Electronic properties of W' twin domain walls in ferroelastic BiVO4

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Background incl. aims
Topological defects in ferroic materials are important in solid state physics since they can exhibit different intrinsic properties from the bulk and act as active sites in device engineering.[1] Investigation of those defects in terms of their structural variations and relevant properties in special materials systems opens a new path for improving materials' performance and developing novel devices. Here, we aim to investigate the structural and electronic properties of the ferroelastic domain wall in a well-known visible-light catalytic material,[2] monoclinic scheelite $BiVO_4$ (ms-BVO), which may be interesting for photochemistry-relevant applications.

Methods
The BF-TEM image and SAED were obtained using a JEOL JEM-F200 S/TEM operated at 200 kV for domain wall determination. HAADF-STEM images and electron energy loss spectroscopy (EELS) were obtained using a JEOL Grand ARM300F2 double-corrected S/TEM operated at 300 kV, for atomic resolution crystallographic structure and electronic structure demonstration. A Digital Instruments Nanoscope-IV Multimode atomic force microscope equipped with a c-AFM application module (TUNA) was used for nanoscale conductivity measurement.

Results
Highly dense twin walls are found in ms-BVO single crystal and identified as ferroelastic W' wall forming along the strain direction.[3] Opposite shear strain is seen in ferroelastic twin domains (A and B) and released at the wall. The W' wall has a kink configuration, and the overall wall width (d) is approximately ~2 unit cells. The W' walls show clear electrical conductivity by c-AFM under a DC tip voltage of −9.8 V while the domains show no obvious current signal. Subsequent STEM-EELS analysis shows that the V eg state of the W' wall shifts downward of 0.12 eV, indicating a lower conduction band minimum (CBM) compared to twin domains. The larger energy splitting at V L_3 and L_2 peaks at the W' wall is consistent with the symmetry of the topological defects. The higher V L_3/L_2 peak ratio indicates a lower oxidation state of vanadium, i.e., a higher density of oxygen vacancies at the W' wall. The higher shoulder peak at ca. 517 eV (compared to V eg state) indicates the possible accumulation of small polarons at the W' wall. The lower conduction band minimum, increased amount of oxygen vacancies and small polarons may be the reasons for the ferroelastic W' wall conductivity.

Conclusions
The present work investigates the structures and electronic properties of the ferroelastic W' wall in ms-BVO bulk crystals. The W' wall is atomically sharp in a zig-zag shape. Compared to non-conductive domains, the W' walls show conductivity in c-AFM measurement under negative bias. The electronic structures revealed by EELS spectra show that the wall has a relatively lowered conduction band minimum, a higher density of oxygen vacancies and

possible accumulation of small polarons compared to the domains, which may contribute to the increased wall conductivity. Since the photocatalytic performance of a semiconductor is highly related to its conductivity,[4] the investigation of W' wall conductivity of ms-BVO crystals may help in designing highly efficient catalytic materials.

Keywords:

ferroelastic domain walls, electronic properties

Reference:

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