



# Disorder–order phase transformation in a fluorite-related oxide thin film: In-situ X-ray diffraction and modelling of the residual stress effects



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## ABSTRACT

This work is focused on the transformation of the disordered fluorite cubic-F phase to the ordered cubic-C bixbyite phase, induced by isothermal annealing as a function of the residual stresses resulting from different concentrations of microstructural defects in the yttrium oxide,  $Y_2O_3$ .

This transformation was studied using in-situ X-ray diffraction and was modelled using Kolmogorov–Johnson–Mehl–Avrami (KJMA) analysis. The degree of the disorder of the oxygen network was associated with the residual stress, which was a key parameter for the stability and the kinetics of the transition of the different phases that were present in the thin oxide film. When the degree of disorder/residual stress level is high, this transition, which occurs at a rather low temperature (300 °C), is interpreted as a transformation of phases that occurs by a complete recrystallization via the nucleation and growth of a new cubic-C structure. Using the KJMA model, we determined the activation energy of the transformation process, which indicates that this transition occurs via a one-dimensional diffusion process. Thus, we present the analysis and modelling of the stress state. When the disorder/residual stress level was low, a transition to the quasi-perfect ordered cubic-C structure of the yttrium oxide appeared at a rather high temperature (800 °C), which is interpreted as a classic recovery mechanism of the cubic-C structure.

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## 1. Introduction

The fluorite related oxide family includes the fluorite dioxides,  $MO_2$  ( $M^{4+} = Zr, Hf, Ce, Th, U, Pu, Am, etc.$ ), which have a cubic fluorite structure and a space group of Fm3m, and their superstructure derivatives, which include the C-type sesquioxides,  $Ln_2O_3$  (lanthanides:  $Ln^{3+} =$  from La to Lu and Y, Sc, In), which have a cubic-C (bixbyite) structure and a space group of Ia3-Th7. The pyrochlore compounds,  $A_2B_2O_7$ , that exhibit a large compositional range are also related to the fluorite oxide structure.

The difference between the fluorite structure (cubic-F) and the bixbyite structure (cubic-C) is due to their oxygen network that, in the case of the cubic-C, exhibits an ordered network of structural oxygen vacancies, which are very sensitive to energetic forces, such as thermal annealing, irradiation, or stress. When this network is fully disordered, the symmetry of the cubic-C is destroyed, and the oxide adopts a disordered fluorite-F structure.

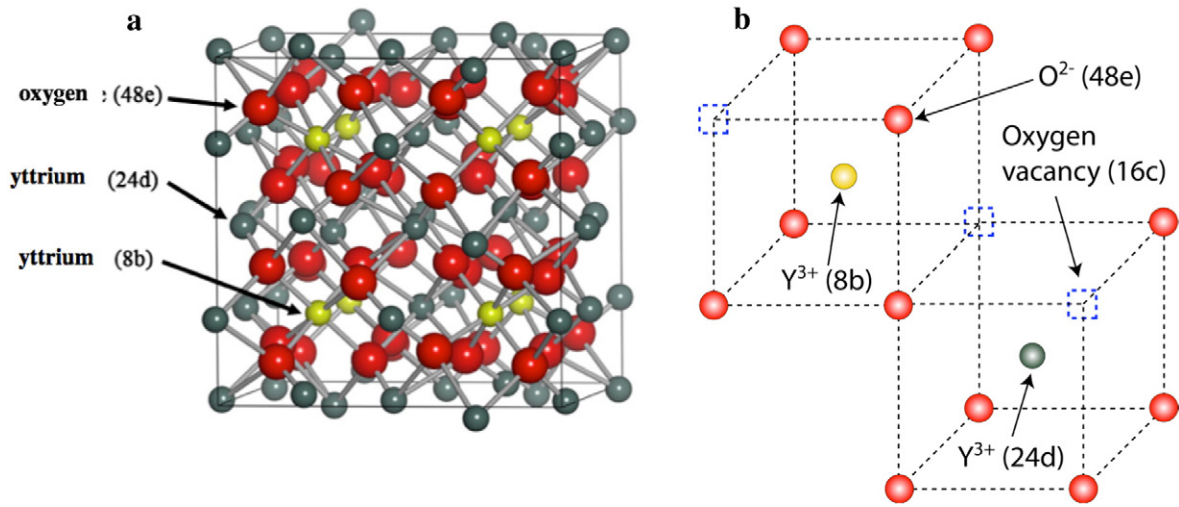
All of these fluorite related oxides exhibit a wide range of physical and chemical properties that enable their potential technological applications. Therefore, it is interesting to determine the effects of the

microstructural defects and the residual stress on the stability of the different structures, which is important for their technological applications.

## 2. Crystallography

The rare earth oxides,  $RE_2O_3$ , exhibit several polymorphic structures: A-hexagonal (P32 m), B-monoclinic (C2/m), C-cubic (Ia3), H-hexagonal (P63/mmc), and X-fluorite (Fm3m). Phase transitions can be observed when the rare earth oxides are exposed to extreme temperature, pressure, or irradiation [1–3]. The fluorite phase of  $Y_2O_3$  has been observed at a very high temperature (2520 K) [4] and exhibits the quenchable nature of the transformation from the C-cubic to the X-fluorite structure. An order–disorder phase transformation was observed in ion-irradiated  $Dy_2O_3$ , a rare earth sesquioxide [5,6], where the oxygen superlattice that was associated with the bixbyite structure was destroyed. Anion disordering induced via ion-irradiation has also been reported in the pyrochlore,  $A_2B_2O_7$  [7]. Thus, we are interested in determining why the high temperature X-fluorite structure, which is considered to be a strongly disordered cubic-C structure, remains stable at room temperature and at atmospheric pressure.

