Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Ferroelastic Domains Improve Photochemical Reactivity: A Comparative Study of Monoclinic and Tetragonal ($Bi_{1\text{-}0.5x}Na_{0.5x}$)($V_{1-x}Mo_x$)$O_4$ Ceramics

Ratiporn Munprom, Paul A. Salvador, and Gregory S. Rohrer

Department of Materials Science and Engineering, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh PA 15213-3890, USA.

Overview

We provide four supplemental figures to support the primary information given in the main document. The first figure (Fig. S1) contains XRD patterns from the two co-doped samples investigated in the ($Bi_{1-0.5x}Na_{0.5x}$)($V_{1-x}Mo_x$)O_4 family. This data shows that the x = 0.05 sample is monoclinic (ferroelastic) and the x = 0.175 is tetragonal (non-ferroelastic). The data (θ – 2θ) was collected using a Panalytical X'Pert Pro MPD diffractometer operated at 45 kV and 40 mA with Cu-Kα radiation. The step size and time per step of the scan were 0.0263 ° and 48 s, respectively. Also, a 1° fixed divergence slit was used in the measurement. In the main manuscript, we highlight the existence or absence of ferroelastic domains, using BSE (Fig. 2) and PFM (Fig. 3), to support this structural assignment at the local grain level.

The second (Fig. S2) compares directly the AFM error signal signals (a, b) and PFM phase signals (c, d) between the monoclinic undoped (a, c) and monoclinic co-doped x = 0.05 (b, d) samples. Contrast in the AFM images corresponds to topographical ferroelastic domains, while contrast in the PFM images is correlated to surface piezoresponse or surface polarity. These images were collected in a similar manner to those given in the main document (Fig. 3). Here we compare the two monoclinic samples, which show that although they have different compositions, these two monoclinic samples behave analogously under PFM measurement; piezoresponsive domains were observed.

The third (Fig. S3) compares reactivities of eight similar-oriented grains of the co-doped monoclinic and tetragonal samples. The orientations of the 8-pair comparison are shown on a stereographic projection in (a). Also, the measured heights of deposits on the given grains are provided in the table (b). Regardless of the orientation, all given surfaces of the co-doped monoclinic sample show quantitatively greater heights of deposits, indicating that they are more reactive.

The fourth figure (Fig.4) shows the one-to-one correlation between piezoresponse (a) and reactivity (b) on the monoclinic co-doped $x = 0.05$ sample. Both PFM contrast and reactivity have similar patterns of parallel laminar strips. This implies that domain-selective reactivity is associated with PFM domains.

