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Final Project Report

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DISCLAIMER

This report describes the findings from the DOE funded research project for the budget period 9/16/00-9/15/03. This budget period extended the original program, which ran for 4 years from September 1996-2000, generated 14 publications (and numerous conference proceedings) in the areas of fundamental atomic scale analysis of interfaces in oxides [1-8], the development of advanced transmission electron microscopy techniques [9-12], and thin film growth processes [13,14]. In addition, 18 invited presentations at research institutions and international conferences and 19 contributed presentations at international conferences were made that feature research funded by this original DOE grant. The grant supported 3 postdoctoral research associates at various times during the grant period (Professor Susanne Stemmer, currently at UC-Santa Barbara; Professor Gerd Duscher, currently at North Carolina State University; Dr Yan Xin, currently a Research Associate Professor at Florida State University).

The current funding cycle has resulted in 16 journal publications [15-30] and numerous conference proceedings following the same lines of research as in the initial program and featuring various aspects of oxide ceramics, and MgB_2. In addition, 18 invited presentations and 20 contributed presentations featuring this DOE supported research have been made at international conferences and research institutions. This cycle of the grant supported 5 graduate students and 1 postdoctoral research associate at various times during the two years (Professor Yasuo Ito, currently at Northern Illinois University; Dr Robert F. Klie, currently a Goldhaber Distinguished Fellow at Brookhaven National Lab; Dr James P. Buban, now a JSPS Fellow at the University of Tokyo; Dr. Yuanyuan Lei, now a postdoctoral fellow at Argonne National Laboratory; Dr. Ilke Arslan, now a postdoctoral fellow at Cambridge University; and Mr. Juan-Carlos Idrobo who is a current graduate student).

One of the main areas of research in the last two years in this program has been the properties of grain boundaries in perovskite and fluorite structured materials. In the case of the perovskites, this research followed the development of the atomic resolution techniques in the first 4 years of funding with an investigation of the vacancy dynamics at grain boundaries. As an example of this work, here we briefly describe the structure, composition and bonding characteristics of a nominally un-doped 58° [001] tilt grain-boundary in $SrTiO_3$. Room temperature and in-situ heating experiments show that there is a segregation of oxygen vacancies to the grain boundary that is increased at elevated temperatures and is independent of the cation arrangement. This is illustrated in figure 1, where images at room temperature and 450°C indicate the cation arrangement at the boundary is unchanged (one of the developments in this program has been the stability of the microscope environment needed to obtain atomic resolution even at high temperature). The corresponding EEL spectra from the grain boundary show a shift to lower energy of the Ti L-edge and a reduced intensity and loss of fine-structure in the oxygen K-edge. This indicates that the Ti valence is decreasing to compensate for the decreasing oxygen concentration. These measurements indicate that the widely observed electronic properties of grain boundaries in perovskites may be due to an excess of oxygen vacancies that segregate in close proximity ($\approx$1 unit cell) to the boundary core.

Similar experimental studies have been performed on fluorite structured grain boundaries. In this case, the aim was to verify whether similar structural and compositional effects occurred in this different type of oxide system, or whether the previous observations were limited to only perovskites. In particular, the study addressed the concept of partial occupancy, oxygen vacancy segregation, and cation valence change

at the grain boundary. The atomic scale structure, composition, and chemistry of grain boundaries in two fluorite structured ceramic materials were characterized by a combination of Z-contrast imaging and electron energy-loss spectroscopy (EELS) that will be the theme of this coming proposal. In the case of a symmetric 24° [001] tilt bicrystal of Yttria-Stabilized-Zirconia (YSZ), a shift in the zirconium M-edge onset and a change in the yttrium and zirconium M-edge ratios at the boundary indicate an increase in the number of electrons in the boundary plane (Figure 2). A detailed study of the structure and composition indicated that this is caused by an increase in the number of oxygen vacancies in the grain boundary core that is partially compensated by yttrium segregation. In a similar manner to the perovskite grain boundaries, partial occupancy was found to feature predominantly at this boundary. Coupled with the study of this "ideal" fluorite grain boundary, studies of grain boundaries in an industrial polycrystalline Gd-doped Ceria ceramics revealed similar changes in vacancy/dopant profiles, indicating that these effects may be generic to grain boundaries in fluorite materials; as they have been observed to be in perovskite materials.

