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Determination of Polymorph Structures in Functional Metal Oxides Using Convergent Beam Electron Diffraction

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In binary metal oxides (BMO), polymorphic transitions can result in various crystallographic structures which have been shown to exhibit very different and distinct physical and chemical properties. Thus, exact structural determination is essential as these changes in their crystal structures offer fine control over a wide variety of different properties and, therefore, open up a wide field of applications. However, distinguishing between different BMO polymorphs is not trivial. A combination of high-resolution X-ray diffraction (XRD), Raman and infrared-ray (IR) spectroscopy might be perform to identify phases. However, this is not a universal approach because strategies for phase identification vary with materials system, and, in the case of BMO polymorphs, might not work at all because of limitations of standard Raman/IR spectrum data of inorganics crystal. Conventional electron-microscopy-based characterization techniques, such as selected area electron diffraction (SAED), nanobeam diffraction (NBE), high-resolution TEM (HRTEM), high-resolution STEM (HRSTEM), provide information that is not always sufficient for polymorph determination, especially in nanocrystalline BMO. A general and universal approach to overcome this and to confirm a specific crystal structure is performing TEM tilt experiments obtaining data from at least 4-6 zone axis orientation (e.g., using SAED patterns, NBE patterns, HRTEM or HRSTEM images). However, this is a complicate experiment and, in case of beam-sensitive materials, this time-consuming approach might not work.

Recent research toward fast and universal phase identification methods shows little progress, but a universal and easy-to-perform method is needed to proceed in the development of functional BMO. Therefore, we propose using Convergent Beam Electron Diffraction (CBED) experiments in one (or a few zone axis orientations) as a direct, easy and universal characterization technique for structure determination of nanocrystalline polymorphic materials. Deficient High Order Laue Zone (HOLZ) lines pattern of different polymorphs (= different space groups) will show distinguishable features. The origin of deficient HOLZ lines is the dispersion surface construction and these line patterns could be theoretically calculated with the help of dynamical scattering theory, enabling accurate determination of accelerating voltages, atomic position, point/space group as well as lattice parameter, [1] as shown in Figure 1. In order to achieve phase identification, we have to compare experimental and computational deficient HOLZ lines in CBED/large angle CBED (LACBED) /Hollow cone beam CBED (HCB-CBED) patterns. [2]

Here, we present results on hafnia (HfO_2) and tungsten trioxide (WO_3) nanoparticles with particle size ranging from 50 - 500 nm. In case of hafnia, there are four published HfO_2 polymorphs that can be stabilized under room temperature (RT) and normal pressure. We attempt to identify and distinguish uniquely between the orthorhombic HfO_2 (o-HfO_2) with space group $Pca2_1$ and tetragonal HfO_2 (t-HfO_2) phase with space group $P4_2/nmc$. The former one exhibits ferroelectric properties while the latter one is a high-permittivity material. [3,4] As for the tungsten trioxide, we attempt to identify hexagonal WO_3 (h-WO_3) with space group $P6_3/mcm$, one monoclinic WO_3 (-WO_3) with space group Pc and the other monoclinic WO_3 (-WO_3) with space group $P2_1/n$ out of 7 published polymorphs. Those three different WO_3 phases show great potential in gas sensor applications, because each polymorph has a distinct response to specific types of gases. For example, -WO_3 is a conventional gas sensor that has been used to detect NO_x, NH_3, H_2S and O_3. [5,6] Our recent work suggests that h-WO_3 shows good sensing property to Isoprene concentration and -WO_3 has high sensitivity to Acetone concentration. [6] Our CBED pattern simulation results in 001 zone axis orientation (Figure 2) suggest that the deficient HOLZ line patterns are unique for the four HfO_2 polymorphs, and therefore enable a unique phase identification of HfO_2 polymorphs. The results of WO_3 polymorphs also support this conclusion. All many-beam CBED patterns are simulated using MBFIT [7]. The CBED experiments are performed using a Tecnai 20 TEM at OSU's Center for Electron Microscopy and Analysis (CEMAS).

