

THE SYNTHESIS OF AN INTERSTRATIFIED LAYERED OXIDE FROM EXFOLIATED PRECURSORS

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ABSTRACT

Aqueous suspensions of exfoliated $\text{Li}_{0.25}\text{MoO}_3$ and Na-montmorillonite have been combined and dried to form interstratified solids. X-ray diffraction patterns of ethylene glycol treated films show that the d-spacing of restacked materials varies with composition between the limits established by the two end members. Based on these data, we conclude that the new materials are composed of individual layers from each of the precursor compounds, arranged in a random fashion. It is likely that other layered solids can be exfoliated and restacked to form new interstratified materials.

INTRODUCTION

A wide variety of low-temperature synthetic processes, including hydrothermal [1], ion exchange [2], pillaring [3], and intercalation [4] reactions have been employed in the search for new layered solids. More recently, approaches involving the synthesis and assembly of single layers have been examined [5]. For example, ordered structures that sandwich organic species between silicate layers can be assembled layer-by-layer from solution [6]. The possibility of forming a new material by combining and flocculating two different single layer suspensions with opposite charges has also been demonstrated by Miramadi and Morrison [7]. These researchers synthesized MoWS_4 , an ordered compound with alternating MoS_2 and WS_2 layers, from equal molar single layer suspensions of exfoliated MoS_2 and WS_2 .

Considering these results, it should be possible to create a variety of interstratified solids, with a range of compositions and properties, by combining the characteristic layers of two or more distinct materials in different ratios. In this paper, we describe how we have applied this principle to synthesize new layered materials. These interstratified solids contain layers of a metallically conducting oxide ($\text{Li}_{0.25}\text{MoO}_3$) and layers of an insulating sheet silicate (Na-montmorillonite).

EXPERIMENTAL

$\text{Li}_{0.25}\text{MoO}_3$ was prepared from $\alpha\text{-MoO}_3$ following the method established by Thomas and McCarron. [8]. Na-montmorillonite (Polar Gel NF) was obtained from American Colloid Company (Belle Fourche, SD). Separate, dilute suspensions of the two layered materials were prepared by dispersing the powders in distilled water with sonication and stirring. Specific volumes of each suspension were then combined, sonicated, and stirred to yield a stable suspension containing a mixture of both layers. The compositions of the mixtures were controlled according to surface area ratios, assuming that the precursors exfoliate into single sheets and that their stoichiometries are $[\text{Li}(\text{H}_2\text{O})_5]_{0.25}\text{MoO}_3$ and

$\text{Na}_{0.3}(\text{Al}_{0.8}\text{Mg}_{0.2})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 7(\text{H}_2\text{O})$. Coincidentally, the surface area to mass ratios of these compounds differ by only 3 %. Because the errors involved in determining the exact surface area to mass ratio (compositional ambiguities and the dissolution of a small amount of the molybdate in the basic silicate sols) are comparable in size to this difference, we assume that the mass ratio is equal to the surface area ratio.

Oriented films of the interstratified solids were prepared by casting approximately 1 ml of the mixed suspension on a glass slide and allowing it to dry in air. After one or two days of drying, the films were saturated with ethylene glycol and X-ray diffraction patterns were recorded with a Rigaku powder diffractometer operating at 25 mA and 35 kV using $\text{Cu K}\alpha$ radiation. Saturating the films with ethylene glycol effectively eliminated the potentially misleading variations in layer spacing that occur with changes in the relative humidity. It has been known for some time that when Na-montmorillonite is saturated with ethylene glycol, its layer spacing swells reproducibly to about 17.4 Å [9]. We found that $\text{Li}_{0.25}\text{MoO}_3$ also readily absorbed ethylene glycol and the interlayer spacing swells to 15.7 Å.

RESULTS AND DISCUSSION

A selection of typical diffraction patterns from the ethylene glycol treated films is shown in Fig. 1. The patterns labeled a and e are from the pure, restacked precursors while the patterns labeled b, c, and d are from interstratified materials. Two peaks, indexed as (001) and (002), were present in all of the patterns. Based on the center of gravity of these two peaks, d-spacings were determined and are plotted in Fig. 2 as a function of composition. Although from a single experiment, these results are representative of several reproducible experiments. There are three possible limiting cases for the arrangement of the restacked layers and these are discussed in the following paragraphs.

