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ABSTRACTS

COMMUNICATIONS

Preparation of nanometer-sized alumina whisker
Z.Q. Yu, Y.W. Du
(Nanjing University)

Alumina whisker reinforced ceramic, metal and plastics composites which have exhibited excellent properties such as low density, high strength, and toughness is a promising structural material for high performance applications. It is necessary to study the preparation process of nanometer-sized alumina whiskers by making use of aluminum alkoxides in order to follow the development of the nanometer-sized grain ceramic composites and inorganic-organic composites. The authors found that the nanometer-sized whiskers could be obtained as an intermediate during preparation of ultrafine spherical alumina powders if the processing parameters could be controlled.

This letter reports some results on the preparation of nanometer-sized alumina whiskers with the aspect ratio and the mean diameter in the range of 10 ~ 40 nm and 2 ~ 4 nm, respectively.

Order No.: JA811-001

Enhanced photoluminescent emission of thin phosphor films via pulsed excimer laser melting
J. McKittrick, G.A. Hirata, C.F. Bacalski, R. Sze, J. Mourant, K.M. Hubbard, S. Pattillo, K.V. Salazar, M. Trkula, T.R. Gosnell
(University of California at San Diego)

Thin-films of $(Y_{0.92}Eu_{0.08})_2O_3$ were synthesized through chemical vapor deposition of β-diketonate precursors onto glass and sapphire substrates. The films were weakly luminescent in the as-deposited condition and were composed of spherical particles 3 μm in diameter. A KrF laser was pulsed for 25 ns from 1–3 times on the surface of the films. One pulse was sufficient to melt the film and repeated pulses caused ablation of the material. Melting of the film smoothed the surface, increased the density and increased the photoluminescent emission intensity.

Order No.: JA811-002

ARTICLES

Sol-gel synthesis and anomalies on magnetic and electric properties of $(Ba_{1-x}La_x)_3Cu_3(O,F)_y$ films
Y. Masuda, J-S. Jin, K. Nakanishi, K. Tanabe
(Superconductivity Research Laboratory-ISTEC)

$(Ba_{1-x}La_x)_3Cu_3(O,F)_y$ films were prepared using a sol-gel method. Phases, the c lattice parameters of which are about 13.8, 13.1 and 11.6 Å, respectively, were formed in the films. The compound with the c parameter of ~13.8 Å is considered to be a $Ba_{2-x}La_xCuO_2F_{2+\delta}$ which has the La_2CuO_4-type structure inserted with fluorine. The compound with the c parameter of ~11.6 Å is thought to have a three-layered structure of the perovskite block which is arisen by ordering between La and Ba elements. The films containing these compounds showed some interesting anomalies in SQUID measurements. However, no film showed a drastic decrease of electrical resistance.

Order No.: JA811-003

A study on the residual stress measurement methods on chemical vapor deposition diamond films
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Diamond films were deposited on the p-type Si substrate with the hot filament chemical vapor deposition (HFCVD). Residual stresses in the films were measured in air by the laser curvature, the x-ray diffraction (XRD) $d_{\phi\psi}$-$\sin^2\psi$, and the Raman peak shift methods. All of the measuring methods showed similar behaviors of residual stress that changed from a compressive to a tensile stress with increasing the film thickness. However, values of residual stresses that were obtained through the Raman and XRD methods were 3 ~ 4 times higher than those of the curvature method. These discrepancies were involved in setting materials constants of CVD diamond film, and determination of a peak shifting on the XRD and Raman method. In order to elucidate the disparity, we measured a Young's moduli of diamond films by using the sonic resonance method. In doing so, the

Raman and XRD peak shift were calibrated by bending diamond/Si beams with diamond films by a known amount, with stress levels known a priori from the beam theory, and by monitoring the peak shifts simultaneously. Results of each measuring method showed well coincidental behaviors of residual stresses which have the stress range from -0.5 GPa to +0.7 GPa, and an intrinsic stress was caused about +0.7 GPa with tensile stress.
Order No.: JA811-004 **© 1998 MRS**

Transformations in undercooled molten $Pd_{40.5}Ni_{40.5}P_{19}$
C.W. Yuen, H.W. Kui
(The Chinese University of Hong Kong)

