Distinguishing crystallite size effects from those of structural disorder on the powder X-ray diffraction patterns of layered materials

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Abstract. Both crystallite size effects and structural disorder contribute to the broadening of lines in the powder X-ray diffraction (PXRD) patterns of layered materials. Stacking faults, in particular, are ubiquitous in layered materials and aside from broadening also induce peaks due to select reflections to shift away from the Bragg positions. The effect of structural disorder has to be suitably discounted before the application of the Scherrer formula for the estimation of crystallite size.

Keywords. Layered double hydroxides; crystallite size; Scherrer broadening; stacking faults.

1. Introduction

The diffraction of X-rays by a crystalline solid results in a pattern of sharp Bragg reflections characteristic of the different *d*-spacings of a solid. Broadening of these reflections beyond that arising due to instrumental factors is generally attributed to crystallite size effects. The line-width in a powder X-ray diffraction (PXRD) pattern is often exploited to calculate crystallite size of nanomaterials through use of the Debye–Scherrer equation.[1]

Another source of line broadening in the PXRD pattern of a solid is structural disorder. Atoms whose positions depart from the ordered arrangement within the solid contribute to diffuse scattering of X-rays. When the bonding is anisotropic as is the case with layered materials, the solids incorporate a variety of structural disorders. We have, in a series of papers[2–5] investigated structural disorder related broadening of PXRD profiles of the layered double hydroxides (LDHs). The LDHs are a class of materials derived from the mineral brucite ($Mg(OH)_2$). Isomorphous substitution of a fraction of the Mg^{2+} ions by Al^{3+} ions results in the layers acquiring a positive charge which may be compensated by the incorporation of anions such as Cl^-, NO_3^-, CO_3^{2-} or SO_4^{2-} in the interlayer region. In these materials bonding within the layers is ionocovalent while adjacent layers are held together by weak van der Waals and hydrogen bonding interactions. Our investigations have shown that different types of disorder induce characteristic broadening of select families of reflections.

In recent years, there has been an emergence of interest in the synthesis of nanoparticulate layered double hydroxides.[6–11] Powder X-ray diffraction has often been used as a tool to estimate crystallite sizes of these materials. It is especially used to estimate crystallite thickness along the *c*-crystallographic axis, also the stacking direction, by measuring the full width at half maximum (FWHM) of the 00ℓ reflections and using it in the Scherrer formula.[6,7,10,11] In isotropic materials where structural disorder related broadening can be safely assumed to be at a minimum, such estimates of crystallite size by use of the Scherrer equation can be relied upon as being fairly accurate. However, the same cannot be assumed of layered materials that are replete with structural disorders. Due to the recent surge in papers related to layered nanomaterials, there is a need to distinguish between crystallite size dependent broadening and structural disorder related broadening in the PXRD patterns of these materials.

2. Experimental

2.1 *Synthesis of layered double hydroxides (LDHs)*

Mg–Al–CO$_3$ LDH was prepared by the slow addition of a mixed metal (Mg^{2+} + Al^{3+}) nitrate solution (total concentration 1·2 M) containing Mg^{2+} and Al^{3+} in the ratio 2 : 1 to a solution containing the stoichiometric requirement of OH^- ions and three times the stoichiometric requirement of CO_3^{2-} taken

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as Na_2CO_3. The precipitation was carried out at 25°C. The resultant precipitate was aged in the mother liquor at 90°C for 24 h before being filtered, washed and dried to constant weight.

An ordered sample of the LDH was prepared by urea hydrolysis. Solid urea was added to 40 ml of a 0·5 M mixed metal [Mg(II) + Al(III)] nitrate solution maintaining the urea/[Mg(II) + Al(III)] molar ratio at 3·3. The clear solution obtained was heated at 150°C in a teflon lined autoclave under autogenous pressure. The solid was recovered by filtration, copiously washed to constant pH and then dried at 65°C.

2.2 *Characterization*

All the samples were characterized by X-ray powder diffraction using a Bruker D8 Advance diffractometer (source CuKα, $\lambda = 1\cdot541$ Å) operated in reflection geometry. Data were collected using a continuous scan rate of $1°2\theta\,min^{-1}$, which were then rebinned into 2θ steps of 0·02°.

Scanning electron micrographs were obtained using a JEOL model JSM 840A microscope. The powder samples were dispersed on a double sided conducting carbon tape. The samples were sputter coated with Pt to improve conductivity.

