (temperature or pressure) in the Landau Free energy is uniform along the material. In radiation experiments, the control parameter associated with the sub cascades formation describing the energy deposition is not uniform. On the other hand, fluctuations of order parameters induced by irradiation can be expected to be violent. A "Landau effective Hamiltonian" could thus not be able to describe the physics of radiation damage at least in alloys [11,12]. Such a harsh treatment leads to the appearance of new unexpected phases under irradiation in alloys [12].

Based on two examples of phase transition in simple oxides irradiated by different ions, we discuss in this paper the validity of such an approach. Two different oxide, pure zirconia and magnesium spinels were irradiated at room temperature with different ions. Their structural evolutions were explained within the Landau theory of phase transition pointing out that such formalism clearly describes the patterning observed in these irradiated ceramics as a function of few well defined experimentally measurable parameters.

EXPERIMENT

The main difficulty to understand the long term behavior of materials under irradiation is due to the fact that radiations damages occur over different length scales. The characteristic penetration depth of Primary Knock on Atoms or incident ions is of about few hundreds of nanometers to tens of micrometers, a highly disordered area is created over few nanometers in thermal spikes and point defects are produced at the atomic scale. Many experimental tools, like optical spectroscopy, positron annihilation and electron paramagnetic resonance have been developed to track point defects and aggregates induced by irradiation in insulators and semi conductors [13]. Few techniques are able to probe the nanometric scale. Rutherford back scattering channeling [14] quantifies the modification of atomic rows due to radiation damage at the nanometric scale but cannot give a clear description of e.g. modifications of the space group associated with the crystal lattice. Despite Electron Microscopy remains a powerful tool to track structural modifications of solids induced by irradiation, an accurate analysis of the diffraction

patterns remains difficult. X ray gives valuable information at different scales. The kinematic approximation permits to describe the atomic structure of the material after irradiation: the Bragg peaks modifications allow describing the evolution of the space group associated with the atomic lattices and the effect of strains induced by irradiation can be measured from the analysis of the lines broadening. On the other hand, Raman spectroscopy gives valuable information on the local environment. These two techniques provide measureable ingredients to describe radiation damages within the Landau framework as pointed out by many authors working on ceramics out and under irradiation [6,8,15,16]

We now illustrate this point describing the evolution of two simple oxides under irradiation.

Behavior of pure zirconia irradiated by low and high energy ions

Many authors[17,18] have shown that pure zirconia exhibits a first order phase transition as a function of the temperature. As irradiation is able to strongly modify the crystal, we can then enhance or inhibit this phase transition under irradiation. To assess this point, various irradiations were performed on pure monoclinic zirconia samples at room temperature [15]. Figure 1 exhibits the Raman spectra (left figure) collected on pure zirconia sample after irradiation by 800 keV Bi ions with a fluence of 10^{15} cm^{-2} at room temperature. The existence of a large Raman peak at about 250 cm^{-1} demonstrates that the tetragonal phase is produced under irradiation in pure monoclinic zirconia at room temperature. From this experimental result, X ray diffraction technique was used both to quantify the amount of the tetragonal phase formed under irradiation (right figure) and the strain field associated with this new phase [15].

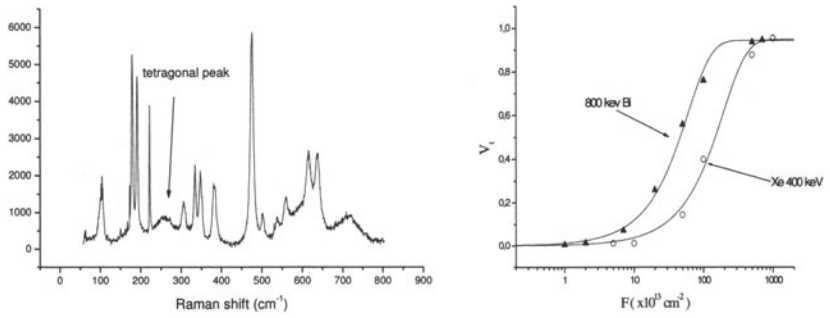

Figure 1. Raman Evidence of the existence of a tetragonal phase induced by 800 KeV Bi impinging ions at room temperature in pure zirconia (left). The appearance of Raman peak at around 260 cm^{-1} (arrow) and the absence of a Raman peak near 600 cm-1 assess that only the tetragonal phase of zirconia is produced. The Right figure displays and quantitative measure of the amount of the tetragonal phase , noticed Vt, versus the fluence F, for different irradiations performed at room temperature. The amount of the tetragonal phase results from a Rietveld refinement of the diffraction patterns collected

under grazing incidence [15].

Figure 2 exhibits the evolution of the strain field as a function of the annealing temperature on the most irradiated sample of pure zirconia irradiated by 92 MeV Kr ions at room temperature [19]. The analysis of Bragg peaks gives quantitative information on the strain tensor.

