Modulated Electrodeposition of Bismuth Based Oxide Superconductors

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This paper provides an overview of parameters relevant to the deposition of crystalline materials and modulated structures in the two classes of bismuth based (non-cuprate) oxide superconductors. Characteristics of the materials produced will also be presented.

Two classes of bismuth based oxide superconductors, one doped at the A site and one doped at the B site in the perovskite structure, are known. These nonstoichiometric materials contain 4 (Ba1-xKx)BiyO3-z, termed BKBO(1)) and 5 ((Ba1-xKx)Pb1-yBiyO3-z termed BPBO) different elements, representing significant compositional complexity. Although there are known mechanisms through which the elemental components of each site may deviate from the ideal perovskite site stoichiometry, the emphasis in this research has been on the sensitivity of the A site composition in BKBO and the B site in BPBO to experimental growth parameters. Parameters of importance include electrode composition, geometry and crystallographic orientation, solution composition, including state of flux hydration, deposition temperature, and electrode potential.

BPBO, the more complex of the two systems studied, was found to be more sensitive to solution composition parameters. Both types of materials were found to be sensitive to deposition potential. Suitable although perhaps not ideal deposition temperatures and levels of flux hydration were maintained in order to minimize the complexity of the studied systems.

Preparation of ideal samples of these materials requires minimizing changes, during lengthy deposition times, in solution temperature and electrode temperature gradient. Problems which have not been resolved include developing a mechanism to avoid solution composition variation during a prolonged, multielement deposition, and maintaining a constant surface potential throughout an extended growth period

Both types of materials were found to display a deposition potential dependent composition. In BKBO, this dependence was found in the A sublattice site, in the Ba/K ratio. In the BPBO material, the major dependence was found in the B sublattice site, in the form of an altered Pb/Bi ratio. In the case of BKBO, this dependence is readily interpreted as counter ion insertion to charge compensate the growing Bi-O polymer backbone. This sensitivity of the composition to deposition potential was employed to produce modulated single crystalline samples of both types of materials. At large modulation length scales, the compositionally induced modulation of the electronic properties in the BKBO system is readily characterized using optical microscopy. The shift of the optical plasma frequency with composition yields materials with different optical properties in the visible region.

"Homogeneous" electrochemically grown samples of BKBO have been the subject of extensive characterization efforts. Methods utilized have included Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis and Mapping, Reflectance Spectroscopy, AC Magnetic Susceptibility, Squid Magnetometry, Vibrating Sample Magnetometry, X-ray and Temperature Dependent Magnetic Neutron Diffraction. The liquid like flux phase, which may be interpreted as indicative of a system lacking strong pinning centers, is notable, since it may influence the domain of applicability of these materials. Modulated structures have been characterized using Optical Microscopy, Scanning Electron Microscopy and Scanning Tunneling Microscopy.

The processability of the materials has been investigated. Solution phase etching of modulated structures has been performed using hot saturated disodium-EDTA, as suggested by Miller (2). Differential etching has been qualitatively demonstrated.

The ability to generate high quality crystalline samples of a relatively high transition temperature isotropic oxide superconductor using common electrochemical methods has been well demonstrated. The environmental sensitivities of this material may be found advantageous, because they can be manipulated to produce compositional, and therefore electronic modulations within a crystalline structure. The unusual magnetic properties which render these materials unacceptable for high current density applications may position them well for magneto-electronic applications.

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References:

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