

MS10.01.06 THE LOW TEMPERATURE WAY TO OXIDES VIA ALCOHOLATE PRECURSORS: STRUCTURE, REACTIVITY, MORPHOLOGY. Heiko Thoms, Matthias Epple, Armin Reller, Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, D - 20146 Hamburg, Germany

Different alcoholates of magnesium and mixed Mg/Si-, Mg/Ti-, Mg/Zr- and Ti/Si-diolates were prepared. A single-crystal X-ray structure analysis was so far only possible for the compound $\text{Mg}(\text{OCH}_3)_2 \cdot 2 \text{CH}_3\text{OH}$ in the orthorhombic space group $Ccca$ with $Z = 64$ [1]. The main structural elements are isolated heterocubane units with Mg^{2+} and OCH_3^- ions in the corner. All magnesium alcoholates follow the same thermal decomposition pathway to magnesium oxide MgO via alkoxy-hydroxy intermediates, a fact also confirmed by EXAFS. Scanning electron microscopy of the magnesium oxides and mixed oxides prepared by thermal decomposition of the alcoholates at temperatures between 500°C and 600°C shows significant differences in morphology and domain size which are important for many applications of these oxides.

[1] H. Thoms, M. Epple, H. Viebrock, A. Reller, *J. Mater. Chem.*, **5** (1995) 589594

PS10.01.07 GLASS-MICA COMPOSITIONS AS AN ELECTRIC HEATER SHELL. L.V. Chilikanova, T.I. Shishelova, T.V. Sozinova, A.V. Shcherbakov, Irkutsk Technical University, Irkutsk, Russia

Glass-mica compositions are successfully used as shells for electric heaters. The long service life, mechanical and electric strength of these materials depend on the interaction of Ni-Cr alloy with fusible glass and mica components under working conditions. The data of x-ray diffraction and thermography have shown that upon thermal activation of these substances the processes of metal oxidation, muscovite decomposition, and interaction between the decomposition products and glass are hindered as a result of the reinforcing effect of the silicate medium on the heater metal. The reinforcing film on the mica-composition-metal interface is formed due to the dissolution of spinels (Ni-Cr alloy oxidation products) in the softened glass, that leads to the formation of iron silicate. The oxidation of heater metal starts with the diffusion of iron ions and the formation of ferros spinels. The latter, known for a wide range of homogeneity with many oxides, dissolve the protective solid layer of oxides. The water which is released during dehydration and dehydroxylation of mica and fills intercrystallite pores serves as an oxidant. The established physico-chemical interactions between mica, glass and the products of Ni-Cr alloy oxidation make it possible to find optimal conditions for the production and modification of electric heaters in a shell of glass mica-composition.

PS10.01.08 CHARACTERIZATION OF EPITAXIAL ZrO_2 BY X-RAY DIFFRACTOMETRY WITH PARALLEL BEAM GEOMETRY. R. Guinebretière, A. Dager, O. Masson, B. Soulestin, Laboratoire de Matériaux Ceramiques et Traitements de Surfaces UA CNRS n°320-ENSCI-47 Av. A. Thomas - 87065 Limoges France

The epitaxial growth of tetragonal zirconia produced via a metal-organic precursor route and deposited on the (h00) planes of MgO substrates was characterized with an original X-ray diffractometer. A parallel $\text{CuK}\alpha_1$ X-ray radiation incident beam is provided by a rotating anode source through a four reflections monochromator made of two channel-cut germanium single crystals. The flat specimen is fixed at controlled incidence angle on the four circle diffractometer. Data are collected with a Curved Position Sensitive Detector (INEL CPS 120). The CPSD angular calibration procedure first proposed for capillary sample setting has been extended to the case of flat plate samples. A specific specimen positioning procedure is used and the d-spacing measurement accuracy has been checked using NIST Silicon standard sample.