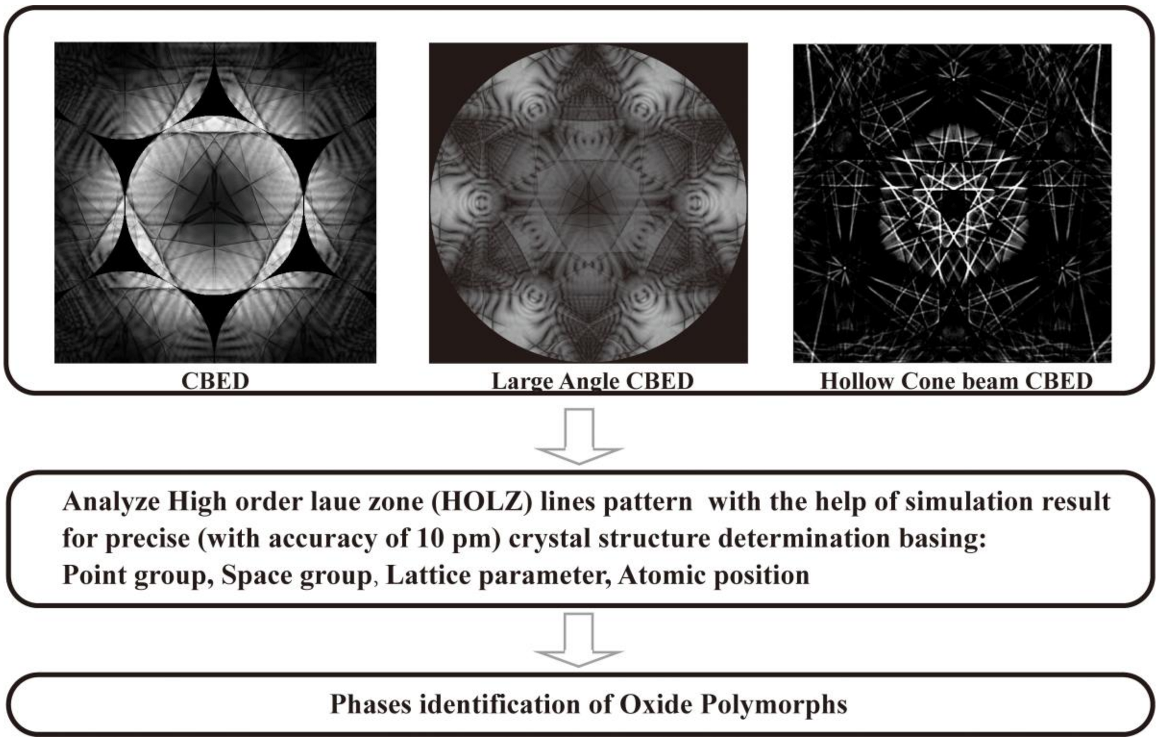

Figure 1. Strategy flow chart of phase identification method

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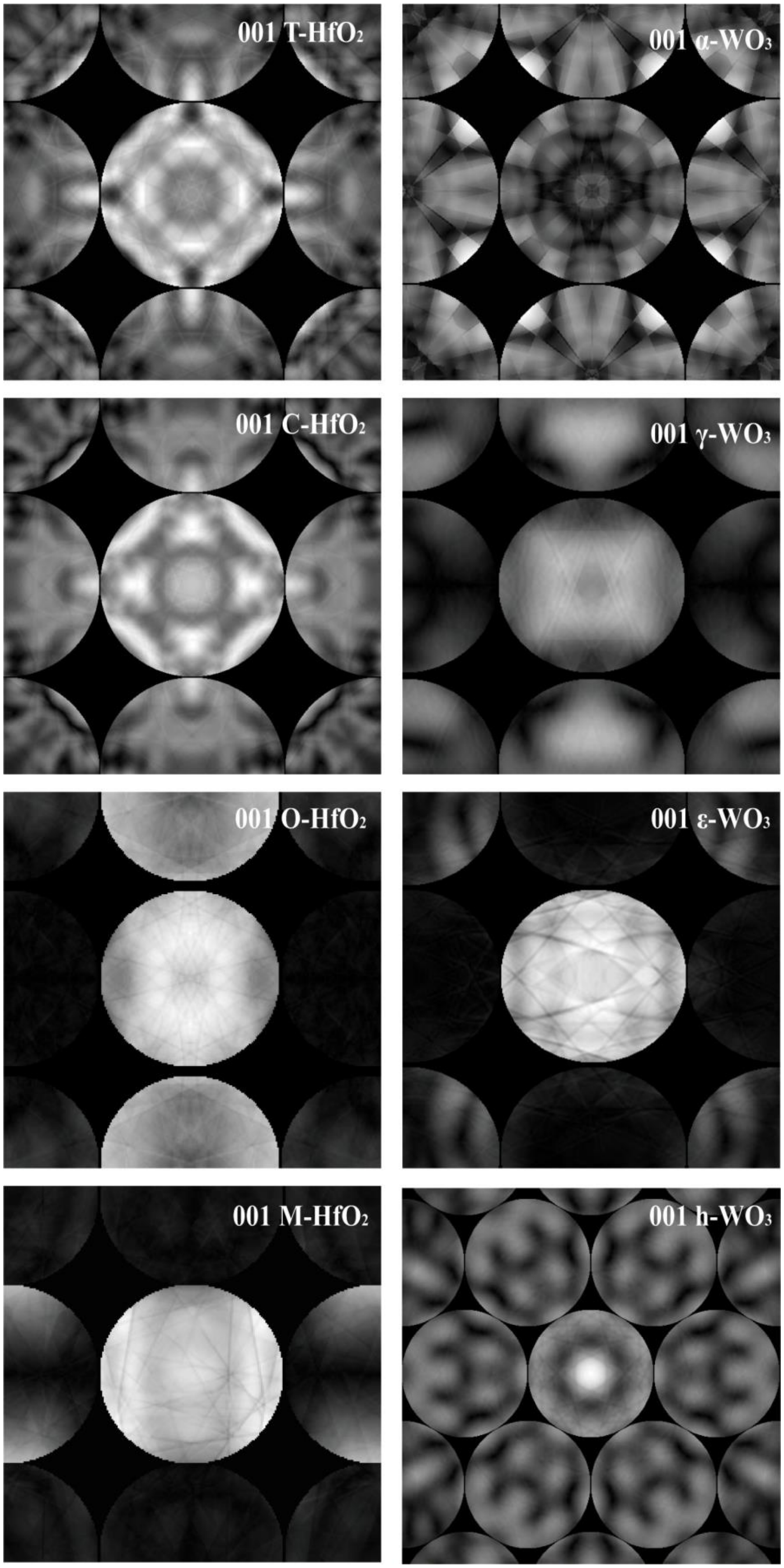

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Figure 2. Simulation results of 001 CBED pattern of HfO_2 and WO_3 polymorphs. The C, T, O and M-HfO_2 represents Cubic, Tetragonal, Orthorhombic and Monoclinic Hafnia

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