

Abstracts of Forthcoming Articles

On the Structure of Evaporated Bismuth Oxide Thin Films. JOHN W. MEDERNACH. New York State College of Ceramics, Alfred University, Alfred, New York 14802. The bismuth oxide films evaporated from bulk Bi_2O_3 are shown to vary in stoichiometry. The as-evaporated low rate (1-5 Å/sec) films are microcrystalline and bismuth rich, relative to Bi_2O_3 , and their optical absorption edge broadens and shifts to lower energies. High rate (15-25 Å/sec) films are amorphous and oxygen rich with an absorption edge shifted to higher energies. Thermal decomposition of the Bi_2O_3 during evaporation produces the variations in film stoichiometry. The high temperature $\delta\text{-Bi}_2\text{O}_3$ observed in the as-evaporated low rate films and thermally treated amorphous films indicates the melt and the films are structurally similar. Thermal treatment of the low rate films results in the formation of the γ -form. Comparison of X ray and stoichiometry results suggests that $\beta\text{-Bi}_2\text{O}_3$ be expressed as $\beta\text{-Bi}_2\text{O}_3 \pm x$, where x is the deviation from trioxide stoichiometry.

Temperature Induced Symmetry Transformation in the Th_3P_4 Type Compounds La_3S_4 , La_3Se_4 , Pr_3S_4 , and Pr_3Se_4 . P. D. DERNIER, E. BUCHER, AND L. D. LONGINOTTI. Bell Laboratories, Murray Hill, New Jersey 07974. From X ray powder diffraction experiments the Th_3P_4 type sulfides and selenides of La and Pr have been shown to undergo a cubic to tetragonal phase transformation with decreasing temperature. The corresponding tellurides show no distortion down to 4.2°K. These results cast some doubt on a possible charge order-disorder mechanism underlying the transition.

Solid State Chemistry of Organic Polyvalent Iodine Compounds. VII. The Relationships between Crystal Packing Modes, Solid-State Intermolecular Interactions, and Infrared Spectra of Benzoxidole Compounds. MARGARET C. ETTER. Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. The importance of intermolecular interactions in determining crystal structures has been investigated for a series of 3-oxo-3H, 2, 1-benzoxidol-1-substituted compounds. These compounds all contain a trivalent iodine atom that is involved in a stereospecific coordination interaction with an electronegative atom (oxygen or halogen) of a neighboring molecule. It has been found that only four basic packing modes occur for these compounds, formally characterized by the nature of the functional group coordinated to iodine. Infrared analysis of solution and solid state samples of these compounds shows that the structurally identifiable intermolecular coordination modes occurring between $\text{I}^{(\text{III})}$ and carbonyl groups do in fact involve chemically stabilizing interactions. Shifts of about 10 cm^{-1} to lower wave number are observed for the carbonyl stretching band of an uncoordinated carbonyl group in solid state samples, as compared to its frequency in solution samples. The carbonyl stretching frequency of a coordinated carbonyl group is lowered from 20-80 cm^{-1} (these bands occur at 1614-1678 cm^{-1} in the solid state). Some of the compounds exist in molecular conformations in the solid state in which a possible intramolecular interaction between $\text{I}^{(\text{III})}$ and a carbonyl may also be contributing to the observed frequency shifts.

Specific Heat Measurement of Cubic Sodium Tungsten Bronzes from 200° to 800°K. HIDEAKI INABA AND KEIJI NAITO. Department of Nuclear Engineering, Faculty of Engineering, Nagoya University, Furo-Cho, Chikusa-ku, Nagoya, Japan. Specific heats of three cubic sodium tungsten bronze samples (Na_xWO_3) with x values of 0.485, 0.698, and 0.794 were measured from 200-800°K. Specific heats per g-atom of three samples at the same temperature were equal within experimental error regardless of the difference of the composition and those at 700°K showed the Dulong-Petit value. λ -type specific heat anomalies were observed around 400°K, showing the existence of a second-order phase transition. The transition temperature increases as the sodium content of the sample increases, and a linear relationship between enthalpy change of the transition and the transition temperature was observed. The entropy increments of the transition were obtained as 0.79, 0.84, and 0.90 J/mole·K for $\text{Na}_{0.485}\text{WO}_3$, $\text{Na}_{0.698}\text{WO}_3$, and $\text{Na}_{0.794}\text{WO}_3$, respectively. It is supposed that the entropy increment of the transition originates from the increase of the number of slightly displaced atoms with respect to the ideal perovskite position.