

**Materials I****Advanced Ceramics and Composites**

**MS10.01.01 CRYSTALLINE MATERIALS WITH VERY SMALL OR NEGATIVE THERMAL EXPANSION** Arthur W. Sleight, Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003

Very low or negative thermal expansion apparently can result from three different mechanisms. In the case of anisotropic materials such as cordierite ( $Mg_2Al_4Si_5O_{18}$ ), thermal expansion in certain directions is coupled with thermal contraction in other directions. The net result can be a very small volume thermal expansion. This behavior can be easily modeled as caused by the thermal expansion of Mg-O bonds. In  $\beta$ -eucryptite ( $LiAlSiO_4$ ), the thermal expansion of Li-O bonds is very important, but the slight negative volume expansion requires that the Li distribution over tetrahedral and octahedral sites change as temperature changes. A third mechanism for very low or negative thermal expansion is based on anisotropic thermal vibration of oxygen in open network structures. This is the apparent mechanism for negative thermal expansion of certain compounds with the cubic  $ZrP_2O_7$  structure such as  $ZrV_2O_7$ . A remarkable example of this behavior is found in cubic  $ZrW_2O_8$ , where negative thermal expansion is observed from 0.3 K to 1050 K. Materials with negative thermal expansion are finding applications in composites to lower the overall thermal expansion of the composite.

**MS10.01.02 RADWASTE INCORPORATION IN SYNROC.** E. R. Vance, B. D. Begg, R. A. Day, C. J. Ball, Materials Division, Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW 2234, Australia

Synroc is a multiphase titanate ceramic designed to immobilize high-level radioactive waste. It is largely composed of hollandite ( $Ba(AlTi)_2Ti_6O_{16}$ ), zirconolite ( $CaZrTi_2O_7$ ), perovskite ( $CaTiO_3$ ) and rutile ( $TiO_2$ ), and incorporates the radwaste ions in dilute solid solution. Early work on Synroc was concerned with waste from reprocessing of spent fuel from commercial power reactors. Recently attention has turned to a variety of other waste compositions, such as defense wastes and actinide-rich wastes arising from chemical partitioning of commercial waste. Defense wastes differ from commercial waste in that they contain large amounts of processing contaminants, notably sodium and aluminum. A modified Synroc formulation can accommodate these contaminants.

Investigations with single phases, mainly zirconolite, have sought to determine the limits of solubility of different elements in different sites. Preliminary work with Ce, Nd and Y established the probable behaviour of Np and Pu in zirconolite, and this has been confirmed at levels of tens of percent. Trivalent rare earths and actinides have extensive solid solubility in the Ca site of zirconolite if sufficient Al, for example, is present to provide charge compensation by substituting for Ti. The solubility in the Zr site depends on ionic size. Tetravalent rare earths and actinides can also substitute in the Ca and Zr sites. The limit of such substitution in the Zr site is 0.15 formula units, and at least 0.2 formula units can also be substituted on the Ca site. X-ray absorption spectroscopy confirms the valency of these ions, but the precise charge compensation mechanism is yet to be determined.

**MS10.01.03 MICROWAVE CERAMICS** T. Siegrist, T.A. Vanderah, R.S. Roth, Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974 NIST, Ceramics Division, Gaithersburg, MD 20899

Modern wireless communication systems incorporate oxide ceramics with unique electrical properties. Cellular phones, for instance, may contain up to the 14 individual pieces of ceramics, mainly as filters. Magnetic ceramics are used where device action is controlled via an external magnetic field. For this purpose, magnetic ions have to be incorporated in good dielectrics. This has led to the detailed study of the Ba-Ti-Fe-O phase diagram. New phases based on hexagonal perovskites were found. These phases can be described by combining octahedra and tetrahedra, resulting in complex stacking sequences. The crystal chemistry of various new phases will be discussed.

**MS10.01.04 AUTOMOTIVE CATALYSTS: NEW STUDIES ON OLD IDEAS.** C. K. Lowe-Ma, M. C. Paput Peck, R. J. Baird, Physics Department, Ford Research Laboratories, Ford Motor Company, Dearborn, MI 48121-2053, USA

The presentation will focus on general aspects of catalyst characterization emphasizing X-ray methods and microscopy techniques. Confounding factors in interpreting, for example particle-size distributions, in complex industrial materials will be discussed.

**MS10.01.05 X-RAY DIFFRACTION STUDY OF THE DOMAIN STRUCTURE AND ITS STABILITY IN  $PbTiO_3$  THIN FILMS GROWN ON  $MgO(001)$  BY MOCVD\*** B.-M. Yen, R.S. Batzer, Haydn Chen, Department of Materials Science & Engineering, University of Illinois, Urbana, IL 61801

Lead Titanate (PT) and Lead Zirconium Titanate (PZT) have generated much interest in electrical and optical industries due to their desirable piezoelectric, ferroelectric and electro-optic properties. Recently, as thin film processing becomes more refined, research and development of PT and PZT materials in the form of thin films have become increasingly active. Several different fabrication methods have been utilized to grow epitaxial PT and PZT films including the MOCVD technique employed by the authors. The purpose of this study is twofold: first, to observe the domain structure evolution of MOCVD-grown epitaxial PT films on  $MgO(001)$  substrate during heating to temperatures above and below the Curie point ( $\sim 490^\circ C$ ); and second, to cycle the temperature in order to study the stability of the domain configuration. The significance of this work lies in the assessment of reproducibility of ferroelectric domain configuration due to thermal cycling. This work was performed using a four-circle x-ray diffractometer *in situ* with a miniature hot stage. Rocking curves were used to monitor the domain evolution. Lattice constants were measured at various temperature to determine the ferroelectric transition temperatures (Curie point) during heating and cooling. The Curie temperatures in the geometrically confined PT thin films were found to be lower than the bulk value. A model concerning the film stress effect on the total free energy is proposed to explain this effect.

\* Research support by the US Department of Energy.