

Fe-rich Phase Separation in Doped BaTiO₃ as Revealed by STEM-EDS

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The flexible structure of perovskite materials makes them an ideal system for developing and tuning multiferroic properties. One attractive multiferroic property is the magnetoelectric effect (ME), where the magnetic and electric effects of a single material become linearly coupled i.e. a magnetic field can induce an electric field in the material and vice versa [1,2]. ME materials are of interest due to their potential for a number of applications, such as magnetic sensing, ferroelectric photovoltaics, memory elements, etc. BaTiO₃ demonstrates a high dielectric constant and high piezoelectric coefficient at room temperature, which alludes to the possibility to introduce magnetic dopants for the purpose of creating a single-phase multiferroic material. BaTiO₃ samples with small concentrations of Fe dopants (less than 2%) have shown success toward this end [3,4].

Here, a powder sample of BaTiO₃ doped with 2% Fe was produced. Transmission electron microscopy (TEM) was employed to study the local structure of the Fe-BaTiO₃. However, the TEM results showed that the Fe phase-separated into a Fe-rich phase rather than forming a doped BaTiO₃. Energy dispersive x-ray spectroscopy (EDS) was used on a JEOL 2200F microscope in scanning mode to gain insight into composition of the as-grown material. Figure 1 shows clear evidence of a Fe-rich phase distinct from the surrounding BaTiO₃. The Fe-rich phase measures > 9 atomic % Fe, much higher than the nominal doping amount. The relative Ba and Ti amounts remain in a 1:1 proportion, and we would expect to see the Ti atomic percent drop if the Fe was substituting in this region. Selected area electron diffraction (SAED) further confirms that this phase is not BaTiO₃. While the SAED does not index to BaTiO₃, it also does not index to magnetite or other common Fe_xO_y phases. This crystallite is on the order of 200 nm, and with only 1% of the material being Fe, it is possible that these Fe-rich nanocrystallites are too small and a too few to be seen in XRD or SEM, demonstrating the value of high-resolution imaging and spectroscopy.

High-angle annular dark field (HAADF) imaging along with electron energy loss spectroscopy (EELS) and EDS was performed in a Nion UltraSTEM200-X to assess the potential Fe doping on an atomic scale. The HAADF (Fig. 2) shows BaTiO₃ with no indication of Fe substituting on the Ti sites. Because the HAADF intensity is roughly proportional to the atomic number of the material, we would expect to see an increase in intensity on atomic columns containing Fe. However, no variation in Ti-column intensity is observed, and neither EELS nor EDS show any Fe [5].

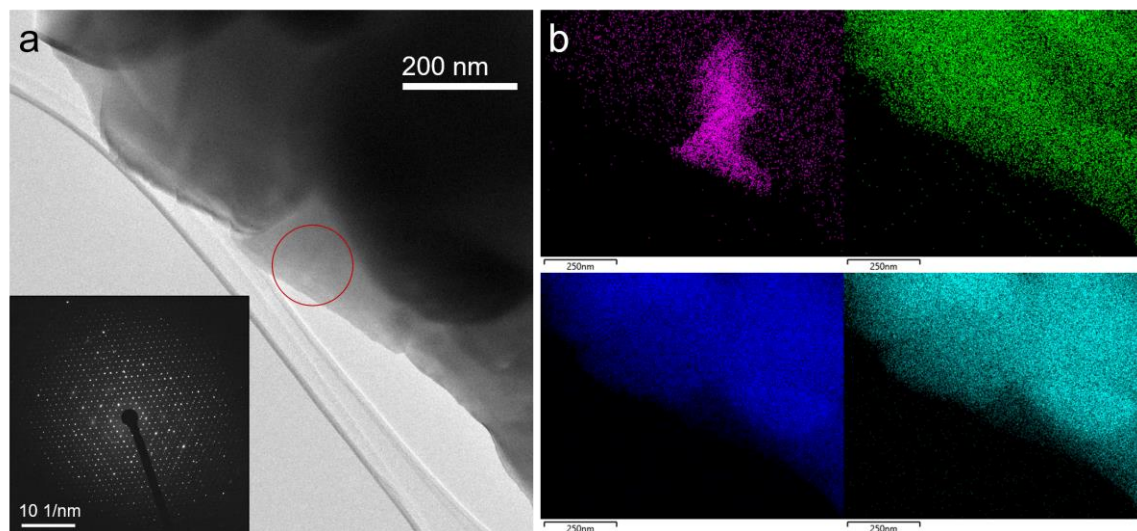


Figure 1. TEM and STEM-EDS of Fe-doped BaTiO₃ as-grown powders. (a) TEM image of BaTiO₃ with a Fe-rich domain. Inset: SAED of region circled in red. (b) STEM-EDS of the region from (a) revealing the presence of a Fe-rich second phase.

