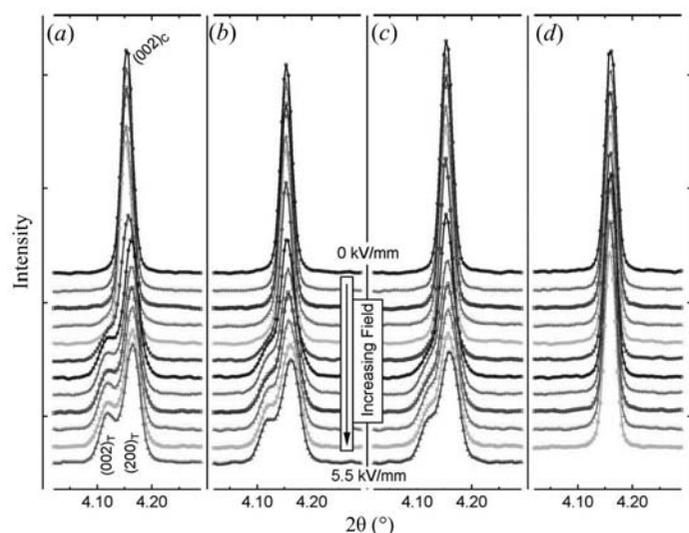


2.8. POWDER DIFFRACTION IN ELECTRIC AND MAGNETIC FIELDS

**Figure 2.8.10**

The pseudo-cubic 002 reflection of (a) 0.93BNT–0.07BT end member, (b) 0.938BNT–0.053BT–0.009KNN, (c) 0.932BNT–0.045BT–0.023KNN and (d) 0.86BNT–0.14KNN end member as a function of electric field from the initial zero-field state (top) to an applied field of 5.5 kV mm^{-1} (bottom). The sample orientation is such that the scattering vector is parallel to the electric field. Reproduced with permission from Daniels *et al.* (2010). Copyright (2010) Elsevier.

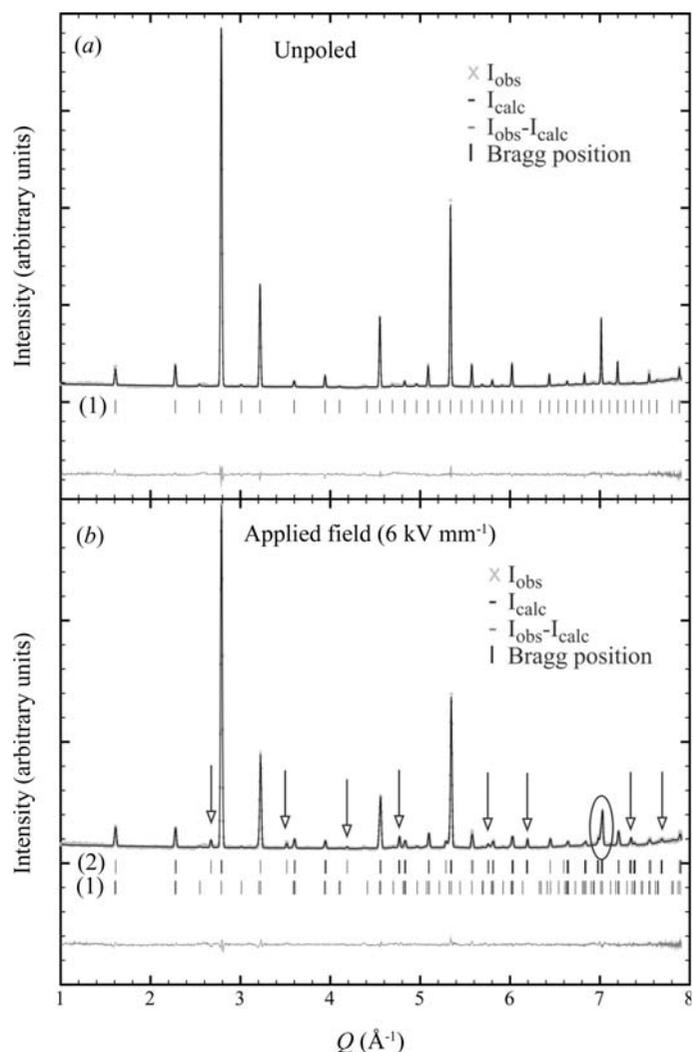
above a threshold of 0.5 kV mm^{-1} , a very pronounced distortion is observed for 0.93BNT–0.07BT, which eventually above 2 kV mm^{-1} develops into a tetragonal structure. In addition to the combination of various compositions, the authors simultaneously measured the X-ray fluorescence spectra, thus confirming the actual composition.