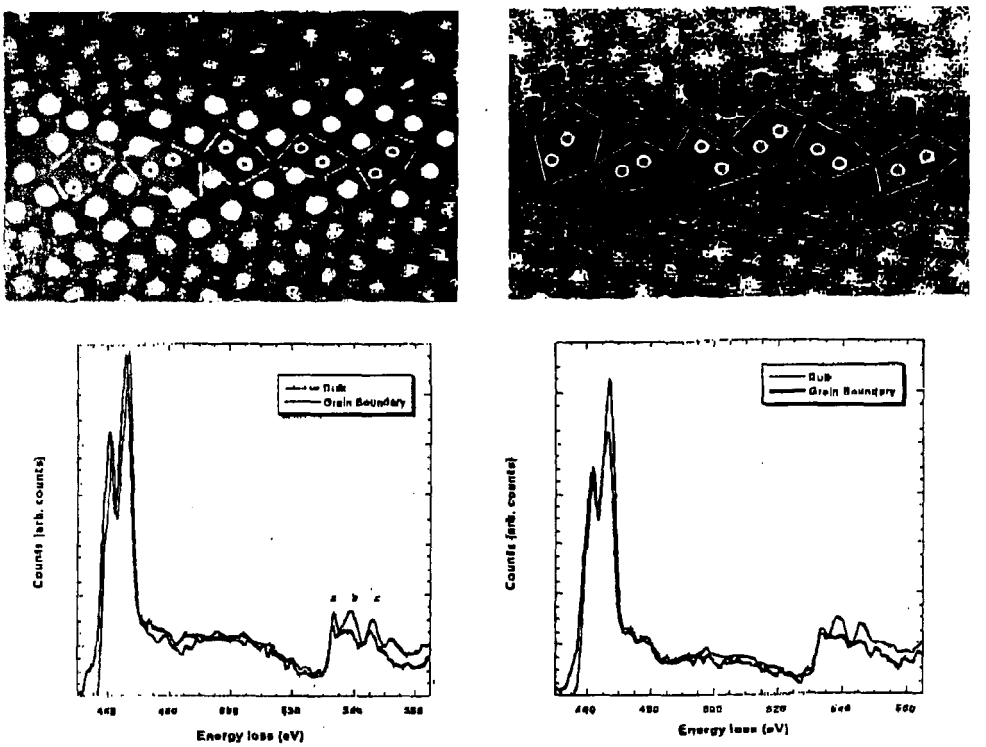

Figure 1: Z-contrast images of the SrTiO3 grain boundary at room temperature and at 450°C. The blue circles are Ti atoms and the empty circles partially occupied Sr columns. At room temperature, Sr atoms are white circles and at 450°C they are red circles. The corresponding EELS spectra show a shift in Ti edge position and decrease in oxygen K-edge intensity and fine-structure.

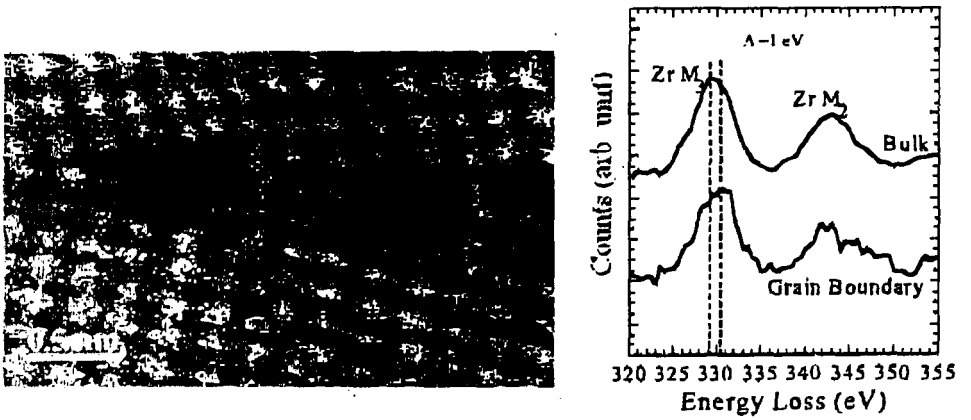

Figure 2: Z-contrast image of a symmetric 24° [001] tilt grain boundary in YSZ and spectrum from the bulk and grain boundary, showing a shift of ~1eV in Zr $M_{2,3}$ edge. The core structure is dark (due to strain) but the structure can be ascertained directly from the image. Oxygen K-edge spectra (not shown) confirm the result from the Zr edge shift.