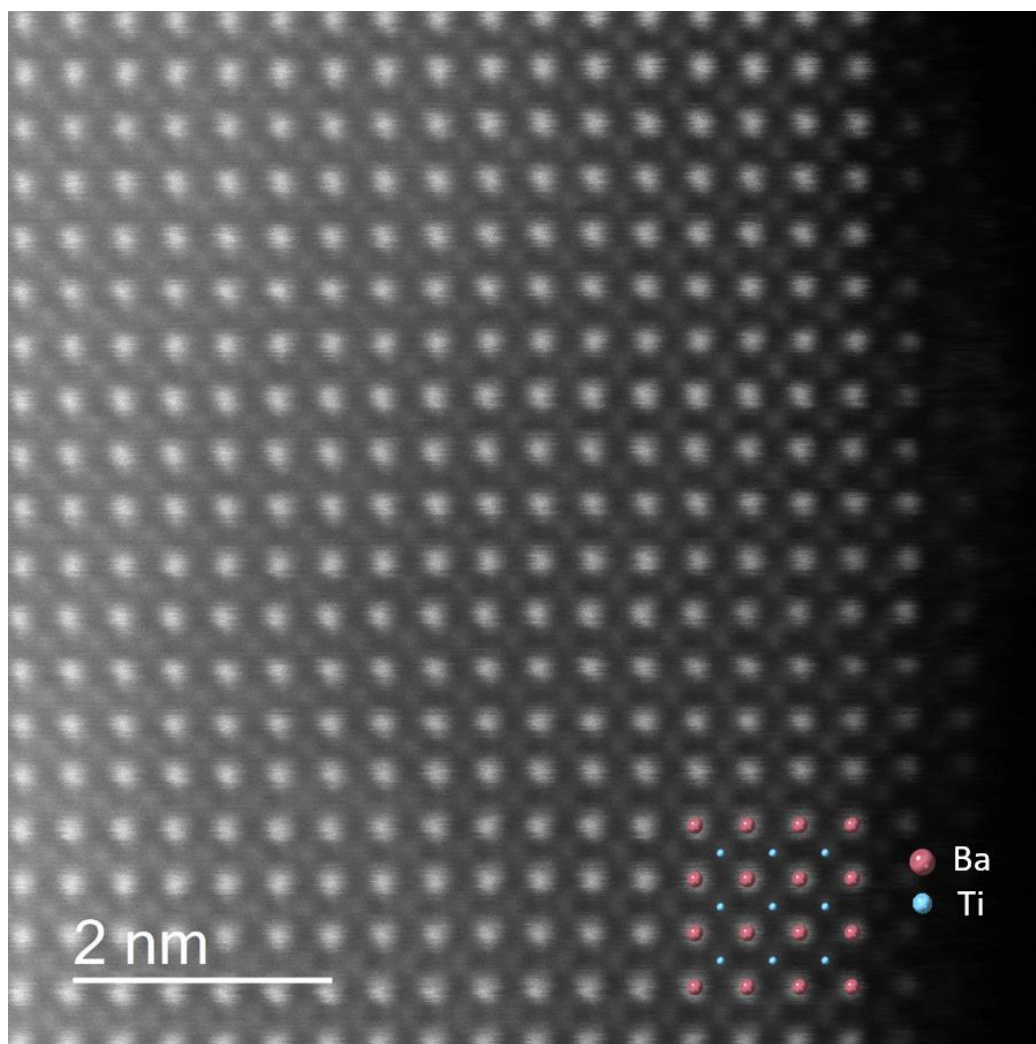


Figure 2. HAADF image of BaTiO₃ [100] displaying a uniform intensity across the Ti columns and no indication of Fe substitution.

References

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