Ceramics, Oxides, Geomaterials

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Aberration-Corrected Microscopy and Spectroscopy of SiAlON Ceramics

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SiAlONs are new generation solid-solution ceramics derived from the same crystal structures of α-β/Si_3N_4 [1]. Depending on the sintering dopants, the desired engineering properties of SiAlONs for many kind of applications from cutting tools to white light emitting diodes (LEDs) can be tailored by microstructure, primarily consisting of two distinct polymorphs (α and β), triple junction phases and grain boundaries [2-4]. Therefore, the atomic-scale characterization is a key step in further developing and designing the SiAlONs. However, over the past three decades, although many researches have been shed light on the micro- to atomic-scale observations of SiAlONs, the atomic-resolved STEM knowledge from α- and β-SiAlON unit-cells as well as grain boundaries has been lacking.

Here, we report the atomic-scale imaging and spectroscopy of gas pressure sintered Yb, Ce and Yb-Ce containing single and double rare-earth cation doped α/β-SiAlONs as well as TiN reinforced β-SiAlON ceramics using Z-contrast and EELS techniques in different type of state of the art aberration-corrected STEMs [5-6]. The results demonstrate that: *(i)* Yb and Ce dopants were preferentially incorporated into the β-SiAlON crystal structure at the atom-specific lattice locations, with higher solubility for Yb than Ce; *(ii)* this observation was also confirmed in the Yb-Ce co-doped system; *(iii)* Ce atoms without any co-doped cation were present in the triangular-like host sites of α-SiAlON unit-cell, accommodating much more atoms than Ce-doped β-SiAlON; *(iv)* Yb and Ce atoms were periodically and differently arranged in the grain boundaries, explaining that they are in semi-crystalline nature, not completely amorphous; and (v) Ti atoms were incorporated into the β-SiAlON unit-cell.

In conclusion, our atomic-resolved microscopy and spectroscopy results demonstrate direct visualization of the sites and solubility of rare-earth and transition metal atoms in α-β SiAlON unit-cells and grain boundaries. This capability offers new atomic-level engineering insights into how appropriate rare-earth types and SiAlON host polymorphs should be chosen for nanoscopic tailoring of both next-generation SiAlON-based structural materials and optical ceramics. We expect our observations of impurity sites and solubilities in SiAlON polymorphs and grain boundaries represents the first step towards a new paradigm for atomic-scale guidance in the production of rare-earth and transition metal atoms doped materials for a wide variety of applications.

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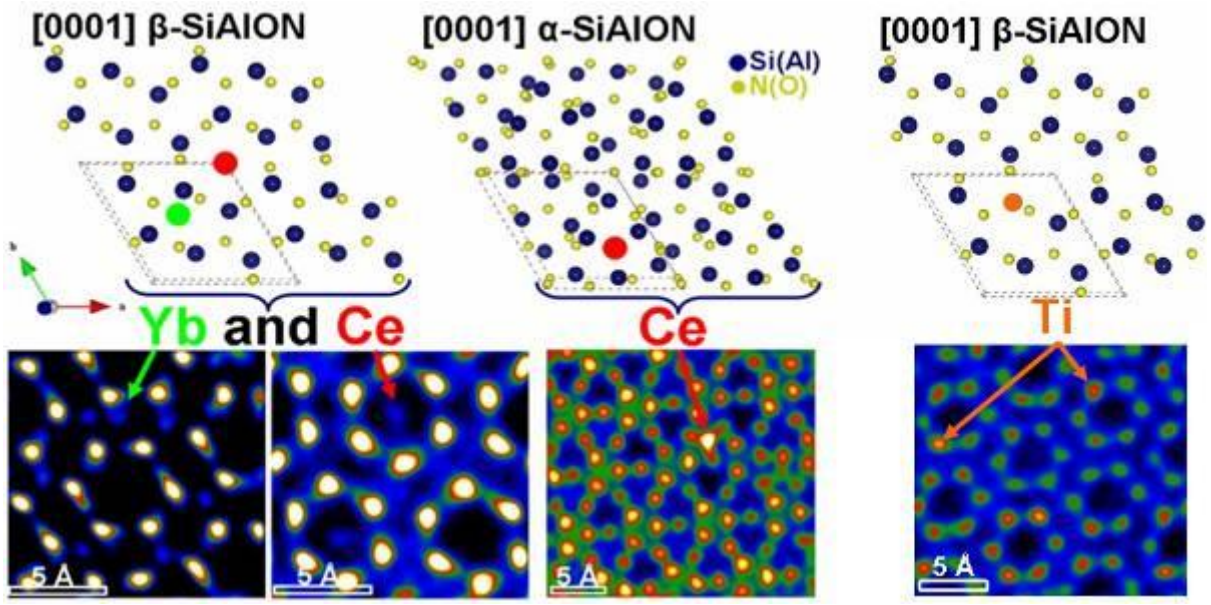

Figure 1. Z-contrast HAADF images of interstitial Yb and Ce rare-earth atoms in α- and β-SiAlON unit-cells as well as substitutional Ti atoms within β-SiAlON crystal structure through Cs-corrected STEM. Please note that unit-cells are shown by dashed parallelograms.

