Grazing-Incidence X-ray Diffraction off a Lanthanum Octadecylphosphonate Langmuir-Blodgett Film

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Introduction

We have prepared a Langmuir-Blodgett (LB) film that incorporates the known layered structure of a lanthanum phosphonate lattice and have characterized the in-plane structure of the film by grazing-incidence x-ray diffraction (GIXD). The results show that the inorganic network formed in this film is isostructural with the corresponding bulk solid derivative.

Materials and Methods

The LB film of lanthanum octadecylphosphonate (LaOPA) was prepared as previously described.[1] GIXD experiments were preformed on a 16 bilayer film and transferred to a glass slide at the MRCAT beamline, sector 10-ID of the Advanced Photon Source. The source wavelength was 1.254 Å and made incident on the glass substrate at an angle below the critical angle for total external reflection.

Results and Discussion

Trivalent lanthanum phosphonates are known to form layered structures in the bulk solid phase. The structures consist of quasi-two-dimensional oxygen-bridged lanthanum networks separated by the organic substituents of the phosphonate group. The methylated derivative crystallizes in the triclinic crystal system. The in-plane unit cell parameters for the lanthanum-oxygen network, as determined by Cao et al.,[2] are a = 5.398Å , b = 8.168Å , $\gamma = 73.5°$, and the unit cell contains two lanthanum ions. The GIXD pattern for the LaOPA LB film is compared to the diffraction pattern obtained for a powdered sample of lanthanum butylphosphonate in Fig. 1. The similarities in the diffraction patterns for the two materials show that the inorganic network formed in the LB film is isostructural with the shorter chain solid-state analogue. In addition to the peaks shown in Fig. 1 at d spacings of 5.00 Å, 4.57 Å, and 3.83 Å, four additional reflections were observed at d spacings of 2.67 Å, 2.59 Å, 2.15Å, and 1.98 Å in the case of the LaOPA film. The diffraction pattern has contributions from the inorganic lattice and the alkyl chain packing. The entire diffraction pattern can be indexed to an oblique cell with a = 12.05 Å, b = 10.55 Å, and $\gamma = 72°$. This is essentially a 1.5*a, 2*b super cell of the one determined by Cao et al.[2] for the lanthanum methylphosphonate derivative. The larger unit cell is necessary to make the organic and inorganic sublattices commensurate. The mean molecular area per phosphonate group is ~20 Å^2 in the LB film, suggesting a close-packed organization of the alkyl chains.

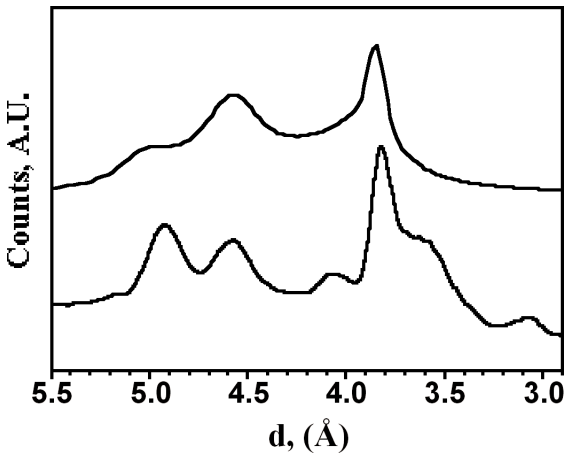

FIG. 1. Comparison of the GIXD pattern for the LaOPA film (top) and the powder diffraction pattern for bulk Labutylphosphonate (bottom).

Acknowledgments

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