Crystallite size analysis was carried out using the Brass 2.0 suite of programs.[12] Investigation of broadening due to structural disorder was carried out using the program DIFFaX.[13]

3. Results and discussion

The PXRD pattern of a coprecipitated Mg–Al–CO$_3$ LDH is given in figure 1a. We compare the experimental pattern with that expected of the crystal structure of the Mg–Al–CO$_3$ LDH (International Crystal Structure Database No. 86655) (figure 1b). Some differences are obvious: (i) While the basal reflections in the experimental pattern are relatively sharp, the peaks in the mid-2θ region (30–55°2θ) are broadened. (ii) The peak positions of the reflections in the mid-2θ region are shifted with respect to the corresponding peaks in the simulated pattern. (iii) The observed pattern cannot be indexed with acceptable figures of merit.

While most preparations of LDHs generally exhibit PXRD patterns similar to that shown in figure 1a, samples whose PXRD patterns match with the expected of an ideal sample (figure 1b) may be synthesized by urea hydrolysis (figure 2). The SEM image of this sample (data not shown) exhibits the sharply faceted hexagonal morphology consistent with the underlying hexagonal crystal structure of these materials. A Rietveld fit of the PXRD pat-
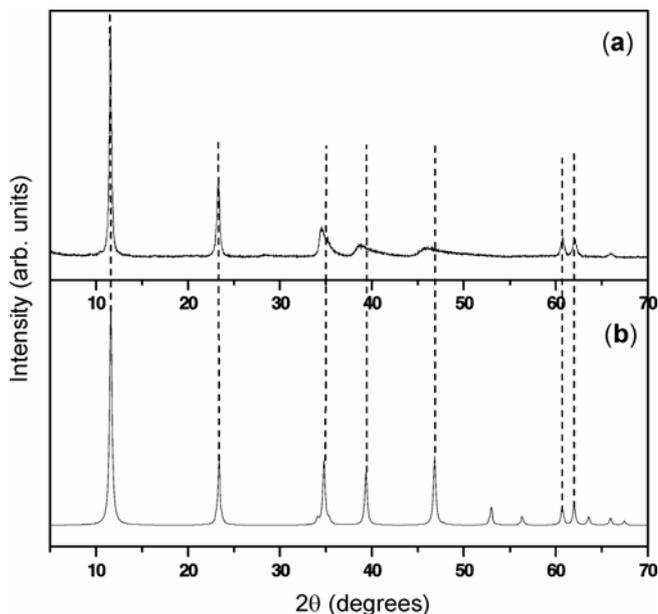

Figure 1. (**a**) Powder X-ray diffraction pattern of an Mg–Al–CO$_3$ LDH prepared by co-precipitation. (**b**) DIF-FaX simulation of the PXRD pattern of an ideal Mg–Al–CO$_3$ LDH assuming no crystallite size effects or stacking disorders.
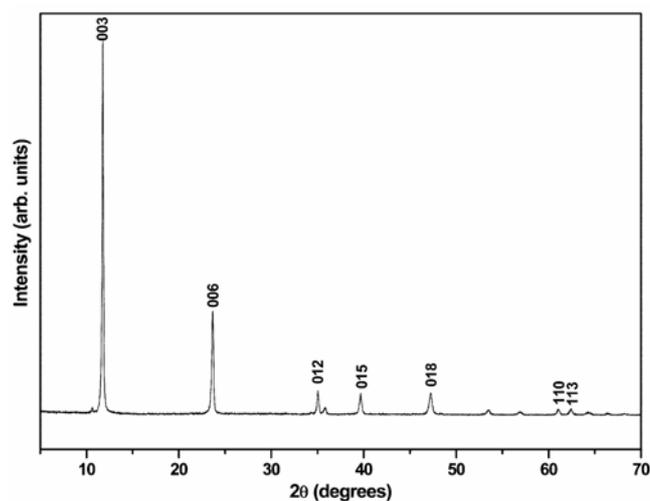