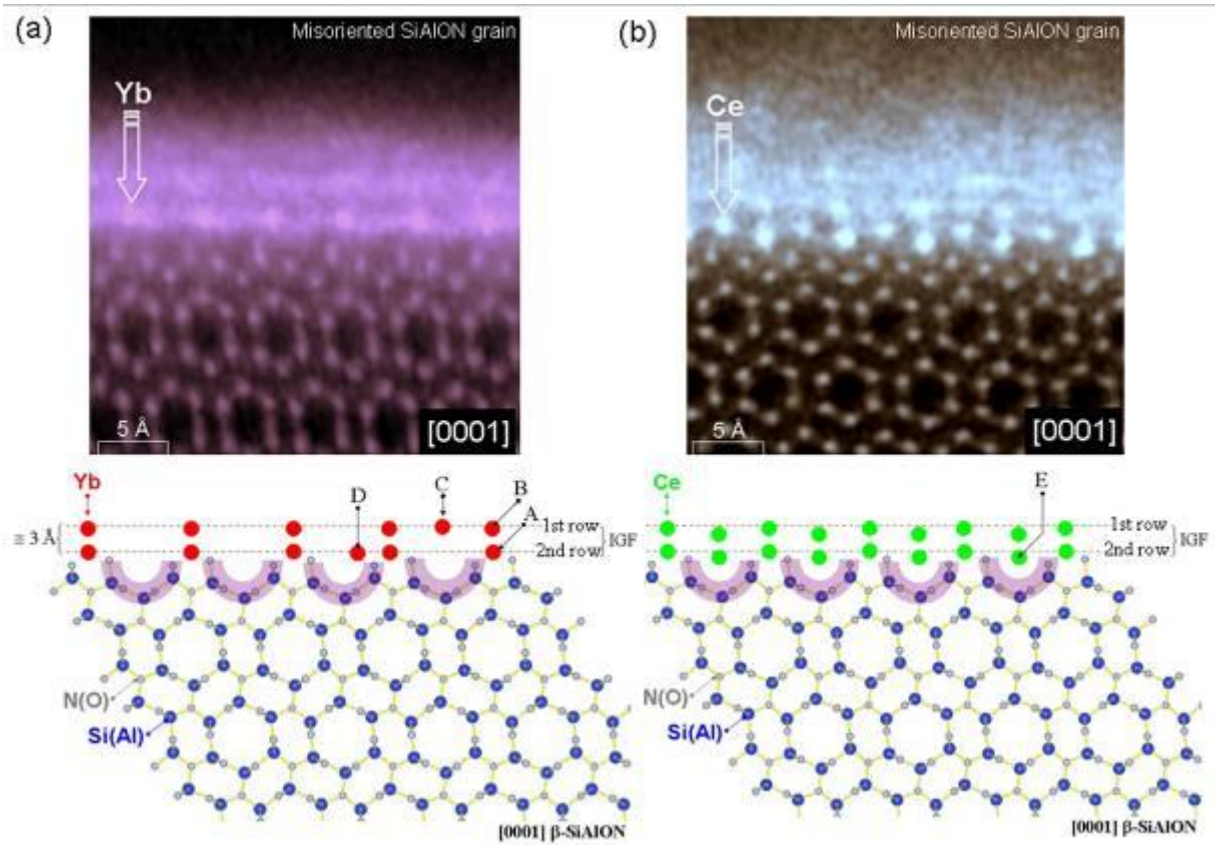

Figure 2. The Z-contrast images obtained from (a) Yb and (b) Ce doped systems using aberration-corrected STEM showing the IGF structures between [0001] β-SiAlON and misoriented SiAlON grains. Here, rare-earth element specific atomic-sites for Yb and Ce are atomically visualized in semi-crystalline IGFs with approximately 7-8 Å thicknesses. Evaluation of specific atomic positions (marked with arrows in the simulation part of Fig. 2(a-b)) on the rows of IGF, it can be deduced that Yb and Ce atoms are attached to the surface of [0001] β-SiAlON grain at the “A”, “B”, “C”, “D” and “E” atomic sites.