What is the origin of a series of low angle XRD peaks which appear following thermal cycling of a gadolinium - doped ceria film – formation of a superlattice or surface contamination?

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Abstract

The structure of non-stoichiometric, gadolinium (Gd) doped, oxygen vacancy enriched ceria ceramics, commonly used in solid oxide fuel cells (SOFC), has been actively investigated in recent years. In particular, in our X-ray diffraction (XRD) laboratory, it was found [1] that when the level of Gd doping reaches 25 mole%, XRD peaks characteristic of the double fluorite structure begin to appear in addition to the original room temperature XRD peaks of fluorite CeO₂. The further observation that at ~90K the dielectric constant of a Ce₀.₈Gd₀.₂O₁.₉ film depends on the applied voltage and displays hysteretic behavior [2] has motivated us to study the low temperature structure of these films by XRD.

Many XRD scans of the Ce₀.₈Gd₀.₂O₁.₉ films were performed in the temperature range 90K to 450K. In approximately 20% of these scans, we observed a series of low angle XRD peaks that appear upon cooling and persist after subsequent heating to room temperature, where they slowly disappear during several hours (Fig. 1). However, upon heating the film directly to 370K, the peaks disappear immediately. Unfortunately, all our efforts to find reproducible conditions have been in vain. First, we succeeded in controlling cooling and heating rates, sample quality, and ice formation on the sample surface. Then, after modification of our variable temperature attachment, we were also able to control gas composition and pressure in the vacuum chamber, as well observe the specimen surface. However, the low angle peaks continued to appear in a random fashion. Obviously, there must be an additional, important parameter that we haven’t taken into account. Our search for this key parameter has centered on conditions for careful freezing of the oxygen vacancies and formation of a superlattice, while one cannot exclude the possibility that these peaks may appear for another, more technical, reason…
Fig1. XRD spectra obtained from a Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ film at different temperatures (start from the top). It can be seen evolution of the peaks formation (between 1-12 degrees) at cooling/heating process. Peak around 28.5 degree is (111) of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$; peaks around 24 degree are the ice peaks (disappeared above ice melting point).

References