It was demonstrated that liquid phase separation by nucleation and growth (LNG) occurs in undercooled molten $Pd_{40.5}Ni_{40.5}P_{19}$ for undercoolings $\Delta T \leq 60$ K (ΔT = T1 - T where T1 is the liquidus and T is the kinetic crystallization temperature), and liquid state spinodal decomposition (LSD) occurs for $\Delta T \geq 100$. For $60 \leq \Delta T \leq 100$ K, it is the transition regime from LNG to LSD. A ternary phase diagram is introduced to summarize the reactions occurred in undercooled molten $Pd_{40.5}Ni_{40.5}P_{19}$. Finally, it is suggested that LSD has a most important impact on glass forming ability of metallic alloys.
Order No.: JA811-005 **© 1998 MRS**

Solidification of undercooled molten spinodal
C.W. Yuen, H.W. Kui
(University of Hong Kong)

When molten $Pd_{40.5}Ni_{40.5}P_{19}$ is undercooled way below its liquidus T_l, liquid state spinodal decomposition is observed. Crystallization of this system is particularly interesting because it has plenty of interfaces. The microstructure of an as-crystallized specimen can be divided into four regions, namely, A: random spinodal; B: aligned and elongated spinodal; C: coarsened spinodal and island structure; and D: rod structure and ternary eutectics. The origin of these different microstructures is discussed.
Order No.: JA811-006 **© 1998 MRS**

Hydrogen embrittlement of B-doped Ni_3Al-based alloy
J-Q. Su, S-J. Gao, Z-Q. Hu
(Academia Sinica)

Environmental and internal-hydrogen embrittlements in stress-relieved and recrystallized Ni-16.5Al-8Cr-0.8Hf-0.1B-0.03Y (at.%) have been studied. The stress-relieved Ni_3Al-based alloy showed environmental embrittlement when tested in air or in hydrogen gas. The embrittlement is more severe in hydrogen gas than that in air. The recrystallized Ni_3Al-based alloy was not susceptible to air, but it was embrittled severely by hydrogen gas and exhibited not only a grain interior but a more severe grain boundary embrittlement. When tested in air, the stress-relieved Ni_3Al was insensitive to internal hydrogen; however, the recrystallized Ni_3Al showed a certain susceptibility to internal hydrogen. With an increase in internal hydrogen content in the alloy, the ductility of the recrystallized Ni_3Al decreased steadily and a certain degree of grain boundary embrittlement was observed.
Order No.: JA811-007 **© 1998 MRS**

Synthesis of ultrafine nickel aluminide particles by the hydrogen reduction of vapor-phase mixtures of $NiCl_2$ and $AlCl_3$
H.Y. Sohn, S. PalDey
(University of Utah)

Fine particles of nickel aluminides were synthesized for the first time by reducing mixtures of $AlCl_3$+$NiCl_2$ vapors by hydrogen. A thermodynamic equilibrium calculation was carried out in the Ni-Al-H-Cl-Ar system to evaluate the effect of the reactant partial pressures and temperature on the formation of intermetallic phases. A single intermetallic phase was found to be feasible only in a very narrow range of the reactant partial pressures. For all other conditions the predicted solid product was a mixture of two phases. Experimentally, Ni_3Al was formed along with metallic Ni. Though the coreduction of $NiCl_2$ and $AlCl_3$ by H_2 to form Ni_3Al is thermodynamically favorable at 1100°C, it did not happen experimentally under the conditions of this work. However, with a small addition of aluminum vapor, the coreduction reaction proceeded as expected by thermodynamics. The effects of reactant partial pressures and temperature were studied. The content of Ni_3Al was maximized to 52 mol% at 1050°C under the partial pressures of H_2, $AlCl_3$, and $NiCl_2$ at 57, 1.4, and 0.5 kPa, respectively. The product particles, as observed by TEM, were very fine, but usually agglomerated. The electron diffraction analysis identified the particles of NiAl and $NiAl_3$ along with Ni_3Al and metallic Ni.
Order No.: JA811-008 **© 1998 MRS**