Another focus of the research has been the study of atomic scale effects in MgB_2. The discovery of superconductivity at 39K in MgB_2 that was revealed to the world in January 2001 presented many new and exciting possibilities to the field of superconductivity. As with many new discoveries, it was hard in the early stages of research to define exactly the materials issues related to defects and interfaces in these materials. However, one of the intriguing issues that was identified early on, was the effect of oxygen impurities in the structure. Analysis of the structures by Z-contrast imaging and EELS revealed that range of oxide interface phases can be induced (and these appear to occur readily in the bulk material and thin films)- MgO, BO_x and MgB_xO_y. Given the enhanced properties that are seen in thin film MgB_2 through alloying with oxygen, these early results suggested that some of these phases may be useful for improving the fundamental superconducting properties of the material.

Further analysis of samples produced by different growth methods indicated that in addition to grain boundary oxide phases, ~20-100 nm sized precipitates are formed by ordered substitution of oxygen atoms onto the boron sub-lattice, while the basic bulk MgB_2 crystal structure and orientation is preserved (Figure 3). The periodicity of the oxygen ordering is dictated by the oxygen concentration in the precipitates and the majority of the oxygen ordering occurs in the (010) plane. The improvement of superconducting properties associated with samples that exhibit large quantities of these precipitates indicates that that the oxide precipitates may act as flux pinning centers, improving the critical current density and the superconducting transition behavior. This is the subject of continuing research in the current funding period.

More recent work on MgB_2 has focused on understanding the location and symmetry of the charge carriers in the material. In this case, the aim was to provide a fundamental understanding of the bulk material, so that the effects of doping on charge concentration could be investigated in the electron microscope. It is important to note here that due to the small grain size (~100nm) and even smaller precipitate size (~10nm), electron

microscopy is the only means to address these issues from individual features. Figure 4 shows the results of the analysis that was performed. In particular, two different crystal orientations, [110] and [001] with respect to the incident electron beam direction, were studied and it was found that significant changes in the near-edge fine-structure of the B K-edge occurred. Density functional theory (DFT) suggests that the pre-peak of the B K-edge core loss is composed of a mixture of p_{xy} and p_z hole states, and the results that were obtained showed that these contributions can be distinguished experimentally only with an experimental energy resolution better than 0.5 eV. For conventional TEM/STEM instruments with an energy resolution of ~1.0 eV the pre-peak still contains valuable information about the local charge carrier concentration that can be probed by core-loss EELS. However, to obtain the information on the charge carriers, considerable analysis must be performed in considering the scattering momentum transfer for different crystal orientations to separate pxy and pz components from the experimental spectra. The results that were obtained highlight the power of EELS to probe the local electronic structure of advanced materials and also the improvements that can be achieved with the next generation of microscopes. These microscopes will therefore lead the way in developing the capability to obtain spectra and the news methods for interpreting the fine-structure in the spectrum.

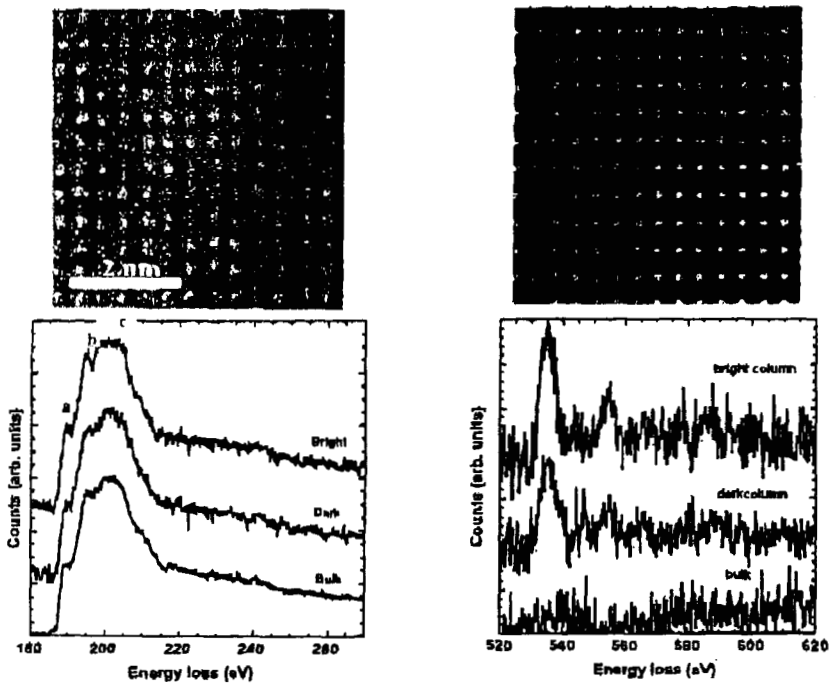

Figure 3: Z-contrast image and multi-slice simulation showing that every second boron column shows an increased intensity caused by oxygen substitution. Boron K-edge and Oxygen K-edge spectra confirm the intensity distribution (note: the spatial resolution had to be degraded to provide enough signal for the spectra, which is why the dark column shows an oxygen signal).