Fig. 2.8.11 depicts a Rietveld refinement of a lead-free ferroelectric material with the composition $0.92\text{Ba}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.06\text{BaTiO}_3\text{--}0.02\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$. New superstructure reflections (Fig. 2.8.11b, arrows) and a lattice distortion (Fig. 2.8.11b, circled) were observed due to a transition from space group $P4bm$ to $R3c$ (Hinterstein *et al.*, 2010).

In an overview, Jones summarized the use of diffraction techniques. Along with the importance of microdiffraction, diffuse scattering and texture effects, the importance of time-resolved studies including stroboscopy was acknowledged (Jones, 2007).

2.8.3.2. *In situ* studies of electrode materials and *in operando* investigations of Li-ion batteries

Rechargeable energy sources in mobile electronics are mainly based on lithium-ion batteries. Their application relies on the mobility of the small Li ions, which move from the cathode through an electrolyte to the anode during charge and back during discharge. Intensive research is underway to improve the performance of such energy-storage technology. High gravimetric and volumetric energy and power densities are required. Other additional challenges are safety, lifetime, the temperature range of stable operation and production costs per unit energy at the battery level. Knowledge of the correlation between the electrochemical functionality and the structure of the electrode materials during Li exchange is essential in order to interpret the underlying mechanisms and degradation processes and to find a promising approach to better materials. The high reactivity of the cell components and the very strong interactions between materials inside an electrochemical cell require studies on complete operational devices by non-invasive *in operando*

**Figure 2.8.11**

Rietveld refinement based on different patterns of $0.92\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.06\text{BaTiO}_3\text{--}0.02\text{K}_{0.5}\text{NbO}_3$ (a) in the unpoled and (b) in the applied field state at 6 kV mm^{-1} . Experimental data are shown by grey crosses, black lines denote calculated profiles, and the lower plot shows their difference. Calculated positions of Bragg reflections are shown by vertical tick marks, where the different rows correspond to the initial tetragonal phase with space group $P4bm$ (1) and the field-induced rhombohedral phase with space group $R3c$ (2). Arrows mark superlattice reflections of type $\frac{1}{2}\{00e\}$ and the circle highlights the rhombohedral split 331_c reflection.

methods. So-called electrochemical ‘half cells’ are often studied to follow structural changes in electrode materials. These are complete operational cells, but the electrode is cycled against an Li-metal counter electrode. Such half-cell studies are sometimes described as *in situ* studies. Limitations might occur with respect to fatigue studies and at very high charge and discharge rates, when the performance is determined by the Li-metal electrode. The classification of *in situ* and *in operando* methods is not unambiguous in structural studies on battery materials. Sometimes the term *quasi in situ* is used for studies where specific states of the materials are prepared electrochemically and handled in an Ar atmosphere with complete protection against humidity and air, but actually investigated *ex situ* (Oswald *et al.*, 2009).

Some early *in situ* setups have been described for neutron diffraction (Bergström, Andersson *et al.*, 1998) and transmission X-ray diffraction (Bergström, Gustafsson & Thomas, 1998), and also at elevated temperatures (Eriksson *et al.*, 2001). Today, for example, good-quality full diffraction patterns can be obtained