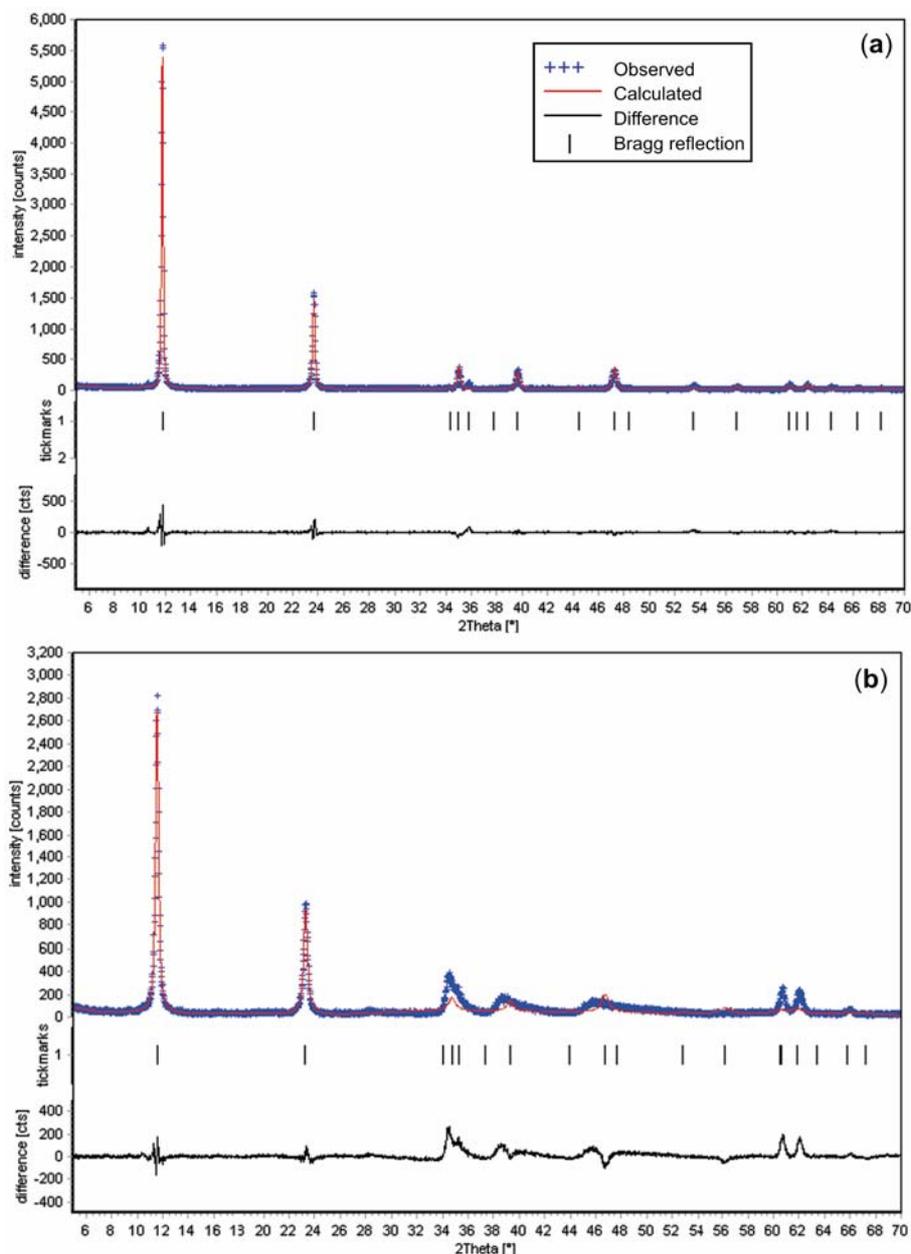**Figure 2.** PXRD pattern of the Mg–Al–CO$_3$ LDH prepared by urea hydrolysis.

Figure 3. (**a**) Rietveld fit of the PXRD pattern of the Mg–Al–CO$_3$ LDH prepared by urea hydrolysis and (**b**) the fit of the LDH prepared by coprecipitation after refinement of crystallite size.

tern of this sample (figure 3a) shows that the broadening of peaks is minimal and therefore this sample may be used as a standard in subsequent analyses. The extensive broadening of the peaks in the PXRD pattern of the co-precipitated (test) sample therefore needs to be examined.