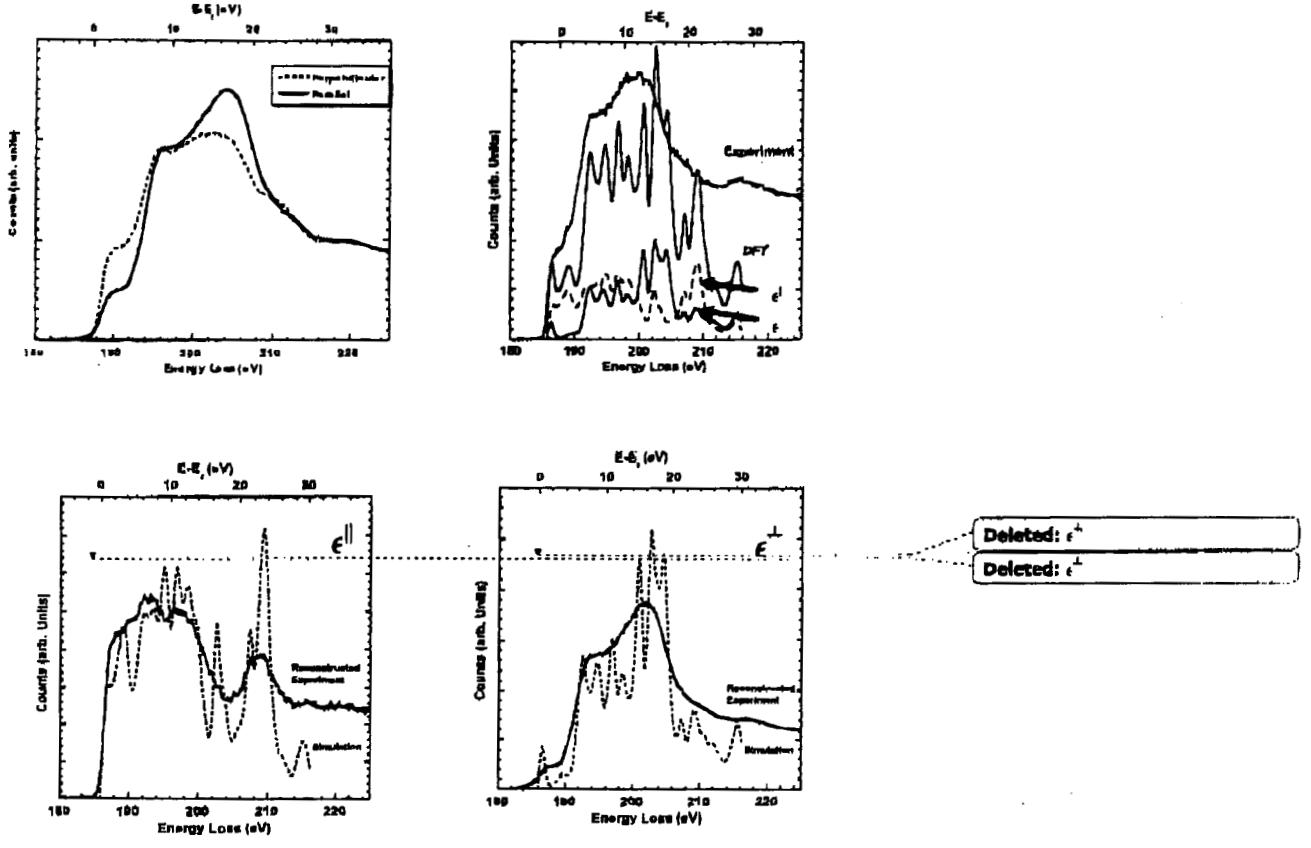

Figure 4: Experimental spectra obtained with the JEOL 2010F in two orientations. The changes in the pre-edge peak, contain contributions from p_{xy} and p_z orbitals. In the spectrum from the VG STEM, these two peaks can be clearly observed in the pre-edge. The spectra from the JEOL can be deconvoluted into p_{xy} and p_z components in good agreement with the DFT calculations.

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