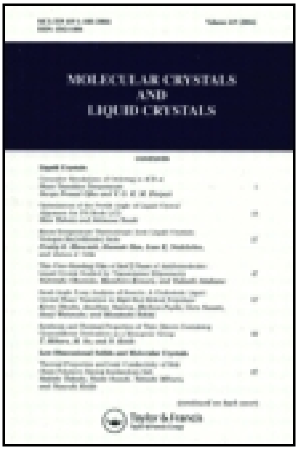

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Layer Rigidity in Layer Double Hydroxides Containing a Fixed Host-Layer

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(In final form July 12, 1999)

We report here the first layer rigidity study which has been performed on layer double hydroxides (LDH's) having a fixed-host layer. The LDH materials studied have the chemical formula $[(CO_3)_{0.195(1-x)}Cl_{0.39x}]:[Zn_{0.61}Al_{0.39}(OH)_2]$, $0 \leq x \leq 1$. An inter-layer rigidity parameter of $p=4.84 \pm 0.06$ was determined for these compounds from a fit of the standard version of the discrete finite layer rigidity model to the composition-dependence of the normalized basal spacing measured using X-ray diffraction. This result validates the previous results obtained from the more complex, variable-host layer LDH materials.

Keywords: layered double hydroxides; layer rigidity; fixed-host

INTRODUCTION

The layer rigidity of an intercalated layered solid vis a vis transverse distortions that are orthogonal to the host layer planes influences many of its physical properties.[1,2] A quantitative value of the layer rigidity is most accurately obtained by measuring the composition-dependence of the basal spacing of a ternary solid-solution system of the form $M_{1-x}M'_x$:L and fitting the result to an appropriate one-parameter theoretical model to extract the inter-layer rigidity parameter, p.[3,4] Here, M and M' represent ions intercalated into the guest layer and L represents a host layer having a fixed composition. The rigidity parameters of fixed-host layered solids such as graphite, layered dichalcogenides, layer perovskites and layered silicates have all been successfully determined using this approach. However, layer double hydroxides (LDH) represent an unusual class of intercalated layered solids in which the guest layer composition can be varied either independent of the host layer (i.e., fixed-host materials) or as a result of cation substitutions within the host layer itself (i.e., variable-host materials). In either scenario, the basal spacing response to the change in concentration of different size ions is governed by the host layer rigidity.

Previous layer rigidity studies of LDH compounds[5] have only been performed on variable-host materials of the form $[(CO_3)_{z/2}(H_2O)_y]:[Ni_{1-z}Al_z(OH)_2]$, $0<z<0.4$, $0<y<1.2$ (hereafter referred to as $(CO_3)(NiAl)$:LDH). In these materials, transverse distortions of the host layer arise as a result of a concomitant change within both the host and guest layers. In the host layer, smaller Al^{+3} ions are substituted for the larger Ni^{+2} ions resulting in an increased positive charge. In the guest layer, additional (larger) CO_3 ions fill previously vacant (smaller) sites in order to balance the net, positive charge of the host layer. In order to properly model the layer rigidity of such materials, a 2-parameter extended version[5] of the finite, discrete layer rigidity model[3] was developed which included an intra-layer rigidity parameter in addition to the inter-layer rigidity parameter. The intra-layer rigidity parameter was determined to be 2.44 and the inter-layer rigidity parameter was determined to be $p \sim 5$. The approximate nature of the inter-layer rigidity parameter arises from the multi-parameter character of the basal response model and from the presence of water molecules in the guest layer. These water molecules solvate the CO_3 ions thus producing an ion who's effective, lateral, size is larger than that of the bare CO_3 ion. The height of both the water molecule and the CO_3 ion are approximately equal since both are essentially defined be the size of the oxygen atom. Hence, the solvated CO_3 ion, though larger laterally, remains equal in height to the bare CO_3 ion. This does not change the value of the basal spacing but does affect its composition-dependence; thus, yielding only an approximate value of p.

