Structural Investigation of an Azobenzene Derivatized Manganese Phosphonate Langmuir-Blodgett Film

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Introduction

We have recently shown that inorganic continuous lattice structures can be incorporated into the hydrophilic regions of Langmuir-Blodgett (LB) films allowing for the tailoring of physical properties such as magnetism.[1,2] In an effort to extend the potential applications for this class of thin films, we have reported the preparation of bifunctional LB films wherein the hydrophobic region consists of a photoreactive azobenzene derivatized phosphonate and the hydrophilic region contains an extended magnetic Mn lattice.[2] Previous studies by our group using synchrotron radiation have shown that the inorganic lattice in the manganese octadecylphosphonate LB film (MnOPA) is isostructural with the solid-state analogues.[3] Here, we show by employing grazing incidence x-ray diffraction (GIXD) that the same manganese network forms in azobenzene derivatized manganese phosphonates films.

Materials and Methods

The preparation of the azobenzene derivatized manganese phosphonate LB film (MnAzo) has been described elsewhere.[2] The film consists of 15 bilayers transferred to a glass slide. The x-ray wavelength was 1.254 Å, and the beam was directed onto the sample under grazing angles to achieve surface sensitivity and minimize bulk background scattering.

Results and Discussion

The GIXD pattern for a 15 bilayer film of MnAzo is compared to the pattern obtained for a 16 bilayer film of MnOPA in Fig. 1. Both films show the expected peaks corresponding to the (2,0) and (0,2) Bragg planes for the manganese phosphonate lattice at d spacings of 2.88 Å and 2.44 Å. The (1,1) peak at 3.71 Å is obscured in the MnAzo film by the strong scattering from the organic lattice. The d spacings for the inorganic lattice yield a centered rectangular cell with a = 5.76 Å and b = 4.88 Å, close to the a = 5.73 Å and b = 4.94 seen in the manganese phenylphosphonate bulk phase. Thus, both films contain the same inorganic network that forms regardless of the organic functionalities. As expected, the packing of the organic moieties is different in the two films. The intense reflection at 4.27 Å in the MnOPA film has been assigned to the (1,0) Bragg plane for the oblique cell resulting from the tilt of the octadecyl chains along the manganese face diagonal. The tilt direction corresponds to the b axis of the oblique unit cell, a = 5.76, b = 6.6, $\gamma = 139.7°$. The intensity of the in-plane Bragg peaks likely results from the tilt organizing the alkyl chains along the b axis. The MnAzo film, in contrast, has a strong peak at 3.79 Å and a weaker reflection at 4.59 Å. These reflections can be assigned to an oblique unit cell with a = 5.75 Å, b = 7.00 Å, $\gamma = 139°$. The azobenzene units are likely tilted along the b axis as in the MnOPA film—but to a lesser degree, 22° in MnAzo as opposed to 28° in MnOPA. The higher intensity in the peak at 3.79 Å in the MnAzo film suggests a packing arrangement in which the azobenzene units are aligned along the (0,1) face of the oblique unit cell. This arrangement would allow for a π–π interaction between the azobenzene groups with only a slight rotation relative to the b axis. This conclusion is further supported by UV-VIS spectroscopy that shows considerable π–π interactions in the MnAzo film.

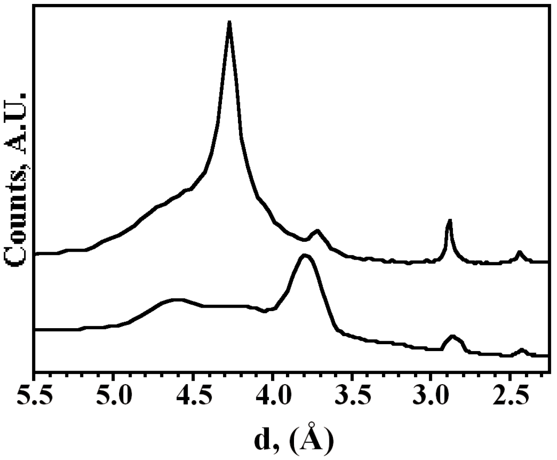

FIG. 1. GIXD patterns for MnOPA (top) and MnAzo (bottom).

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References

[1] C.T. Seip, G.E. Ganroth, M.W. Meisel, and D.R. Talham, J. Am. Chem. Soc. **119**, 7084-7094 (1997).

[2] M.A. Petruska, and D.R. Talham, Chem. Mater. **10**, 3672-3682 (1998).

[3] J.T. Culp,H. Tostmann, R.S. Duran, and D.R. Talham, Argonne National Laboratory Report ANL-00/5 (2001).