We first examine the possibility that the broadening may be due to crystallite size effects. An accurate estimation of crystallite size requires one to first

correct for instrument-related broadening. The residual broadening may then be attributed to sample related factors which include broadening due to crystallite size, strain and absorption. To accomplish this, we use the Brass suite of programs which enable a rigorous separation of instrument and sample contributions to the peak profiles. In a typical application of this methodology, the instrumental contribution to line broadening is obtained by
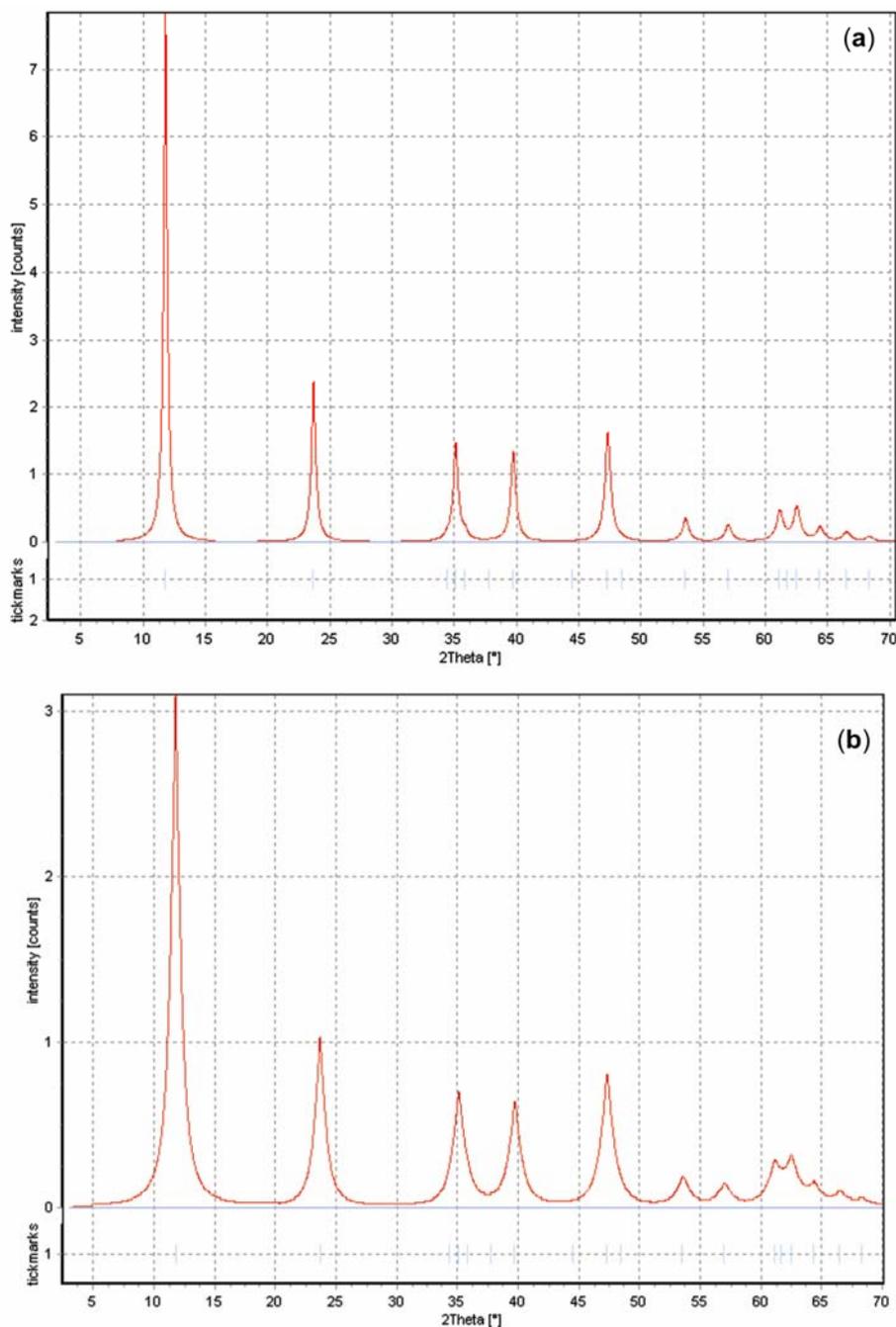
Figure 4. Simulation of the PXRD pattern of an Mg–Al–CO$_3$ LDH assuming crystallite size along 003 direction to be (**a**) 30 nm and (**b**) 10 nm.

refining the profile parameters to fit the line shape of a standard. The refinable profile parameters include U_G, V_G, W_G and U_L, W_L for the Gaussian and Lorentzian contributions respectively. Subsequently, these parameters are used without further refinement to fit the profile of the test sample. Any mismatch in the fit is then corrected by accounting for sample related factors, including Scherrer broadening due to

crystallite size effects. We have successfully used this methodology to evaluate the crystallite size of nanocrystalline Cu$_2$O samples.[14]