In order to obtain a more direct and accurate measure of the inter-layer rigidity parameter for LDH's, both the host layer cation substitutions and the solvating water molecules need to be addressed. Accordingly, we report here the first fixed-host layer rigidity studies of dehydrated LDH's, namely materials of the form $[(CO_3)_{0.195(1-x)}Cl_{0.39x}]:[Zn_{0.61}Al_{0.39}(OH)_2]$, $0 \leq x \leq 1$ (hereafter $(Cl/CO_3)(ZnAl)$:LDH). These materials contain no solvating water molecules in the guest layer and have a fixed cation substitution within the host layer. With the host layer charge and composition fixed, the relative concentration of the smaller to larger ions in the guest layer can be varied independent of the host layer composition.

EXPERIMENTAL PROCEDURE

The synthesis of a series of LDH compounds having the chemical formula $[(CO_3)_{0.195(1-x)}Cl_{0.39x}(H_2O)_y]:[Zn_{0.61}Al_{0.39}(OH)_2]$, $0 \leq x \leq 1$, $y=0.4+0.2x$ has been previously reported.[6] The dehydration procedure described below was determined from a previous study[7] of the hydration dynamics of the end member compounds $[Cl_{0.39}(H_2O)_y]:[Zn_{0.61}Al_{0.39}(OH)_2]$ (hereafter Cl:LDH) and $[(CO_3)_{0.195}(H_2O)_y]:[Zn_{0.61}Al_{0.39}(OH)_2]$ (hereafter CO_3:LDH). The x-ray diffraction (XRD) apparatus has also been described elsewhere.[8] The (003) and (006) Bragg reflections measured in the powder pattern were used in a q-plot[9] to determine the basal spacing. A sample was dehydrated by putting it into an N_2 purge at room temperature for two days and then slowly heating it to 70 °C. Additionally, thermal gravimetric analysis data was used to study the dehydration dynamics of individual samples.

RESULTS AND DISCUSSION

The full XRD patterns for each of the dehydrated (Cl/CO_3)(ZnAL):LDH samples are shown in Fig. 1. The prominent (00L) reflections at low angle are characteristic of layered materials and the narrow width of all the reflections indicate that the samples exhibit a high degree of crystallinity. Reflections from the sample holder are marked with an asterisk (*). It has been determined from simulated XRD patterns[10] generated using DIFFaX[11] that the reflections for all but the x=1.0 XRD pattern correspond to an $R\bar{3}m$ space group having a 3R stacking sequence with 10% faulting and have been so labeled in the figure. The remaining XRD pattern of the x=1.0 sample has also been compared to simulated XRD patterns and corresponds to the same space group but with a mixed stacking sequence comprised of 30% 3R stacking with 10% stacking faults and 60% 2H stacking with no faulting. The term 3R refers to an ABCABC sequence of layer stacking and 2H refers to an ABAB sequence of layer stacking. The labeled reflections for the x=1.0 sample are associated with this change in stacking sequence.

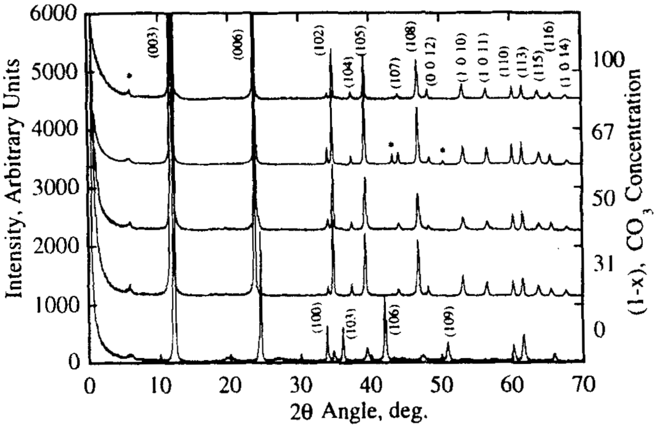

FIGURE 1. CuKα X-ray powder diffraction patterns of $[(CO_3)_{0.195(1-x)}Cl_{0.39x}]$:$[Zn_{0.61}Al_{0.39}(OH)_2]$ shown as a function of CO_3 ion concentration. The patterns have been displaced vertically for clarity. The reflections marked by an asterisk (*) are from the sample holder.

