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Real-Time Observation of Two-Phase Separation in $LiFePO_4$ at Elevated Temperature

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A wide spectrum of studies on how two phases separate in binary-phase systems can be found in the literature, ranging from the modulated structure in metallic alloys and oxides to a variety of peculiar separation morphologies in block-copolymer-based soft materials. Among the numerous factors affecting the phase separation behavior, elastic strain at interfaces between two phases plays a major role during microstructure evolution when two phases having similar crystal structures and lattice parameters construct coherent interfaces. Following the work by Cahn on spinodal decomposition, theoretically and experimentally notable results have been reported on the relationship between the coherency elastic strain and the phase-separation morphologies over the past five decades.

Crystal twinning can take place without any crystal deformation by external shear stress, as extensively studied in various metals and alloys (annealing twins) and also as frequently observed in many oxide minerals during crystal growth (growth twins). Because these twins are two-dimensional planar interfaces, quadruple junctions form when phase boundaries intersect the twinning planes during phase separation. A key aspect that should be taken into account at the quadruple junctions is that four interfacial tensions from the phase boundaries and the twin interfaces should satisfy their force equilibrium. Therefore, a complex correlation between the force balance and the coherency elastic strain is anticipated when the lattice coherency is maintained at the quadruple junctions, and direct experimental observations of the quadruple junctions at atomic resolution and the resultant phase-separation morphologies with crystal twins are necessary to shed light on this correlation.

By taking olivine-type $LiFePO_4$, which is used for cathodes in Li-ion batteries, as a model crystalline system, we show that a comprehensively different phase-separation morphology is induced in order to release the high coherency strain confined to quadruple junctions, at which twin boundaries and phase boundaries intersect with each other (Figure 1). High-temperature *in situ* transmission electron microscopy [1–4] revealed that phase boundaries with a new crystallographic orientation emerged over twinned crystals to provide strain relaxation at quadruple junctions in contrast to the phase separation in twin-free crystals. As shown in Figure 2, the high coherency strain and the formation of different phase boundaries can be understood in terms of the force equilibrium between interface tensions at a junction point [5]. Visualizing the quadruple points at atomic resolution in a crystalline system, our experimental observations emphasize the impact of nanoscale multiple junctions on the morphology evolution during phase separation

Conventional HREM images were acquired using a transmission electron microscope (JEM-2100F, JEOL) operated at 200 kV. BF-STEM and HAADF-STEM images were also obtained using the same electron microscope with a spherical aberration corrector (CEOS GmbH) for probe-forming lenses. For *in situ* observations during heating and after quenching, a hot-stage heating holder was utilized in a transmission electron microscope capable of a high specimen tilt. The heating system based on a ring-type furnace made from tantalum in the holder enables homogeneous and rapid heating up to 1000°C. Cooling from 350°C to room temperature could be achieved in ~10 sec by turning off the furnace in the holder [6].

References

[1] SY Chung *et al*, Nature Phys. **5** (2009), p. 68.
[2] SY Chung *et al*, Nano Lett. **12** (2012), p. 3068.
[3] SY Chung *et al*, J. Am. Chem. Soc. **135** (2013), p. 7811.
[4] SY Chung *et al*, ACS Nano **9** (2015), p. 327.
[5] SY Chung *et al*, Nature Commun. **6** (2015), p. 8252.
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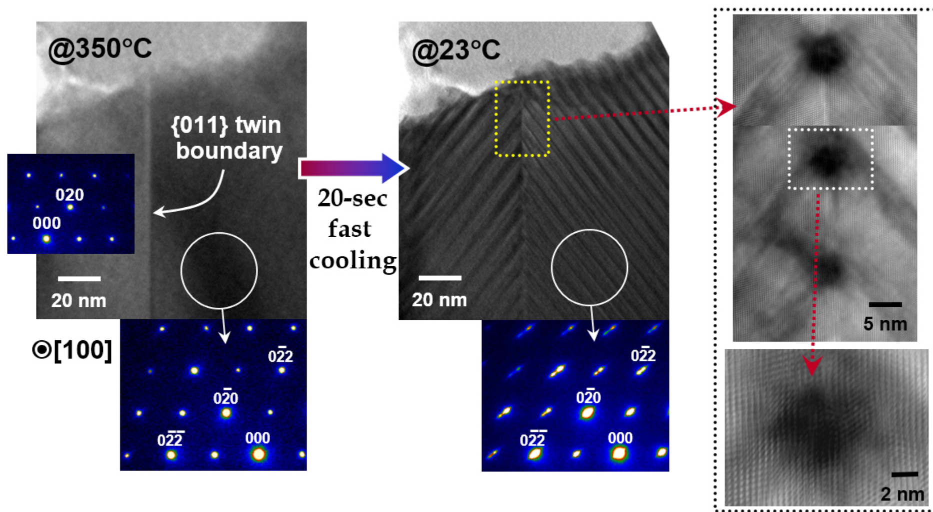

Figure 1. Observation of phase separation with a twin interface in $LiFePO_4$. A symmetrical › -shape morphology across a twin boundary can be identified. Appearance of the periodic black image feature along the twin boundary is noted (right panel).

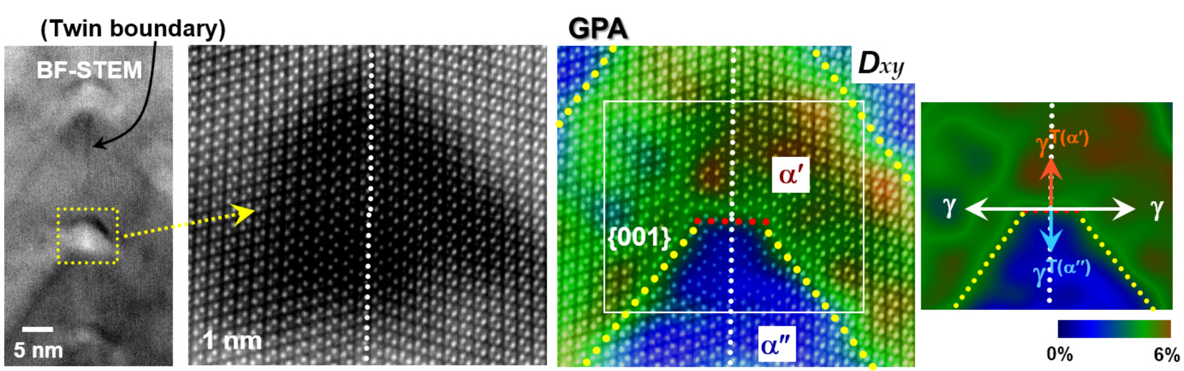

Figure 2. Atomic-column images at a quadruple junction and GPA for phase discrimination. Formation of a phase boundary with a different orientation (red dotted line) is identified on the D_{xy} map obtained from the GPA.

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