In this work a similar methodology is used to analyse the pattern of the test sample of LDH obtained by coprecipitation. The sample synthesized by urea hydrolysis is used as a standard to obviate the need to explicitly model sample-related broadening aris-

ing from absorption. In a procedure similar to that described above, the instrument related parameters are determined by a Rietveld fit of the PXRD profile of the standard Mg–Al–CO$_3$ LDH (figure 3a). These parameters are then kept fixed when refining the PXRD profile of the coprecipitated LDH. The residual is accounted for by refining crystallite size. However unlike in the case of the isotropic Cu$_2$O, attempts to account for the residual broadening by refining crystallite size fails as shown in figure 3b. The difference profile clearly indicates significant residual intensities.

We then ask the question: how will PXRD pattern of the LDH look like under the influence of crystallite size effects. To answer this, we simulate the PXRD pattern of the LDH assuming an illustrative crystallite size of 30 nm along the *c*-crystallographic axis**.** The profile parameters are taken from the Rietveld refinement of the standard Mg–Al–CO$_3$ LDH sample. The resulting simulation is shown in figure 4a and the broadening of peaks is seen to be negligible. Simulation of the PXRD pattern assuming the crystallite size to be 10 nm is shown in figure 4b. Here we make two observations: (i) Unlike in the test sample (figure 1a) the broadening is seen across all classes of reflections. (ii) Although all the reflections are broadened, there is no shift in the peak positions from that expected of the standard (figure 2).

The above analysis rules out the possibility that the broadening observed in the test pattern is due to crystallite size effects.
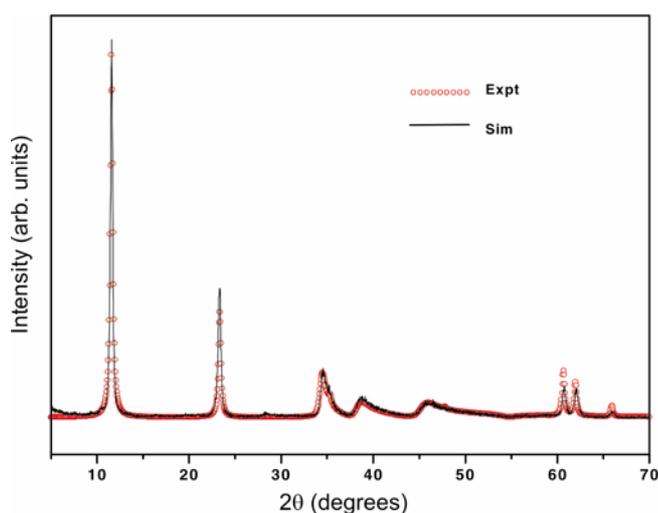
We, therefore examine whether the broadening is due to structural disorder. We have, in our earlier papers shown that the DIFFaX formalism[15] is best suited to study stacking faults in layered materials. In DIFFaX, a crystalline solid is treated as consisting of a stacking of sheets of atoms interconnected by stacking vectors. Different kinds of stacking faults may be engineered into the solid by varying the stacking vectors and the resulting changes in the PXRD pattern can be computed. Details of the procedure have been dealt with in detail in earlier papers[2–5] and therefore will not be discussed here. Stacking faults affect the line shapes of the $h0\ell/0k\ell$ class of reflections, turbostraticity affects the $hk0$ reflections and interstratification affects the non-$hk0$ reflections. Using DIFFaX, we are able to simulate the PXRD pattern of the test LDH sample by incorporating 20% stacking motifs having a local hexagonal symmetry (2H$_1$: stacking sequence AC CA AC---) in a matrix of rhombohedral crystal symmetry (3R$_1$: stacking sequence AC CB BA AC---) (figure 5). The good match of the observed with the simulated pattern is self evident and is superior to the one shown in figure 3b.

4. Conclusions

Stacking disorders are ubiquitous in layered materials. They contribute significantly to the broadening of lines in the PXRD patterns of layered materials. Any uncritical use of the measured line-widths for the estimation of crystallite size by the use of the Scherrer formula leads to severe underestimation of the crystallite size and calls into question the validity of the estimated crystallite sizes in the so-called 'layered nanomaterials'.

Figure 5. DIFFaX simulation of the PXRD pattern of the coprecipitated Mg–Al–CO$_3$ LDH by inclusion of 20% 2H$_1$ faults in a 3R$_1$ polytype.

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