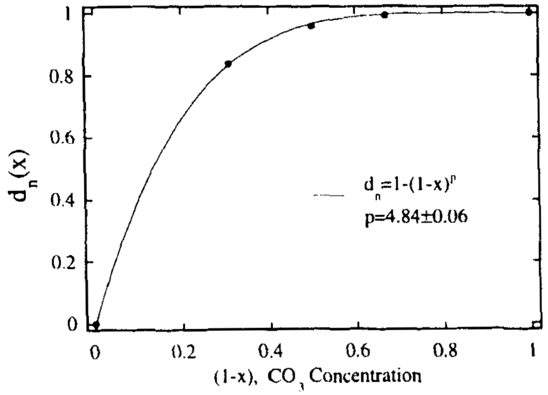

FIGURE. 2. The normalized basal for $[(CO_3)_{0.195(1-x)}Cl_{0.39x}]$:[$Zn_{0.61}Al_{0.39}(OH)_2$ (data points). The solid curve represents a fit of the discrete finite layer rigidity model to the data points. The inter-layer rigidity parameter used in the fit is shown.

The normalized basal spacings[12] for the dehydrated (Cl/CO_3)(ZnAL):LDH samples are defined as

$$d_n(X) = \frac{d(X) - d(0)}{d(1) - d(0)} \tag{1}$$

and shown as data points in Fig. 2. These basal spacing data for the dehydrated (Cl/CO_3)(ZnAL):LDH samples are unique because the spacing is largest for the end member containing the smaller CO_3 ion and smallest for the end member containing the larger Cl ion. This phenomenon occurs because, even though the Cl ion (3.62 Å)[13] is larger in height than the CO_3 ion (3.09 Å)[5], it is smaller in its lateral (in-plane) dimension. This allows the Cl ion to be nested into the trigonal pockets of the host layer; thus, producing an effective height for the Cl ion which is actually smaller than the height of the CO_3 ion.

The discrete finite layer rigidity model can be applied to the normalized basal spacing data independent of the reversal of the basal spacing response provided that the height of each ion is independent of concentration. The normalized basal spacing within this model[14] is shown in Eq. 2 where X is the concentration of the larger ion and p is the inter-layer rigidity parameter.

$$d_n(X) = 1 - (1 - X)^p \tag{2}$$

The only caveat in using this equation is that, because of the nesting of the larger Cl ion, X is now the concentration of the smaller CO_3 ion. The solid line in Fig. 2 is a fit of the finite layer rigidity model to the dehydrated (Cl/CO_3)(ZnAL):LDH data with an inter-layer rigidity parameter of p=4.84±0.06.

This result can be compared to that obtained by applying the extended (2-parameter) version of the finite layer rigidity model to the variable-host LDH compound $[(CO_3)_{z/2}(H_2O)_y]:[Ni_{1-z}Al_z(OH)_2]$, $0<z<0.4$, $0<y<1.2$ discussed above. In that case (and for reasons discussed above) an approximate value of p ~ 5 was obtained. Nevertheless, the value of the inter-layer rigidity parameter determined for the fixed-host layer (Cl/CO_3)(ZnAl):LDH compound is in good agreement with the value determined for the variable host layer

$(CO_3)(NiAl)$:LDH compound and thus further validates the extended version of the discrete finite layer rigidity model. It is also interesting to note that the LDH hosts are more rigid than either graphite (p = 2) or layer dichalcogenides (p = 3.5) but less rigid than layer silicate clays (p = 6.5).

CONCLUSION

The $(Cl/CO_3)(ZnAl)$:LDH (fixed-host) materials constitute a less complex LDH system than the previously investigated $(CO_3)(NiAl)$:LDH (variable-host) materials for the study of transverse layer rigidity properties of layered solids. The inter-layer rigidity parameter for these fixed-host layer LDH's has been determined to be $p=4.84\pm0.06$. This result validates the similar result of p~5 obtained from the variable-host layer materials. The $(Cl/CO_3)(ZnAl)$:LDH materials exhibit additional unique properties in that the larger Cl ion produces a smaller basal spacing than the smaller CO_3 ion. This reverse basal spacing response has been attributed to a nesting of the Cl ion into the trigonal pockets of the host layer.

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