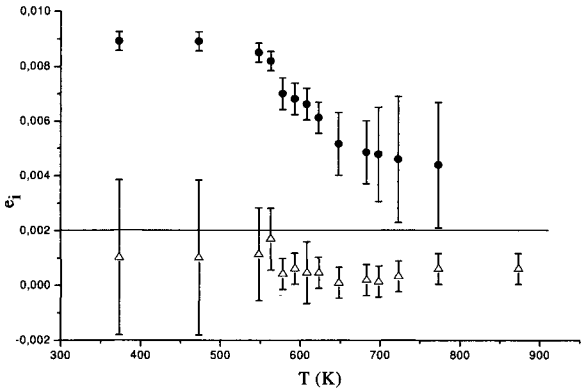

Figure 2. Evolution of the different components of the strain tensor (I varies from 1 to 3 in Voigt notation) extracted from the broadening of Bragg peaks versus the temperature during isochronal annealings on zirconia samples irradiated by 92 MeV Kr ions [18].

Combined analysis of Raman and XRD measurement will then permit to draw a clear picture describing the evolution of zirconia under irradiation [19,20].

Behavior of spinels irradiated by low and high energy ions

The impact of radiation has also been studied on magnesium aluminates, magnesium chromites and zinc aluminates spinels. This family exhibits a very simple phase diagram out of irradiation. These samples were irradiated at room temperature by both high and low energy ions to detect a possible phase transition induced by irradiation. The damaged are were then scanned using both Raman spectroscopy and XRD. Figure 3 displays the evolution of XRD patterns and Raman spectra on $MgCr_2O_4$ samples irradiated by 92 MeV Kr ions [18].

The XRD diffraction patterns clearly exhibit that many Bragg peaks vanish on the most irradiated samples whereas Raman analysis shows all normal modes associated with the usual spinel space group (Fd-3m) remain. The vanishing of these odd Bragg peaks could be understood as a phase transformation induced by irradiation at the atomic scale. However, TEM patterns collected on different scales give the experimental evidence that no change of the space group occurs in irradiated spinels in agreement with results of Raman spectroscopy which does not reveal any structural change at this scale. Figure 3 highlights the fact that irradiation can modify materials over different scale lengths. Moreover, no clear broadening is observed on odd Bragg peaks insuring that no strain appears during irradiation in the materials.

Since intensities of Raman peaks do not evolve during irradiation, the stiffness of bonds remains unaffected by irradiation. At first approximation, Raman frequencies can be considered as a simple function of the average mass of the cation lying on the octahedral and tetrahedral sites. Assuming the stiffness constant of the cation oxygen bond unaffected by irradiation, it is then possible to estimate the fraction of Mg atoms lying at the center of octahedral sites. From the measure of the Raman shifts, this fraction of Mg atoms in octahedral positions is roughly equal to 20% in the most irradiated samples. This point has been discussed in detail [23].

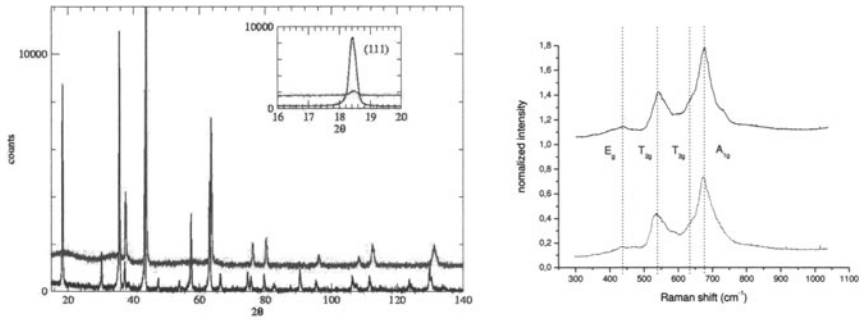

Figure 3. Comparison between Raman spectra (right figure) and XRD patterns collected on non irradiated (black line) and on the most irradiated (red line) sample of $MgCr_2O_4$.

DISCUSSION

All information given by Raman spectroscopy and X ray diffraction collected on irradiated samples can be clearly described with the phase transition Landau theory framework. Whereas this theory remains phenomenological, it can be used to describe the microstructural evolution of ceramics under irradiation taken account all experimental facts. We illustrate this point below.