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**Fig. 1.** Structure of the cubic C-type  $\text{Y}_2\text{O}_3$  (bixbyite). The lattice parameter is  $a_0 = 1.0604$  nm. (a) Unit cell representation. (b) Environment of the two Y sites (the actual position of the O atoms is slightly shifted from the corners of the cubes). The small squares are structural oxygen vacancies.

Here, we focused on the transition from the disordered fluorite cubic-F phase to the ordered cubic-C bixbyite phase, which was induced by isothermal annealing as a function of the residual stresses resulting from different concentrations of microstructural defects in the yttrium oxide  $\text{Y}_2\text{O}_3$ .

This transition was studied using in-situ X-ray diffraction (XRD) and the Kolmogorov–Johnson–Mehl–Avrami (KJMA) model [8–10].

There is a strong crystallographic similarity between the cubic-C (bixbyite) and the fluorite structure. The unit cell of the  $\text{Y}_2\text{O}_3$  cubic-C structure is composed of 80 atoms with a bulk lattice constant of  $a_0 = 1.0604$  nm.

The oxygen atoms are located on the (48e) sites, and yttrium atoms are located on two non-equivalent cation sites,  $\text{Y}_1$  (8b) and  $\text{Y}_2$  (24d) (Fig. 1-a). All of the cations are six-fold coordinated: the  $\text{Y}_1$  atoms are surrounded by six neighbouring oxygens at the same distance (0.230 nm), whereas the  $\text{Y}_2$  atoms have three pairs of neighbouring oxygens at three different distances (0.225, 0.228, and 0.236 nm). This structure results in a specific arrangement of structural oxygen vacancies that form a network in the (16c) position along the body diagonal and face diagonal of the cubic cell (Fig. 1-b). When the structural oxygen vacancies are fully filled by oxygen ions, the bixbyite structure becomes a disordered fluorite structure. It is particularly interesting to consider the oxygen network of both the bixbyite and the fluorite structure by considering their dense {111} oxygen planes (Fig. 2).

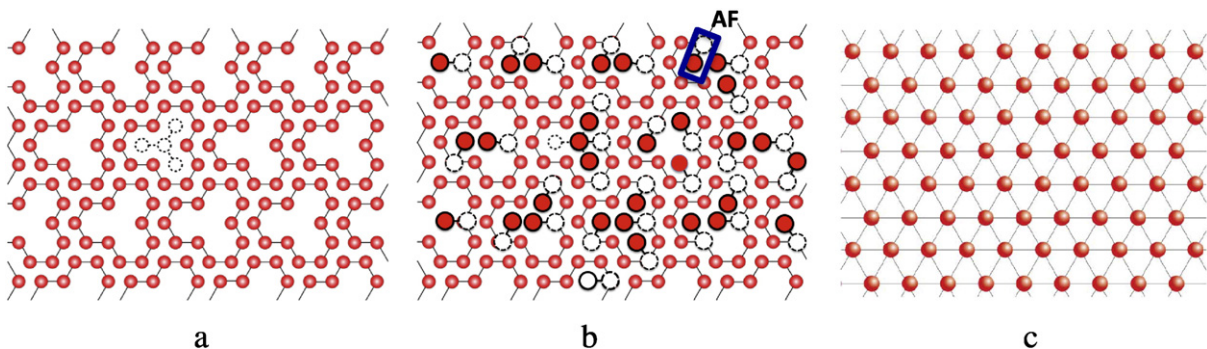
In rare earth oxides, the oxygen vacancies have the smallest energy barrier for diffusion [11], and the minimum energy of interstitial oxygen

has been determined to be in a structural vacancy site (16c in Fig. 1-b) that generally produces anti-Frenkel pairs. Thus, the oxygen network of the rare oxide is particularly sensitive to energetic forces that induce either a strong diffusion mechanism or/and internal stress that can strongly decrease the free energy of the oxide, resulting in a phase transformation and stabilization of the new phase.

### 3. Experiments

$\text{Y}_2\text{O}_3$  thin films were grown on a Si (100) substrate via the Ion Beam Sputtering deposition technique, which uses an argon beam of different energies (600, 800, 1000 and 1200 eV) to sputter a  $\text{Y}_2\text{O}_3$  sintered stoichiometric target [12]. A thickness of 100 nm was attained at 700 °C. The XRD analysis was performed using a Bruker D8 diffractometer with a  $\text{Cu K}\alpha$  radiation source in the Bragg–Brentano geometry. This diffractometer is equipped with an Anton-Paar heating chamber that allows in-situ annealing in air up to 1100 °C with a controlled heating/cooling rate of  $1^\circ\text{C s}^{-1}$ .

The  $\text{Y}_2\text{O}_3$  thin films were strongly textured along the  $\langle 111 \rangle$  direction of the cubic-C structure. Fig. 3-a shows that the profile of the (222) Bragg peak was significantly modified when the primary Ar ion beam energy increased from 600 to 1200 eV to produce an asymmetrical profile (Fig. 3-a). This asymmetrical profile is due to the mixture of different phases, as shown in Fig. 4, in which the components,  $\text{C}_1$  and  $\text{C}_2$ , are ascribed to the {111} planes of the fluorite structure and the {222} planes of the cubic-C structure, respectively.



**Fig. 2.** Dense {111} oxygen planes in (a) a perfectly ordered bixbyite, (b) a strongly disordered bixbyite/fluorite, and (c) a perfect fluorite structure. The ordered network of structural oxygen vacancies is shown in (a). In (b), this order is destroyed. The majority of the defects are anti-Frenkel (AF) pairs.

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