THE ROLE OF DEFECTS IN MICROWAVE-ASSISTED SYNTHESIS OF CUBIC ZRO_2

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Microwave radiation (MWR) is capable of inducing rapid, low-temperature crystallization and potential non-equilibrium phase formation in ceramic oxide materials.[1] However, the mechanisms by which MWR influences phase transitions and atomic ordering are not well understood. Theories to explain the influence of MWR range from purely thermal effects (e.g., rapid heating rate) to purely MWR-driven, non-thermal effects (e.g., enhanced defect generation).[2] To take full advantage of the opportunities provided by field-assisted methods, it is necessary to understand the underlying mechanisms. One limiting factor in determining how MWR affects phase formation has been the ability to effectively characterize the effects of an applied field on both long range (crystalline) and short range (amorphous/disordered) atomic order. Here, we utilize synchrotron x-ray pair distribution function (PDF) analysis, coupled with molecular dynamics (MD) and density functional theory (DFT) to explore the role of MWR-induced defects and local atomic disorder on low-temperature cubic phase formation in ZrO_2 thin films. PDF analysis is an experimental technique capable of quantitatively characterizing both local and long range atomic order, and thus can characterize the effects of MWR on atomic structure beyond the capabilities of conventional x-ray diffraction. We find the application of MWR can stabilize cubic ZrO_2 at temperatures as low as 225°C, about 2000°C lower than conventionally required. Our PDF analysis suggests that distortions in the local atomic structure may be responsible for the stabilization of the cubic phase, and these distortions are consistent with increased oxygen vacancy formation (Fig. 1). Interestingly, higher MWR power levels and faster heating rates do not correspond to more crystalline phase formation, suggesting that thermal effects may not be the sole driving force. To further explore the idea of MWR-induced, defect-mediated phase transitions, we utilize MD and DFT simulations to investigate how oxygen vacancy concentrations affect the relative phase stability of various ZrO_2 polymorphs, and compare the resultant simulated structures with our experimental PDF data. Through analysis of both crystalline phase formation and local atomic order, we investigate how defects and local atomic distortions are influenced by MWR exposure, and how these structural effects can impact low-temperature phase transitions.

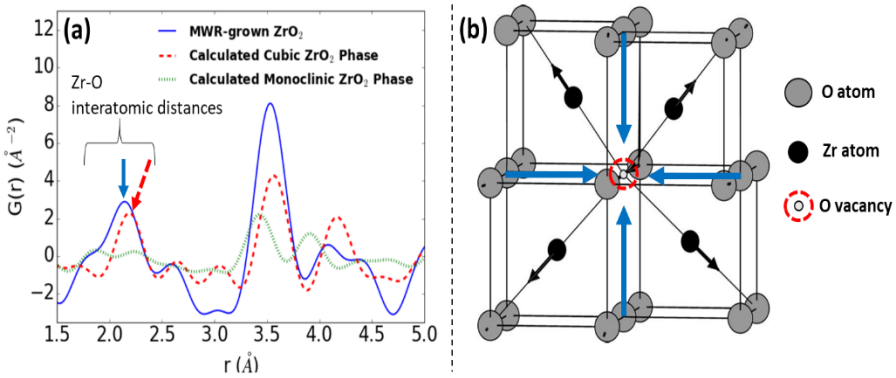

Figure 1 – (a) Experimental PDF data from an MWR-grown film (solid) compared with calculated PDFs from an ideal cubic (dashed) and monoclinic (dotted) structure. PDF peaks correspond directly to interatomic distances. The shift in the Zr-O nearest neighbor peak to shorter average interatomic distances observed in our experimental data relative to the cubic phase indicates structural relaxations consistent with oxygen vacancy formation. (b) Structural relaxations around an oxygen vacancy in cubic ZrO_2, modified from Ref.3

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