Study of Order-Disorder Transformations in Yttria-Rich Tantalate Using Transmission Electron Microscopy

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The YO1.5-TaO2.5 system contains phases of technological interest in applications as diverse as ionic conductors, catalysts, phosphors, lasers, and potentially thermal barrier coatings. The phase equilibria in this system have been recently re-examined experimentally, elucidating some of the controversies in prior literature. Specifically, the structures and phase transformations in the region around the Y3TaO7 composition had been the subject of significant debate in prior studies owing to the ambiguity resulting from the interpretation of X-ray, synchrotron, and electron diffraction patterns. While the most recent study provided understanding of the phase relationships between the orthorhombic Ccmm (W) and Cmmm (O) structures below 1500°C, it also revealed intriguing features of their evolution at higher temperature [1]. Both phases are ordered derivatives of fluorite (F), with W originally proposed to disorder peritectoidally into F + O above ~1580°C and O decomposing by a similar reaction into F and tetragonal $YTaO_4$ at ~1870°C [2]. Nevertheless, it has now been established that the fluorite phase is stable at temperatures as low as 1250°C [3], much lower than previously reported, but the earlier descriptions of its structure at higher temperatures [4,5] remain unclear.

The goal of this study is to provide insight into the phase evolution above 1500°C in $Y_{3-x}Ta_{1+x}O_{7+x}$ compositions for $0 \leq x \leq 0.12$, clarifying arguable interpretations of previous reports. Accordingly, $Y_{3-x}Ta_{1+x}O_{7+x}$ samples with x=0 (75Y25Ta) and x=0.12 (72Y28Ta) were isothermally heat treated from 1500°C to 1700°C and investigated using selected area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM), and high-angle annular dark-field (HAADF) imaging in scanning transmission electron microscopy (STEM). In particular, for HAADF imaging with reasonable signal-to-noise ratio while concomitantly reducing scan and specimen drifts, 30 fast-scan images were sequentially recorded and aligned using cross-correlation algorithm. The aligned images were subsequently averaged out. To specifically obtain Ta and Y ion orderings in the given structures atomic-level electron energy loss spectroscopy (EELS) and energy dispersive X-ray (EDX) spectroscopy were additionally performed.

The formation of domain structures was observed in both compositions. The long-period superstructures in the 75Y25Ta and the 72Y28Ta composition were formed at 1600°C and 1700°C, respectively, suggesting the effect of chemical composition on the transformation temperature (Fig. 1). The atomic arrangements of the modulated layers were also affected by chemical composition. An incommensurate superstructure with antiphase boundaries was formed in the 72Y28Ta composition, while in the 75Y25Ta composition a commensurate superstructure was built with no antiphase boundary (Fig. 1). The detailed structure of the fluorite phase with a short-range ordering of cations, potentially accompanied by anion ordering above the transformation temperature, was exclusively explained by combining SAED analysis with an atomic resolution HAADF imaging (Fig 2). In this study, deeper understanding of the structural evolution from orthorhombic to fluorite phase during the order-disorder transformation and the fluorite structure remained unclear in prior studies were provided using suitable TEM imaging and spectroscopy techniques.

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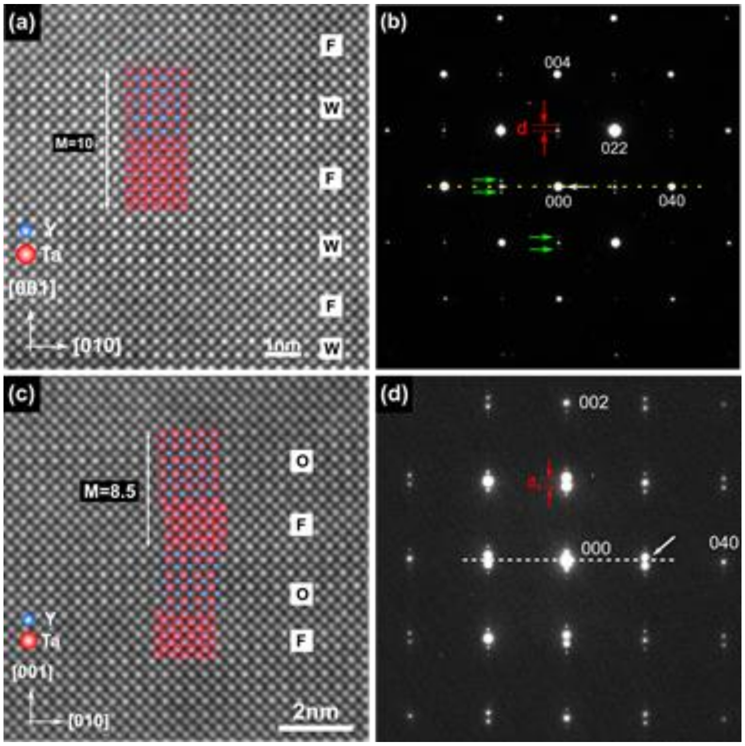

Figure 1. HAADF images (a, c) and corresponding SAED patterns (b, d) along the [100] direction of the long period superstructure in the 75Y25Ta and 72Y28Ta compositions, respectively. The modulation thickness (M) in the 75Y28Ta and 72Y28Ta composition were $10 \cdot d_{004}$ (commensurate) and $8.5 \cdot d_{002}$ (incommensurate), respectively. A splitting and slight shift of (020) reflection along the [001] direction (white arrow) in (d) suggest antiphase relationship between modulated layers. The HAADF image of the 72Y28Ta in (c) confirms this antiphase relationship.

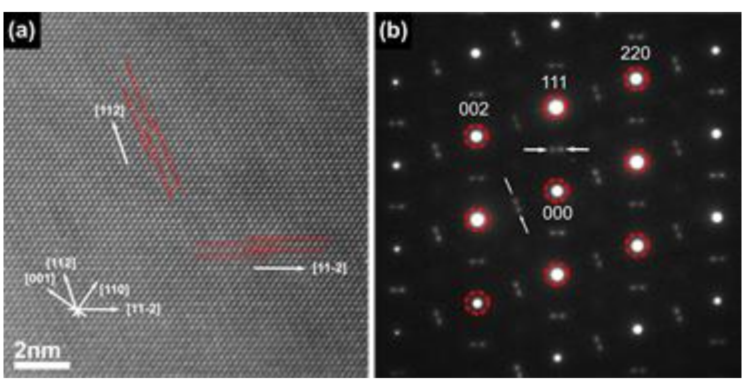

Figure 2. HAADF image (a) and corresponding SAED pattern (b) of the 75Y25 composition annealed at 1700°C. A Splitting of reflections at the (111) equivalent positions along the [112] direction (white arrows) is evident in (b), suggesting antiphase boundaries. The HAADF image in (a) confirms antiphase boundaries arising from the short-range ordering of cations.