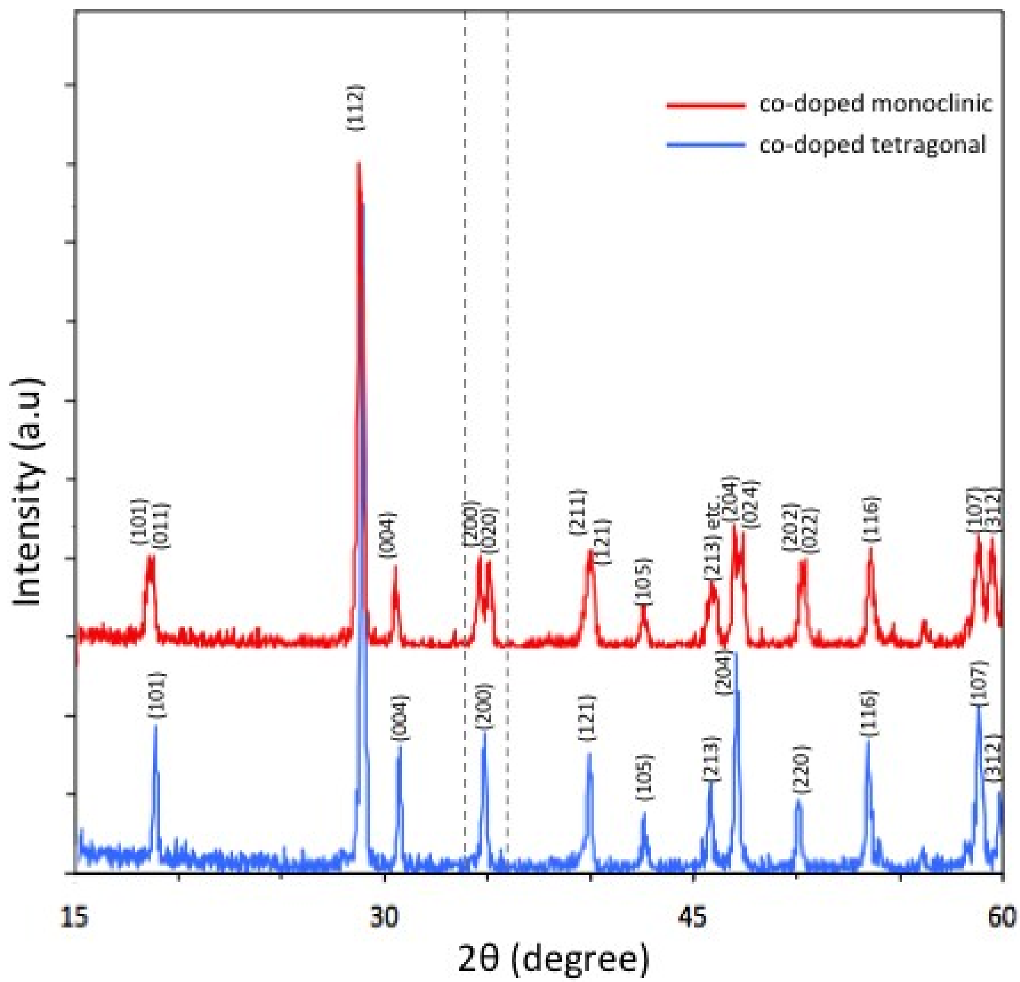


Fig. S1. XRD patterns of $(Bi_{1-0.5x}Na_{0.5x})(V_{1-x}Mo_x)O_4$ samples, with x = 0.05 (upper red line) and x = 0.175 (lower blue line) samples. These patterns can be indexed as monoclinic, for the x = 0.05 sample, and tetragonal, for the x = 0.175 sample. The peaks in the angular range around ~35° are accentuated with vertical dashed lines, as these peaks can clearly distinguish the symmetry of the phases.

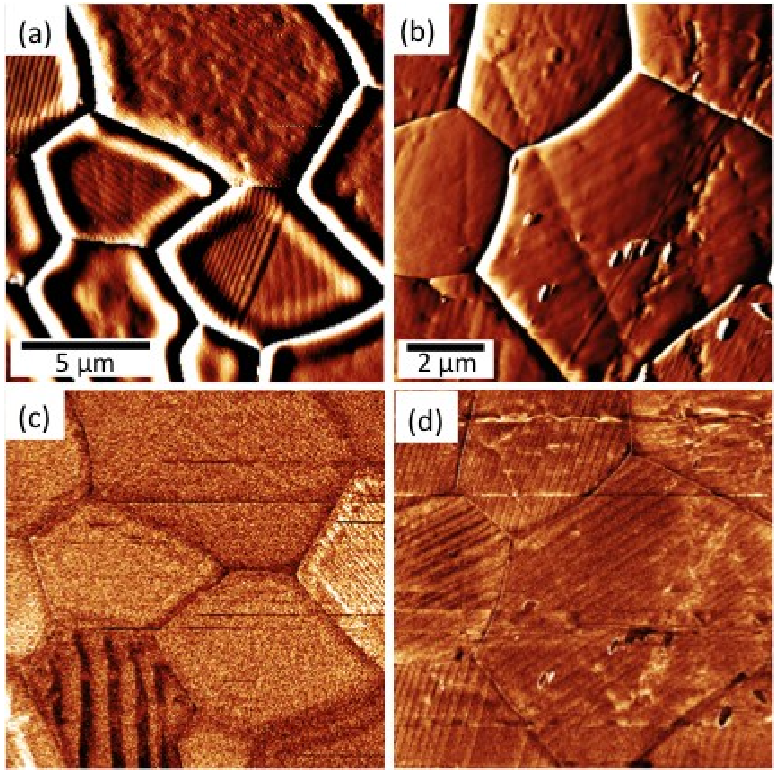
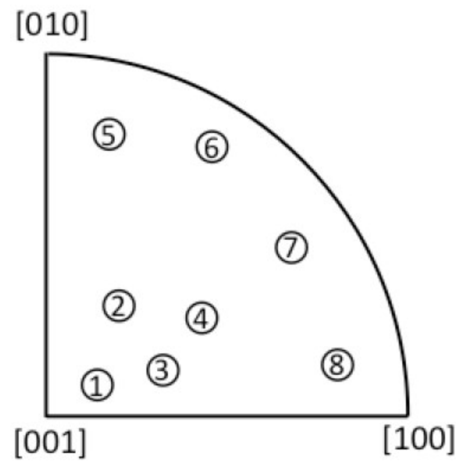


