

## 2.8. POWDER DIFFRACTION IN ELECTRIC AND MAGNETIC FIELDS

the spatial resolution is significantly affected by the sample dimensions because of self-collimation. The appropriate choice of diffraction method is defined by the particular scientific challenge and has to take into consideration the different amount of sample that is needed for each experiment.

Very high absorption cross sections are desirable for shielding purposes. In X-ray diffraction, lead or tungsten are widely used. Only a few isotopes have a nuclear resonance in the thermal neutron range and thus a high absorption cross section. The most prominent are  $^{10}\text{B}$ ,  $^{113}\text{Cd}$  and  $^{157}\text{Gd}$ , which are used in neutron optics as collimators, attenuators and beam-shaping devices.

## 2.8.2.3. Sample fluorescence and incoherent neutron scattering

Sample fluorescence is a common problem for laboratory X-ray powder diffractometers, which are neither equipped with an analyser nor use detectors with a narrow energy resolution. In powder diffraction using synchrotron radiation, this problem is often solved either by adjusting the energy of the incident beam or by an adjustment of the dynamic range of the detector, or by a combination of both.

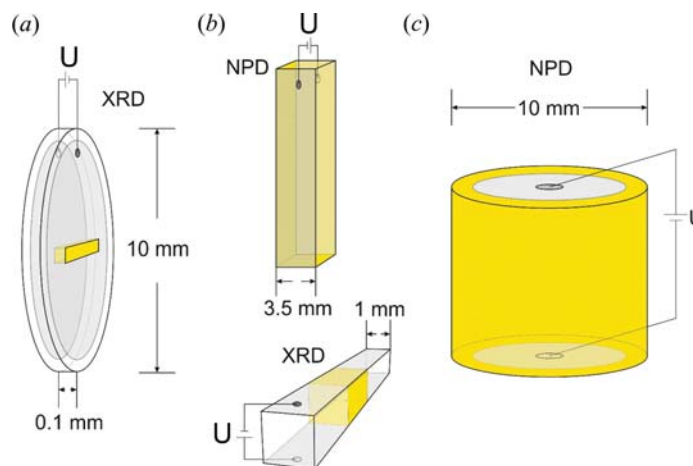
Like absorption cross sections, the incoherent neutron scattering lengths for different elements and isotopes do not vary in any obviously systematic way throughout the periodic table. Among the known stable isotopes,  $^1\text{H}$  has the largest incoherent scattering length (25.274 fm) and has a small and negative coherent one ( $-3.7406$  fm). The situation is very different for  $^2\text{H}$  (deuterium), for which the incoherent and coherent scattering lengths are 4.04 and 6.671 fm, respectively. Differences between the coherent scattering lengths of hydrogen and deuterium form the basis of the isotopic labelling technique, called contrast matching; this is particularly important in applications of neutron scattering to hydrogen storage, structural biology and polymer science. Deuteration of samples is a challenging task, but obtaining high-quality powder diffraction data from hydrogenated samples is far more difficult. Use of neutron polarization analysis is a reliable way to subtract the incoherent scattering contribution from the diffraction data (Mikhailova *et al.*, 2012), but it is often accompanied by significant losses of incident neutron flux and, consequently, of data quality. Both sample fluorescence and incoherent neutron scattering are isotropic and, therefore, are often considered as a background in powder diffraction experiments.

## 2.8.3. Examples

2.8.3.1. *In situ* studies of ferroelectrics in an external electric field

The function of ferroelectrics as stress sensors, high-frequency microphones, medical injectors or large strain actuators is based on electric poling. A polycrystalline material exhibits a zero net polarization. When an electric field is applied to the sample, the spontaneous electric polarization of the ferroelectric material is reoriented along the electric field vector. This occurs by a reorientation of domains. Additional polarization is obtained by an increase of the spontaneous polarization induced by the applied electric field. With *in situ* experiments, the field-induced changes in the powder diffraction reflections are measured. Fig. 2.8.1 is a schematic representation of some *in situ* sample geometries. The electric field is applied *via* electrodes on the sample surface.

Many of these ferroelectric materials crystallize in a structure derived from the cubic perovskite type, but in a crystal system with lower symmetry and with a non-centrosymmetric space group. The most widely used material is lead zirconate-titanate ( $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ , PZT), which exhibits the highest strain response



**Figure 2.8.1**

Sample geometries for *in situ* experiments with an applied electric field. Samples are poled *via* an applied voltage (U) at the sample electrodes (grey). Different sample geometries are necessary to account for different beam sizes, absorption and detector concepts. Yellow indicates the irradiated sample volume. (a) Flat-plate samples for X-ray experiments with strip detectors, limiting photon energies to around 30 keV. (b) Bar-shaped samples for high-intensity neutron powder diffraction (NPD) or high-energy X-ray diffraction (XRD). (c) Cylinder-shaped samples for high-resolution neutron diffraction with fixed detector collimators.

at the so-called morphotropic phase boundary with a composition of about 50% for Ti and Zr. It is generally accepted that the phase on the Ti-rich side of the PZT phase diagram has a tetragonal structure with space group  $P4mm$ . On the rhombohedral Zr-rich side, two ferroelectric phases can be identified, with space groups  $R3m$  for high and  $R3c$  for low temperatures. A considerable amount of work has been devoted to the elucidation of the crystal structure of the material close to the morphotropic phase boundary. Neutron and synchrotron diffraction detected monoclinic symmetry at low temperatures and nanometre-sized regions (the so-called polar nanoregions) were inferred from diffuse scattering (Noheda *et al.*, 2000; Hirota *et al.*, 2006). Alternative interpretations explained the new reflection found in the pattern between the  $111_C$  and  $200_C$  reflections (where the subscript 'C' corresponds to the cubic archetype structure) as diffuse scattering from diffuse incoherent scattering by small domains (Jin *et al.*, 2003).

Unique information on structural changes during poling is obtained from *in situ* studies in applied external electric fields (Hoffmann *et al.*, 2001). Fig. 2.8.2 displays two groups of powder reflections (Schönau, Schmitt *et al.*, 2007) observed by synchrotron X-ray diffraction. They are directly compared with the domain structure from TEM observations (Schmitt *et al.*, 2007) for a range of compositions near the morphotropic phase boundary. One group of reflections is derived from the cubic  $111_C$  reflection, the other from the archetype  $200_C$  reflection. The transition from the rhombohedral splitting to the tetragonal one with increasing Zr content is correlated with the forms of ferroelectric domains in TEM. Close to the morphotropic phase boundary, nanodomains (ranging in width from 20 to 200 nm) are observed in addition to the well known microdomains. The nanodomains react immediately under the influence of an electric field to become microdomains. Fig. 2.8.3 shows the intensity changes observed for the  $110_C$  group of reflections. The changes under an electric field are pronounced and depend on the *c/a* ratio (Schönau, Knapp *et al.*, 2007), the formation and disappearance of nanodomains, and the local symmetry of these domains.