Direct observation of intermediate twinning in the phase transformations of ferroelectric potassium sodium niobate

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The substitution of toxic lead-containing state-of-the-art ferroelectric materials is an intensely worked topic [1]. It covers a broad variety of applications from piezoelectrics to caloric [2], including energy harvesting applications. The $K_{0.5}Na_{0.5}NbO_3$ (KNN) [3] ceramic, exhibiting first-order phase transitions and ferroelectricity and is one of the most prominent material systems in line for such substitutions. Its combination of properties makes it highly interesting with regard to electrocaloric cooling or pyroelectric energy conversion [4,5]. Naturally, this has created a demand for deeper knowledge of the underlying mechanisms to enable further improvement of fatigue behaviour, dielectric strength and crystallographic homogeneity.

As for the rigid nature of ceramics, fatigue is of special interest among those properties and has been subject of many theoretical approaches to describe matching criteria between phases to minimize inelastic interface energies and thus improving the materials fatigue life. The theory of phase compatibility [6,7] has shown to predict hysteresis narrowing and ultra-low fatigue in metal alloys [8], and recently even ceramics [9,10]. The compatibility theory provides a set of mathematical conditions, which – once satisfied – predicts several unstressed interfaces between the transforming phases.

In this study, temperature-dependent X-ray diffraction and transmission electron microscopy have been combined to reveal the mechanisms in the first-order phase transitions of ferroelectric $K_{0.5}Na_{0.5}NbO_3$. Direct observation of the orthorhombic to tetragonal and tetragonal to cubic phase transitions and twinning mechanisms in homogenously-grained, excess alkali $K_{0.5}Na_{0.5}NbO_3$ between room temperature and ~440 ∘C was made (Figure 1). We discovered that the two first-order phase transitions in the presented ceramic are multi-step processes exhibiting an intermediate twinning stage, which precedes the austenitic (high-symmetry) phase, and is yet to be described theoretically. The examination of grain boundary and single grain lamellae enabled a precise analysis of optical and crystallographic features of the phase transition. We believe that these findings can fuel novel investigations on the twinning mechanisms in ferroelectric ceramics.

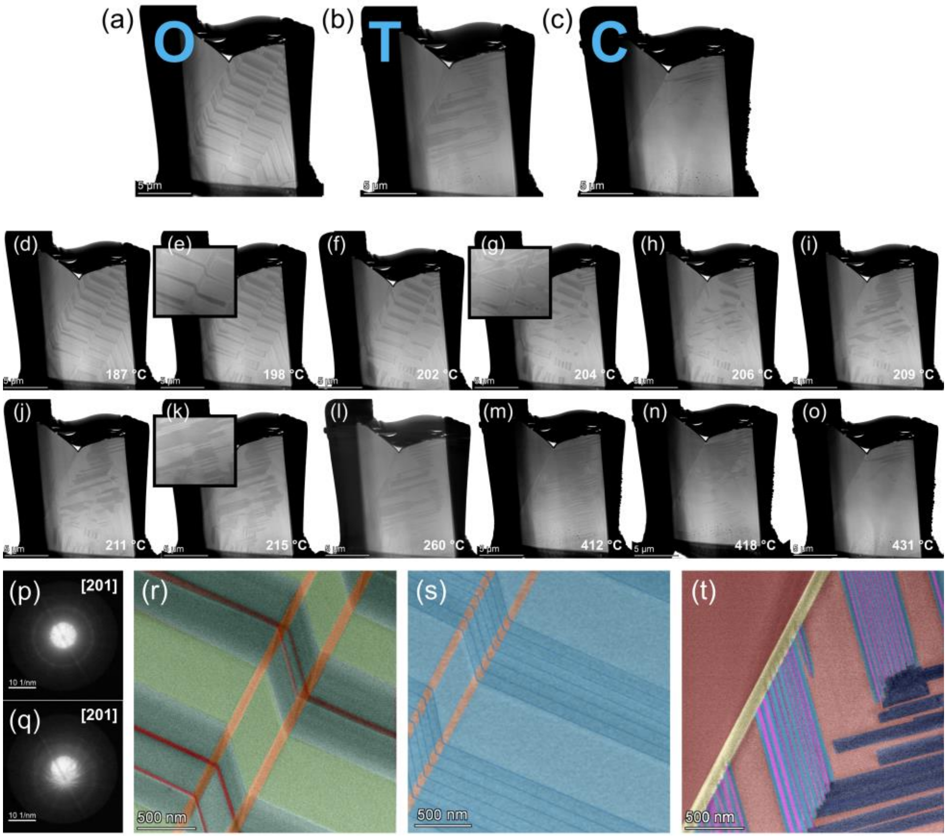

Figure 1: In-situ temperature-dependent TEM on KNNex. The first three BF STEM images show a KNNex lamella incorporating a grain boundary in the (a) orthorhombic (177 ◦C), (b) tetragonal (260 ◦C) and (c) cubic phase (432 ◦C) respectively, while (d)–(i) and (j)–(o) illustrate the intermediate twinning mechanism, which was found reproducibly in all lamellae. (p)–(s) Crystallographic twinning in ferroelectrics. (p) Kikuchi lines of twin 1 (light green) in zone axis, compared to the (q) off-axis Kikuchi lines of twin 2 (dark green) in the same zone axis and correlated twinning in the orthorhombic phase (r,s). (r) illustrates 90◦ and 180 ◦C ferroelectric twinning, while (s) shows 180 ◦C twinning within a crystallographic domain. (t) Twinning in the tetragonal phase of KNNex, colors have been added for illustration purposes.

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