Structural evolution of pure zirconia under irradiation

The phase transition Landau theory gives the natural framework to describe evolution of these ceramics as a function of the temperature and the pressure out of irradiation. Some authors have clearly shown that the monoclinic to tetragonal phase transition occurring in pure zirconia can be described by a phonon condensation [22]. The description of this transition within the Landau theory agrees with experimental results. Moreover, this description explains the stability of the tetragonal phase, the high temperature phase, in nanocrystals of pure zirconia at room temperature [23], pointing out the role of the strain field induced by the surface free energy. Such a model explains also the appearance and the stability of the tetragonal phase under irradiation [24]. Neglecting Ginzburg terms in Landau free energy and focusing our attention only on the leading terms, it is possible to write the free energy density as:

$$F(I) = \frac{\alpha_T}{2}\left(T - T_c - \frac{\alpha_e}{\alpha_T} H\left(e - e_{Threshold}\right)\right) I - \frac{1}{4} I^2$$

where α_T and α_e are phenomenological positive constants. The function I is the Landau invariant responsible for the displacive transition out of irradiation and 'e' is the trace of the strain tensor.

The analysis of the stability of zirconia nanocrystals as a function of the temperature out of irradiation and XRD patterns of irradiated zirconia samples give experimental evidence to include this term in the Landau free energy [23,24]. The value α_e embodies then the correction to the free energy density associated with the strain field induced by oxygen vacancies (deduced from optical analysis) in low energy irradiation and dislocation loops (as observed by TEM) in high energy irradiations. Once the concentration of defects is high enough, the strain fields becomes superior to a threshold value and the tetragonal phase is stabilized. This point clearly shows that radiation damages can be easily integrated in the PT Landau formalism.

Moreover, it is important to notice that Bright field TEM pictures clearly display the fact that the tetragonal domains produced under irradiation are not uniformly distributed in the irradiated sample. This point highlights the fact that different length scales exist under irradiation as expected from the fractal feature of the energy deposition under irradiation. [16,17]..

Structural evolution of spinels under irradiation

Out of irradiation, many authors attempted to describe the cation exchange occurring as a function of the temperature in many spinels within the mean field approximation. Careful analyses of neutron diffraction data prove that this thermodynamic of non convergent cation ordering in spinels can be better described within the Landau phase transition framework [7]:

$$F(I) = -hI + \frac{\alpha_T}{2}(T - T_c) I^2 + \frac{c}{6} I^6$$

Where I is the order parameter related to the cation exchange along tetrahedral and octahedral sites. The constants h, α_T and c are positive phenomenological constants.

This Landau free energy explains the evolution of the cation exchange as a function of the temperature out of irradiation without evoking any strain field effects, this in agreement with XRD results (no Bragg peaks broadening). Such a free energy can also explain the behavior of these materials maintained far from equilibrium by irradiation. The analysis of Raman spectra on spinels irradiated by low and high energy ions clearly displays the appearance of different shoulders in irradiated samples indicating andifferent domains characterized by different values of the order parameter I. This point can be understood if we correlate these domains with existence of displacement cascades induced by irradiation in spinels as pointed out by Molecular Dynamic simulation [24].

It is important to notice that XRD patterns clearly reveal the fact that the domains produced under irradiation are not uniformly distributed in the irradiated sample. As pointed out

in our previous example, this point highlights the fact that different length scales exist under irradiation in agreement with the fractal nature of the energy deposition [14,15].

CONCLUSIONS

As pointed out by numerous authors [25-27], the state of the knowledge on the behavior of oxides and more generally of ceramics under irradiation is far from satisfactory, despite their important role in these conditions, either as electric insulators, as nuclear fuels and structural materials in reactors or as storage matrices for radioactive wastes from nuclear industry. The origin of this situation can be attributed to:

- Experiments in ceramics are more complex than in metals and alloys due to the higher characteristic temperatures involved.
- the complex nature of the bonding, partly ionic [24] and partly covalent [27],in ceramics are less known than in alloys. This point has for long precluded any relevant quantitative calculation.

Based on studies of two simple oxides, pure zirconia and spinels, this paper demonstrates that the specific energy deposition modes induce modifications of materials over different length scale. On the other hand, we prove that the Landau phase transition theory largely used to explain the structural stability of materials out of irradiation can give a general framework to describe the behavior of these oxides under irradiation. The major point of this paper is clearly to show that no new phases, unexpected from the classical P-T thermodynamic diagram of these solids, are produced under irradiation with different fluxes at least at room and low temperatures.

Moreover, the Phase Transition Landau theory succeeded to explain the behavior of these materials under irradiation. Even if this theory remains phenomenological, the use of diffraction techniques coupled with the Raman spectroscopy allows defining in a quantitative way parameters leading to predictive results. On the other hand, this framework can be easily extended to take into account inhomogeneities due to irradiation in larger length and time scales. Even if this description of radiation damage remains phenomenological, it gives some clues to capture key parameters controlling the microstructure of these irradiated simple oxides, overcoming difficulties associated with the complex nature of chemical bonds in ceramics. Such a phenomenological approach may be used to understand the radiation resistance of many crystalline ceramics under irradiation like for instance the zirconium based americium ceramics [30] or the amorphisation of SiC [5].

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