A zirconia precursor sol was first prepared in the zirconium n-propoxide - acetylacetone - n-propanol system, deposited by dip coating on the polished (100) face of a MgO crystal and then heat treated for 1.5 hour at successive temperatures ranging from 600 to 1400°C. A polycrystalline thin film of tetragonal zirconia nanosized grains first appeared. Sintering and normal grain growth simultaneously occurred. Then the film began to break up into isolated islands. At high temperature, the size of single grained islands increased rapidly, up to about 1 μm after 1.5 hour at 1400°C, and complete epitaxial orientation with respect to the substrate was observed: $\langle 100 \rangle_{\text{ZrO}_2} // \langle 100 \rangle_{\text{MgO}}$ and $\{ 100 \}_{\text{ZrO}_2} // \{ 100 \}_{\text{MgO}}$. The breadth of t- ZrO_2 (200) rocking curve demonstrated the very low level of misorientations. The modification of the substrate (200) and (400) rocking curves was related to surface strains. The interface was imaged by transmission electron microscopy on cross sectional thin samples.

PS10.01.09 DETERMINATION OF SiC POLYTYPES DISTRIBUTION WITH HIGH ACCURACY. By Hongchao LIU and Changlin KUO, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050.

Quantitative determination of SiC polytypes distribution is very difficult from traditional X-ray powder diffraction quantitative analysis methods. SiC polytypes seem to form as the result of stacking faults introduced into the parent structures, the main reflections will overlap with those of the parent polytype and the differences will be relative small. So many efforts have been concentrated on this topic (see L. K. Frevel, et al, *J. Mater. Sci.*, **27**(1992)1913-1925). However, it was still hard to obtain accurate results of SiC polytypes distribution by these traditional methods for various reasons.

The whole pattern fitting Rietveld method (H. M. Rietveld, *J. Appl. Crystallogr.*, **2**(1969)65-71) is introduced to determine SiC polytype distribution. With the scale factors and cell parameters given by the Rietveld program, equation

$$x_j = \frac{S_j \cdot \rho_j \cdot V_{oj}^2}{\sum_{k=1}^n S_k \cdot \rho_k \cdot V_{ok}^2} \quad , \text{ where } S,$$

ρ and V are scale factor, density and unit cell volume of each polytype, can be used to calculate the relative weight percentag-

es of each polytypes. The simulated data by Warren and Averbach method (B.E. Warren & B.L. Averbach, *J. Appl Phys.*, **21**(1950): 595-599; **23**(1952): 1059) with 4H, 3C, 6H and 15R polytypes and two specimens from the same nano material were used to test this approach.

The results show that the distribution of SiC polytypes can be accurately and reliably determined by this approach. It can be applied in nano-material case.

PS10.01.10 ISOTROPIC MATERIALS WITH LOW OR NEGATIVE THERMAL EXPANSION. Nazy Khosrovani, Arthur W. Sleight, Department of Chemistry, Gilbert Hall, 153 Corvallis, Oregon, 97331-4003

Materials which contract on heating (negative thermal expansion materials) are of great importance since they can be mixed with other materials (positive thermal expansion materials) to make composites which have zero thermal expansion. Materials with zero or low thermal expansion have many applications in electronic devices, space telescope mirrors, stove tops, cook wares and so on.

There are two types of low or negative thermal expansion materials. The first type have anisotropic thermal expansion which means that on heating, the structure will expand in one or two dimensions and contract in the other dimension(s). Examples of anisotropic materials are β -eucryptite, cordierite, and NZP ($\text{NaZr}_2\text{P}_3\text{O}_{12}$). The problem with anisotropic materials is that microcracking occurs during the heating cycle. The second type of materials have isotropic thermal expansion which means that on heating, the structure will contract (or expand) in all dimensions. Examples of isotropic materials with low or negative thermal expansion are ZrP_2O_7 and ZrV_2O_7 respectively.

We have solved the structures of ZrP_2O_7 and ZrV_2O_7 , and found that ZrP_2O_7 shows normal thermal expansion up to about 290°C at which the phase transition occurs, and very low and positive thermal expansion after 290°C. However, ZrV_2O_7 shows positive thermal expansion up to about 100°C, and very strong negative thermal expansion after 100°C up to about 800°C at which the material decomposes. There are two phase transitions observed for ZrV_2O_7 before 100°C which makes the structure more challenging.