Fabrication and characterization of concentric-tubular composite micro- and nanostructures using the template-synthesis method
V.M. Cepak, J.C. Hulteen, G. Che, K.B. Jirage, B.B. Lakshmi, E.R. Fisher, C.R. Martin
(Colorado State University)

The template-synthetic method is a general approach for preparing tubular micro- and nanostructures. This method has been used to prepare micro- and nanostructures composed of metals, carbons, semiconductors, polymers, and Li^+-intercalation materials. This paper describes the use of the template method to prepare composite tubular micro- and nanostructures. These composite structures consist of an outer tubule of one material surrounding inner tubules of different materials. Chemical strategies used to prepare these composite tubular structures include electroless deposition of Au; electropolymerization of conductive and insulating polymers; electrodeposition of metals and semiconductors; carbonization of polymer precursors; chemical vapor deposition synthesis; and sol-gel synthesis.
Order No.: JA811-009 **© 1998 MRS**

Electromechanical study of carbon fiber composites
X. Wang, X. Fu, D.D.L. Chung
(State University of New York at Buffalo)

Electromechanical testing involving simultaneous electrical and mechanical measurements under load was used to study the fiber-matrix interface, the fiber residual compressive stress and the degree of marcelling (fiber waviness) in carbon fiber composites. The interface study involved single fiber pull-out testing while the fiber-matrix contact electrical resistivity was measured. The residual stress study involved measuring the electrical resistance of a single fiber embedded in the matrix while the fiber was subjected to tension through its exposed ends. The marcelling study involved measuring the electrical resistance of a composite in the through-thickness direction while tension within the elastic regime was applied in the fiber direction.
Order No.: JA811-010 **© 1998 MRS**

Interfaces and properties of Al-Si alloy zircon particulate composites
J.U. Ejiofor, R.G. Reddy
(The University of Alabama)

Zircon-particle-dispersed Al-13.5Si-2.5Mg is a structural composite material being investigated for lightweight, tribological applications. The conventional, powder-processed material, in the temperature range of 22–100 °C, yielded a low coefficient of linear thermal expansion (CTE) of 7.8×10^{-6}°C at 0.15 volume fraction (V_f), a 64% reduction of that of the alloy. The dry sliding wear rate and the coefficient of friction measured by the pin-on-the-plate technique at 4 kg load decreased significantly by 99% and 35.5%, respectively. A significant reduction, by 29%, in wear rate of the alloy was observed to occur only when more than $0.03V_f$ zircon was dispersed. An x-ray study showed that the interface reaction products consist of compounds of Mg, Ce, Cu, and Nb. Tensile failure of the reaction-sintered parts revealed a ductile mode of fracture, with the path traversing both through voids and the bonded particles while interface failure was observed in parts without Mg. An analysis of both the tribological and tensile properties showed that an optimal performance of this alloy at $0.15V_f$ zircon is achieved when the Mg content is between 2.5 and 3.5 weight percent.
Order No.: JA811-011 **© 1998 MRS**

Effect of volume fraction of dispersed SiO_2 particles on intermediate-temperature embrittlement in Cu-SiO_2 polycrystals
H. Miura*, T. Sakai*, G. Gottstein+
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Several kinds of Cu polycrystals with dispersed SiO_2 particles of different volume fractions were tensile tested at high temperatures from

473 K to 1023 K. All of the alloys showed clear intermediate-temperature embrittlement (ITE). Although the temperature of minimum elongation was almost the same in all the alloys, temperature dependence of fracture strain depended strongly on the SiO_2 volume fraction: 1) At a fixed temperature, the fracture strain tended to first decrease with increase in SiO_2 volume fraction, showed minimum in an alloy with certain volume fraction, and increased again with increase in volume fraction. 2) With increase in SiO_2 volume fraction, the temperature range of ITE became narrower and sharper. These results were reasonably understood by considering the occurrence of stress concentration at around grain-boundary particles induced by grain-boundary sliding (GBS), occurrence of dynamic recrystallization and stress relaxation by Cu/SiO_2 interfacial diffusion.
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Growth structure of yttria-stabilized-zirconia films during off-normal ion-beam-assisted deposition
Y. Iijima*, M. Hosaka*, N. Tanabe*, N. Sadakata*, T. Saitoh*, O. Kohno*, K. Takeda+
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Biaxially aligned YSZ thin films with strong [100] fiber texture were formed on a polycrystalline Ni-based alloy by off-normal ion-beam-assisted deposition. Growth structures were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM) etc., and the alignment mechanism was discussed using a selective growth model. Peculiar structural evolution of the crystalline orientation was observed and its development was well described by an exponential equation. It was explained as a collaboration of an anisotropic growth condition and epitaxial crystallization. The [100] fiber texture was formed by columnar structures of diameter of 30–100 nm, which were composed of 5–10 nm diameter crystallites. Very smooth surfaces were observed by AFM imaging with a roughness of 2–3 nm and a peculiar ripple structure. The origin of the azimuthal alignment was discussed with emphasis on the surface structure of YSZ films produced using IBAD and the etching rate measurements of (100) surfaces of YSZ single crystals.
Order No.: JA811-013 **© 1998 MRS**