Fig. S2. Topographic AFM images of the monoclinic (a) $x = 0$ and (b) $x = 0.05$ samples, each plotted as error signals with a vertical scale of 0.2 nA. (c) and (d) are PFM phase images from the same areas as given in (a) and (b), respectively. The ranges of the vertical scale for the PFM images in (c) and (d) are 17° and 2.4°, respectively.

(a)



(b)

Pair no.	Average height of deposits (nm)	
	co-doped monoclinic	co-doped tetragonal
1	20	8
2	16	5
3	15	4
4	14	3
5	15	3.5
6	10	2
7	15	3
8	13	3.5

Fig. S3. Reactivity comparison of similar-oriented monoclinic and tetragonal grains (8 pairs): (a) the orientation of the 8-paired grains in the orientation space and (b) the actual average height of deposits on the given grain. Note: the average value is measured from the baseline (no deposit area).

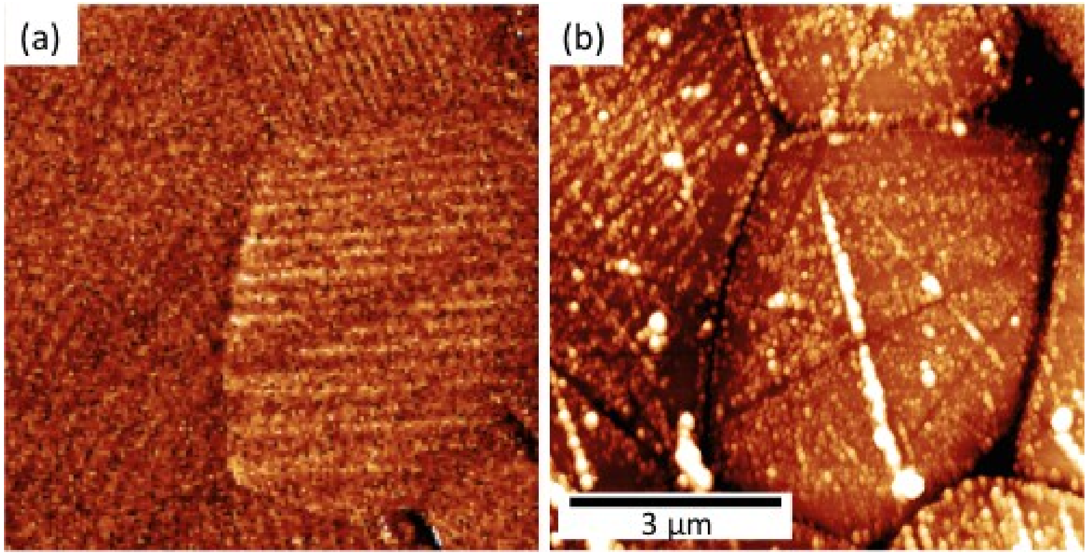


Fig. S4. A correlation between (a) piezoresponsive domains and (b) photoreduction of Ag^{+} on the x = 0.05 sample. The vertical scale of PFM image in (a) is 2° and that of AFM topographic image in (b) is 50 nm.