doi:10.1017/S1431927616005560
Microsc. Microanal. 22 (Suppl 3), 2016

Determining Interplanar Distances from STEM-EDX Hyperspectral Maps.

Jeffrey Ditto[1], Gavin Mitchson[1], Devin R. Merrill[1], Douglas L. Medlin[2], Nigel D. Browning[3] and David C. Johnson[1]

[1.] University of Oregon, Department of Chemistry, Eugene, OR, USA
[2.] Sandia National Laboratories, Energy Nanomaterials Department, Livermore, CA, USA
[3.] Pacific Northwest National Laboratories, Fundamental and Computational Sciences Directorate, Richland, WA, USA

Since the first demonstration of atomically resolved energy dispersive x-ray spectroscopy (EDX) using a scanning transmission electron microscope (STEM) in 2010 [1], theory based simulations established that EDS hyperspectral maps could be used to measure atomic distances. That is, EDX is an incoherent imaging mode and signal intensity corresponds directly to the structure of the sample [1]. It has also been demonstrated that fractional occupancies of chemical species can be quantified [2]. Here we present results exhibiting statistically significant atomic species-dependent differences in interplanar distances in addition to quantification of planar occupancies.

It has been observed that rock salt structured 2D layers exhibit systematic variability in structure associated with thickness [3,4] and adjacent constituents [5]. To observe these effects in the context of an alloy system, a series of layered $(Pb_xSn_{1-x}Se)_{1+\delta}TiSe_2$ films were self-assembled from designed precursors using a modulated elemental reactant (MER) method in a custom physical vapor deposition system [6]. These films consist of alternating bilayers of $Pb_xSn_{1-x}Se$ and monolayers $TiSe_2$. Prior results indicated that the films form a solid solution through the bulk miscibility gap [7]. Present in the alloy samples are occasional formations of rock salt-like $Pb_xSn_{1-x}Se$ hexalayers with segregation of Pb to the outermost layer.

Consistent with prior observations of low-dimensional rock salt structures, our in-depth analysis of the heterostructured hexalayer and bilayer alloys finds systematic element specific interplanar distances of the different chemical species (Pb, Sn, and Se). These results are corroborated with refinement of (00l) x-ray diffraction patterns and density functional theory calculations. Additionally we corroborate the finding that EDX peak intensities from off zone axis (rotationally disordered) atomic planes can be used for quantification [8] as the quantified intensities from our calibrated $Pb_xSn_{1-x}Se$ alloy series scale as expected. [9]

References:

[1] D'Alfonso, A. J.; Freitag, B.; Klenov, D.; Allen, L. J., Phys. Rev. B - Condens. Matter Mater. Phys., **81** (2010), p. 2–5.
[2] Lu, P.; Romero, E.; Lee, S.; MacManus-Driscoll, J. L.; Jia, Q., Microsc. Microanal, **20** (2014), p. 1782–1790.
[3] Beekman, M.; Disch, S.; Rouvimov, S.; Kasinathan, D.; Koepernik, K.; Rosner, H.; Zschack, P.; Neumann, W. S.; Johnson, D. C., Angew. Chemie - Int. Ed. **52** (2013), p. 13211–13214.
[4] Anderson, M. D.; Heideman, C. L.; Lin, Q.; Smeller, M.; Kokenyesi, R.; Herzing, A. A.; Anderson, I. M.; Keszler, D. A.; Zschack, P.; Johnson, D. C., Angew. Chem. Int. Ed. **52** (2013), p. 1982–1985.
[5] Falmbigl, M.; Alemayehu, M. B.; Merrill, D. R.; Beekman, M.; Johnson, D. C., Cryst. Res. Technol.,

135 (2015), p.11055–11062.
[6] Fister, L.; David, C., J. Am. Chem. Soc., **114** (1992), p. 4639–4644.
[7] Merrill, D. R.; Sutherland, D. R.; Ditto, J.; Bauers, S. R.; Falmbigl, M.; Medlin, D. L.; Johnson, D. C., Chem. Mater., **27** (2015), p. 4066–4072.
[8] Lugg, N. R.; Kothleitner, G.; Shibata, N.; Ikuhara, Y., Ultramicroscopy, **151** (2015), p. 150–159.
[9] The authors acknowledge funding from National Science Foundation under grant DMR-1266217. Coauthors MF and SB acknowledge support from the National Science Foundation through CCI grant number CHE-1102637. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC0494AL85000. We acknowledge support through the Collaborative Access Team (CAT): Pooled Resources for Electron Microscopy Informatics, Education and Research (PREMIER) Network Program and the Chemical Imaging Initiative at Pacific Northwest National Laboratory (PNNL) and the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research at PNNL. PNNL is a multiprogram national laboratory operated by Battelle for DOE under Contract DE-AC05-76RL01830.

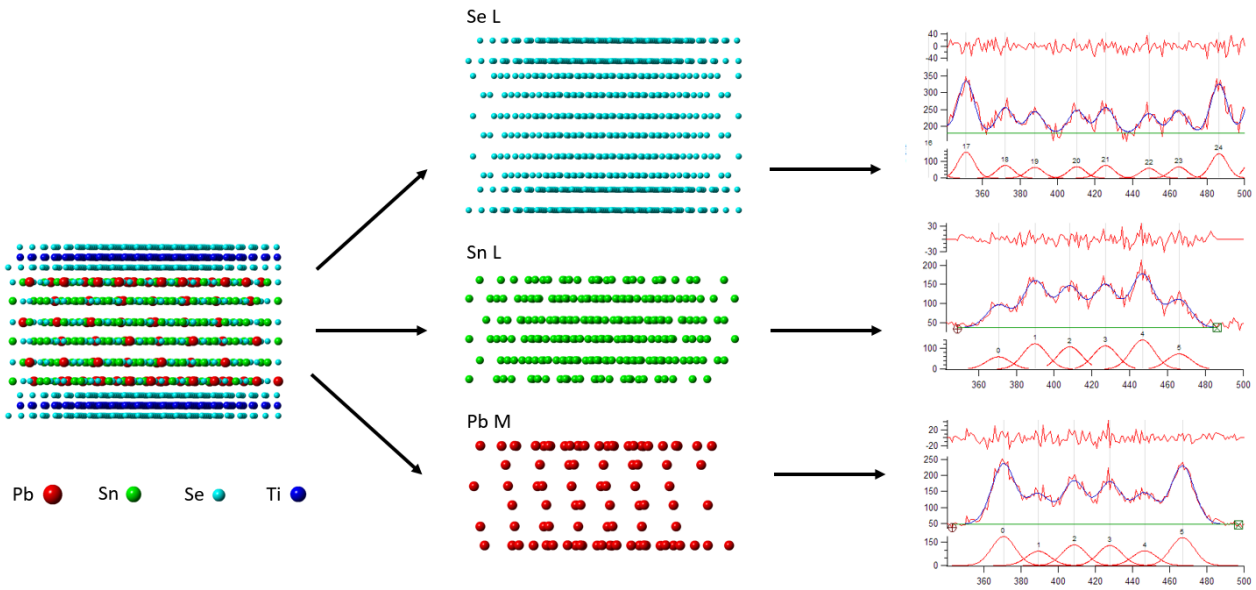

Figure 1. A schematic illustrating the extraction of EDX peak intensities from a hyperspectral data cube and the Gaussian peak fits and residuals for extracting element specific interplanar distances and intraplanar composition.

https://doi.org/10.1017/S1431927616005560