Antiphase Ordered Domains and Optical Diffraction for Copper-Gold and Samarium-doped Ceria: Reflections on Gareth Thomas

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The first article co-authored by one of us (RS) with Professor Gareth Thomas concerned the use of the then relatively new high resolution “lattice imaging” technique to study antiphase boundaries in ordered Cu₃Au [1]. As this approach was still not universally accepted at that time, a follow-up article used optical diffraction from the lattice images to demonstrate that the latter contained equivalent information to those revealed in electron diffraction patterns of the original specimens in the transmission electron microscope [2]. Nowadays, forty or so years later, high resolution TEM imaging is well established and, since the images are recorded digitally, the optical diffractogram can be generated simultaneously using fast Fourier transformation (FFT) programs.

In this paper we present aberration-corrected high resolution TEM images and their FFT analyses of Sm doped ceria thin films prepared by pulsed laser deposition, for possible fuel cell application. The images show a superlattice structure related to the base fluorite lattice, comprising small ordered domains (Fig 1a). This physical situation is similar to that described in ref. [1] in which approximately 2.5 nm ordered domains with the L1₂ structure exist within a disordered Cu₃Au FCC matrix. The domains are in antiphase, which gives rise to splitting of the superlattice reflections [1]. The same phenomena is observed in the new results on the Sm-doped ceria: the FFT clearly illustrates split superlattice reflections from the ordered domains in antiphase (Fig 1b). In the present case, image matching calculations (reported separately) show that the superlattice arises from an ordering of oxygen anion vacancies which are created during the electron beam irradiation. The influence of the imaging electron beam must always be taken into account, which we have emphasized in recent articles on in situ observation of gas-solid reactions during environmental TEM [3, 4].

The present article shows that the techniques being developed during the early days of high resolution TEM are still relevant for materials analysis today, albeit with significantly improved instrumentation. The conclusion of ref. [1], that lattice fringe imaging “should find increasing importance in the investigation of ordering reactions in materials”, has clearly been borne out. Professor Thomas’s vision in supporting and promoting this approach can thereby be recognized, and we are pleased to dedicate this work to his long-lasting contributions. [5]

References:

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Figure 1. (a) Cross-section aberration-corrected high resolution TEM image of Sm-doped ceria on yttrium stabilized zirconia taken along [100] direction, showing the domains of oxygen vacancy ordered phase within the film. Arrows indicate offset planes. (b) Fast Fourier transformation of the HRTEM image in (a), showing the splitting of superlattice reflections (inset).