The structure of both ZrP_2O_7 and ZrV_2O_7 is cubic and the space group is Pa3. A $3 \times 3 \times 3$ superstructure is observed for both compounds at room temperature. The $3 \times 3 \times 3$ superstructure disappears after the phase transition is achieved in ZrP_2O_7 , but it doesn't fully disappear until the second phase transition is achieved in ZrV_2O_7 . We believe that the unusual thermal expansion of these compounds is a result of frustration in bending some of the P-O-P or V-O-V angles away from 180°.

Khosrovani, N.; Sleight A.W., *Inorg. Chem.* **35**, 485 (1996)

PS10.01.11 STRUCTURE OF CUBIC YTTRIA DOPED ZIRCONIA BY SYNCHROTRON RADIATION. Y. Matsushima, M. Hayashi, K. Suda, Y. Tabira, N. Ishizawa, Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan

The structure of yttria-doped zirconia, $(\text{Zr}_{1-x}\text{Y}_x)\text{O}_{2-x/2}$ with $x=0.242$ has been studied by both the synchrotron radiation single-crystal diffraction and EXAFS. The diffraction experiment on a spherical crystal with 35 μm in diameter was carried out using a horizontal-type four circle diffractometer at the beam line 14A, KEK-PF. Two wave lengths of 0.7281 Å and 0.75 Å, corresponding to the energies 10 eV and 500 eV below the Y K absorption edge respectively, were employed to enhance the scattering contrast between Y and Zr. The EXAFS spectra of the powdered sample near the Y and Zr K absorption edges were also measured at BL14A employing the transmission mode. The refinements using 83 independent reflections for the 0.75 Å data set and 90 for the 0.7281 Å data set converged with R/Rw factors of 0.0053/0.0051 and of 0.0074/0.0066 respectively. In contrast to the conventional understanding of the fluorite-type structure of this compound, Zr atoms are presumably displaced by about 0.17 Å along $\langle 111 \rangle$ from the origin, while Y atoms stay at the origin. In addition, about one third of oxygen atoms are displaced by about 0.35 Å along $\langle 001 \rangle$ from the ideal position at 8c site $1/4, 1/4, 1/4$ of the space group Fm3m. The final residual electron density maps indicated that the oxygen atoms near the 8c sites suffer a conspicuous third order enharmonic vibration along $\langle 111 \rangle$, suggesting a possible diffusion path toward the nearest vacant sites of $4b \ 1/2, 1/2, 1/2$. EXAFS results indicated that Zr-O bond is 2.15(1) Å that is much shorter than the Y-O of 2.32(1) Å. The coordination number of Zr-O is 8.2 and that of Y-O is 6.2. Combining the results of the EXAFS and the single crystal diffraction, it is suggested that Y and Zr atoms have local structures similar to those found in their parent end-member oxides respectively.

PS10.01.12 STRUCTURE AND PROPERTIES OF COMPLEX PEROVSKITE MICROWAVE CERAMIC DIELECTRIC RESONATORS. H. Sreemoolanadhan, R. Ratheesh, M. T. Sebastian, P. Mohanan, Electronic Ceramics, Regional Research Laboratory, Thiruvananthapuram-695 019, India *Electronics Department, Cochin Univ. of Sci. & Tech., Thrikkakara-682 022, India

Ceramic materials with high dielectric constant and low loss called 'dielectric resonators (DR)' have become indispensable components for both active and passive devices in modern microwave systems. $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$ [$\text{B}' = \text{La, Pr, Nd, Sm, In, Tb, Y, Gd, Er}$] complex perovskites have been prepared as a microwave dielectric ceramic resonator material. They have high ϵ_r (30-45), low loss and very small temperature variation of resonant frequency in the microwave range. Several earlier workers reported that these materials have cubic symmetry with $(\text{NH}_4)_3\text{FeF}_6$ structure. Recent studies show that these materials have a cubic symmetry at high temperature and transforms to one with a lower symmetry (tetragonal, orthorhombic or monoclinic) on cooling. The mechanism of the transition and its relation to the tolerance factor, difficulties of X-ray diffraction to find the transition and the correct symmetry and dielectric properties of these materials are discussed.