The first possibility is that like layers associate with one another and phase separation occurs. In this case, the film would have two distinct restacked phases at all intermediate compositions. The diffraction pattern from such a two phase mixture would be a superposition of the patterns characteristic of each phase (1a and 1e) and the d-spacing would be constant with composition. We simulated the diffraction pattern from hypothetical two phase mixtures by summing the data in Figs. 1a and 1e (properly weighted to reflect different compositions) and compared the results to our observations. Because the molybdate scatters X-rays better than the silicate, its pattern completely dominates the summation at all compositions with at least 25 % $\text{Li}_{0.25}\text{MoO}_3$ surface area. The low angle Na-montmorillonite peak is always hidden in the tail of the first molybdate peak and the measured d-spacing are, thus, identical to restacked $\text{Li}_{0.25}\text{MoO}_3$. The continuous evolution of the d-spacing that we observed in our data can not be explained by a two phase mixture.

The second possibility is that the unlike layers associate strongly with each other and an ordered layer arrangement forms. If this happened, we would expect to see new peaks characteristic of the increased repeat distance (the sum of the two individual layers). Because this was not observed, we conclude that the layers do not order.

The third possibility is that the layers restack more or less at random, forming a random interstratification. This is illustrated schematically in Fig. 3. Naturally occurring [9] and hydrothermally synthesized [10] randomly interstratified clay minerals have been known for decades and there are well established theories [11, 12] that can be used to interpret the diffraction patterns from such materials. In accordance with experimental observations, the theory predicts that if layers from compounds A and B (individually characterized by d-spacings d_A and d_B , respectively) are randomly stacked, the d-spacing of the interstratified solid is intermediate between d_A and d_B and depends on the relative concentration of each type of layer. Furthermore, the (00 l) peaks from the randomly interstratified material are not expected to always form a rational sequence. Because our data has exactly these characteristics, we assume that the mixtures of exfoliated $\text{Li}_{0.25}\text{MoO}_3$ and Na-montmorillonite form a random interstratification.

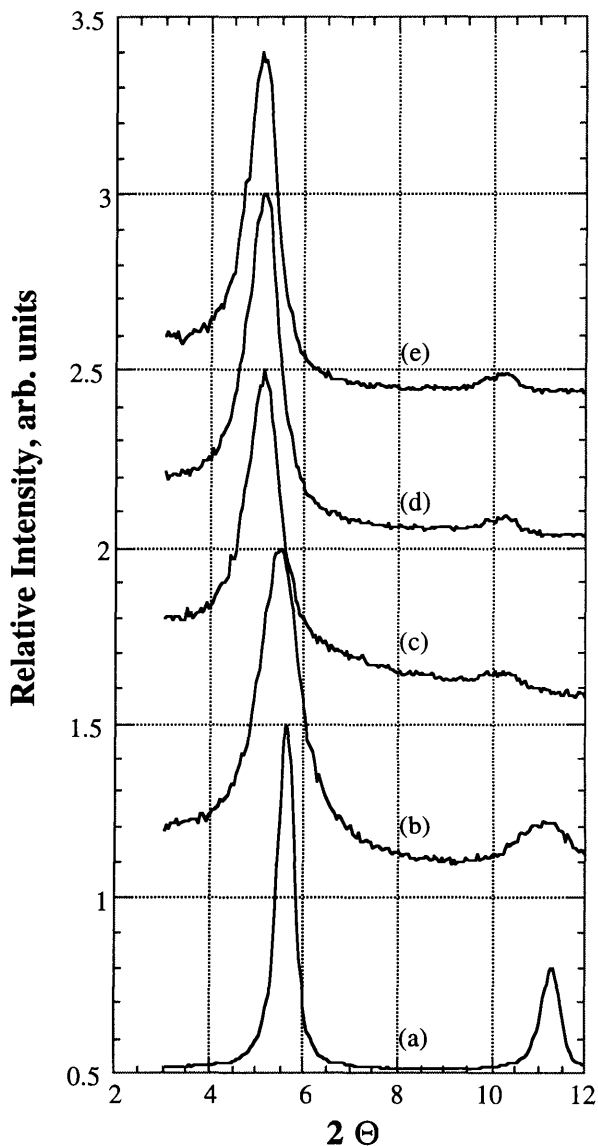


Figure 1. Selected diffraction patterns from restacked molybdate-silicate interstratifications after treatment with ethylene glycol. The pattern labeled (a) was obtained from pure, restacked $\text{Li}_{0.25}\text{MoO}_3$ and the pattern labeled (e) is from pure restacked Na-montmorillonite. The pattern labeled (b) is from a film containing 70% $\text{Li}_{0.25}\text{MoO}_3$ layers, (c) is from a film containing 50% $\text{Li}_{0.25}\text{MoO}_3$ layers, and (d) is from a film containing 25 % $\text{Li}_{0.25}\text{MoO}_3$ layers. The low angle peak is indexed as (001) and the higher angle peak as (002).

