Investigating multiferroic phase change dynamics using in-situ electron counted spectrum imaging with synchronized holder control

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Improper ferroelectrics have strong potential for use in low power domain wall nano-electronic devices, as the formation and motion of conducting domain walls in such materials is governed by strain as opposed to their electric polarization [1,2]. Multimodal STEM spectrum imaging performed in the (scanning) transmission electron microscope (S)TEM is ideal for characterization of the ferroelectric domain dynamics in improper ferroelectrics, as the technique enables correlation of local chemistry and bonding information, with crystallographic and strain information determined from identical specimen regions at micro to (near) atomic scale.

The ferroic phase changes of the improper ferroelectric: Co-Cl, Cu-Cl and Fe-I based boracites ($M_3B_7O_{13}X$) are complex, with the materials undergoing multiple phase transitions from low temperature up to Tc. For example, Co-Cl boracite undergoes a trigonal to monoclinic transition at 296 K, monoclinic to orthorhombic transition at 500 K and orthorhombic to cubic transition at 673 K. No memory effect is apparent through the paraelectric to ferroelectric transition though memory effect from trigonal to monoclinic phases are observed [3].

MEMS based heating-biassing and cooling-biassing holders can be used to investigate phase change dynamics in these materials as a function of applied temperature and bias, though manual holder control becomes impractical if high stimuli resolution is required, due to the large number of temperature steps required for meaningful analysis in combination with the large number of individual biassing steps required at each temperature.

Here we present a holder automation strategy that takes advantage of the high-level communication Python library, ZMQ, to generalize external stimulus control within the DigitalMicrograph Python scripting framework. Control commands from the embedded in-situ SI data acquisition routine are sent via a generalized modular framework, enabling synchronized control of any external device supporting Python and ZMQ.

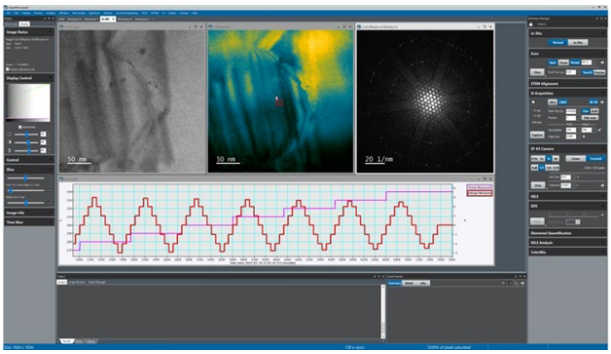
In-situ spectrum imaging was performed on Co-Cl, Cu-Cl and Fe-I based boracites ($M_3B_7O_{13}X$) with a 50-80 pA probe at 300 kV, using a counted mode EELS / energy filter system (GIF Continuum K3, Gatan) and flexible scan control system (Digiscan3). Domain wall dynamics were investigated as a function of applied bias at variable temperature using MEMS based in-situ heating-biassing, and cryogenic cooling-biassing holders (Lightning & Lightning-Arctic, DENSSolutions). Holder control and synchronization to data capture was performed using Python scripting in the DigitalMicrograph and DENSSolutions Impulse software packages. This scripting allowed multiple pass in-situ spectrum image (SI) data acquisition with all SI passes acquired at fixed holder stimuli conditions. Full voltage sweeps were applied at each temperature step in a temperature series. All data acquisition and holder control was fully automated . Data processing was performed using a combination of DigitalMicrograph (EELS, 4D STEM) and the Py4DSTEM (4D STEM) software packages.

Gatan's eaSI platform and DigitalMicrograph 3.60, allowed multipass single electron counted SI data capture with zero dead time between passes, at SI pixel rates of up to 3000 pix/s with continuous drift tracking in real time. A software screenshot showing the results of an in-situ energy-filtered 4D STEM data acquisition from Co-Cl boracite is shown in figure 1. Heating

was applied in 10 ^{o}C steps from 270 ^{o}C – 340 ^{o}C. Biassing was applied at each temperature step in increments of 1 V from 0 V to Vmax = + 3.0 V and Vmin = -3.0 V and back to 0 V. The in-situ dataset comprises three primary data objects. An ADF image time series, a simultaneously acquired energy-filtered (EF) 4D STEM time series, and a holder auxiliary data plot. Measured temperature is shown in the auxiliary plot in pink. Voltage (holder bias) is shown in red. Both profiles are stepped, indicating SI passes are acquired at fixed holder stimuli conditions. A summed EF-CBED image from the highlighted region is also shown. In spite of the low probe current, the SNR of this image is high due to the high sensitivity of the counting detector. Two HOLZ rings are clearly visible.

Python scripting was successfully utilized to customize in-situ spectrum image capture, allowing synchronized control of a remote application using the ZMQ Python library. and a client-server design pattern. This design strategy was found to be a powerful means of leveraging the strengths of the native software application such as zero dead time multipass scanning, sub-pixel scanning, continuous drift tracking, etc. while also enabling holder control options not yet natively supported. In the case of Co-Cl, Cu-Cl and Fe-I based boracites ($M_3B_7O_{13}X$), this allows the setup of complex heating and biassing conditions at high temperature and bias resolution that would be unachievable if a manual approach was adopted. Such setups allow exploration of the FE memory affect at specific phase transitions in addition to complex analyses such as the correlation of strain mapping with local chemical and coordination environment changes at micro and macro domain walls in these materials.

Graphic:



Keywords:

ELNES, 4DSTEM, InSitu, Ferroelectric

Reference:

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