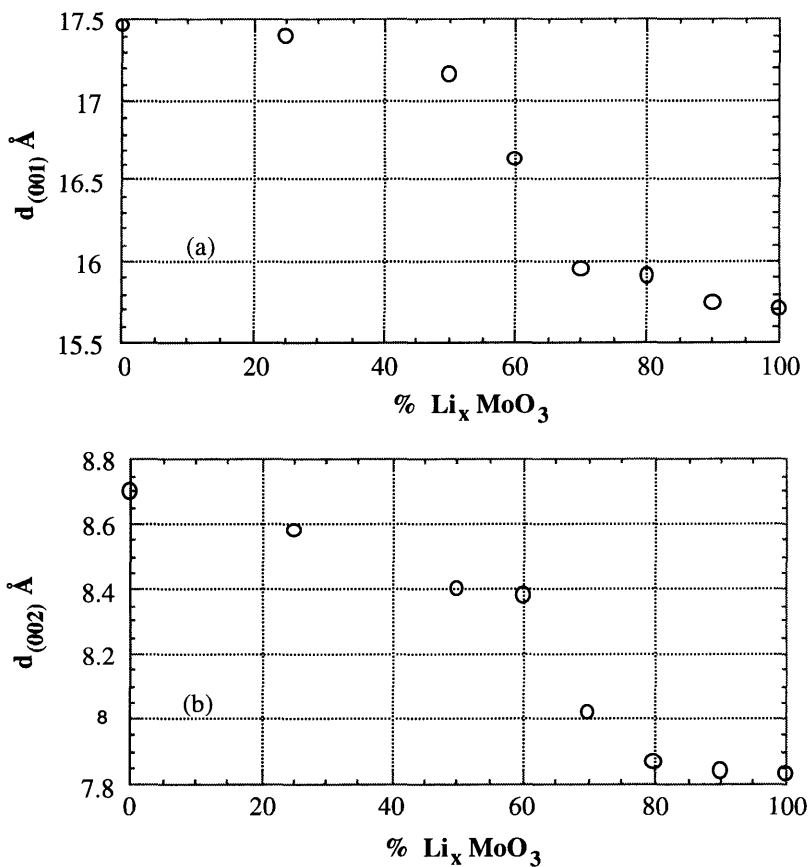


Figure 2. Layer spacing vs. composition for molybdate-montmorillonite interstratifications after ethylene glycol treatment. In (a), the d-spacing determined from the 001 peak is shown and in (b), the d-spacing determined from the (002) peak is shown.

Considering the fact that both of the layers possess a negative charge that is compensated by interlayer alkali cations, it is not surprising that the layers restack at random. The molecular-scale mixing of the layers implies that the interlayer cations are also mixed at this scale. To insure that the observed changes in d-spacing were not simply caused by an ion exchange reaction in which the Na ions from the montmorillonite replace some of the Li ions in $\text{Li}_{0.25}\text{MoO}_3$, we measured the d-spacing of pure $\text{Na}_{0.25}\text{MoO}_3$ films after treatment with

ethylene glycol. We found that the interlayer spacing is 15.63 Å. Because this is essentially identical to the ethylene glycol treated $\text{Li}_{0.25}\text{MoO}_3$ films, we assume that an ion exchange reaction can not account for the observed change in the d-spacing.

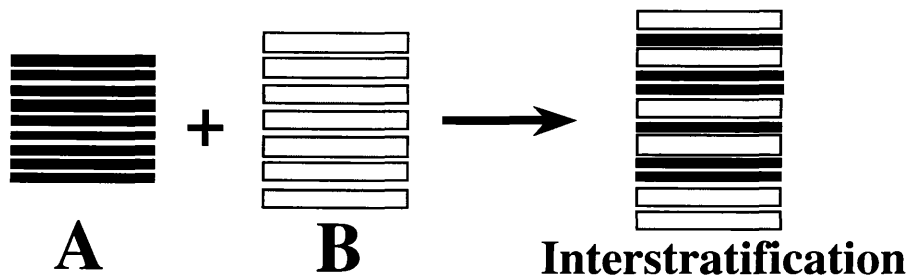


Figure 3. Schematic model for the randomly interstratified solid.

Tests have shown that the interstratified films are electronic conductors when they contain a significant fraction of the conductive molybdate. Future research will be aimed at measuring the composition dependence of the electronic conductivity of the films and their thermal stability. Finally, we note that because there are numerous materials that are known to exfoliate to stable single layer suspensions [13], it is probably possible to restack a wide variety of new layered materials that might have unique properties.

CONCLUSION

Based on X-ray diffraction data, we have found that aqueous single layer suspensions of Na montmorillonite and $\text{Li}_{0.25}\text{MoO}_3$ can be combined to form randomly interstratified materials. Because the layers restack in a random fashion, solids can be formed with any composition. If the other inorganic compounds that are known to exfoliate behave in a similar way, it might be possible to design a range of new layered materials.

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