Diamond growth by hollow cathode arc plasma chemical vapor deposition
G-T. Liang, F.C-N. Hong
(National Cheng-Kung University)

Hollow cathode arc plasma chemical vapor deposition was employed to grow crystalline diamond films using 1.5% to 7% of methane in hydrogen. The growth rate was as high as 3.2 μ/h when using 5% CH_4/H_2 at a pressure of 15 Torr and a substrate temperature of 1083 K. However, an intermediate layer of several hundred nanometers was observed at the film substrate interface by cross-section SEM. Raman and XPS characterizations showed that the interfacial layer consisted of sp^2 carbon and TaC with Ta vaporized from the hot cathode tube. XRD and XPS results further showed that the deposited diamond films also contained TaC. Ta composition in the film increased with the increase of growth pressure, the reduction of substrate temperature and the increase of H_2 flow in the Ta tube. The diamond films deposited by using $CHCl_3$ as carbon source had Ta concentrations one order of magnitude higher than those using CH_4, as shown by XPS results, but the nucleation densities using $CHCl_3$ were always higher than those using CH_4.
Order No.: JA811-014 **© 1998 MRS**

Synthesis of $BaAl_2Si_2O_8$ from solid Ba-Al-Al_2O_3-SiO_2 precursors: III. The structure of $BaAl_2Si_2O_8$ formed by annealing at ≤ 650°C and at 1650°C
X-D. Zhang, K.H. Sandhage, H.L. Fraser
(The Ohio State University)

Analytical TEM and HREM have been used to examine the structure of $BaAl_2Si_2O_8$ crystals produced within oxidized Ba-Al-Al_2O_3-SiO_2 precursors upon annealing: i) at ≤ 650°C and ii) up to 1650°C. A $BaAl_2Si_2O_8$ polymorph with a c-axis parameter of 15.6 Å was detected after annealing at ≤ 650°C. Stacking faults and antiphase boundaries were detected within this polymorph after the 650°C treatment. After a 15 h heat treatment at 1650°C, convergent beam diffraction patterns and HREM confirmed that the predominant phase was β-hexacelsian. Although antiphase boundaries were absent in the β-hexacelsian crystals, dislocations and stacking faults were detected after the 1650°C anneal. The generation of defects in $BaAl_2Si_2O_8$ crystals within specimens annealed at ≤ 650°C and at 1650°C is discussed in light of prior structural analyses.
Order No.: JA811-015 **© 1998 MRS**

Synthesis of sinteractive single-phase microstructure yttrium disilicate precursor powder using hydrothermal processing
P.A. Trusty, K.C. Chan, C.B. Ponton
(The University of Birmingham)

This paper is the first report of the synthesis of a sinteractive single-phase microstructure yttrium disilicate precursor powder using hydrothermal processing. The effect of the pH of the precursor chemicals on the ease of formation of a single-phase material was investigated using x-ray diffraction, TEM and SEM. Under very acidic conditions (pH 1), the formation of yttrium chloride in addition to the yttrium disilicate precursors, produced a powder which absorbed moisture, did not sinter well, and produced a two-phase interpenetrating microstructure after sintering. At pH 6, yttrium chloride no longer formed, but the interpenetrating network persisted after sintering. Only under basic conditions (pH 10) did single-phase yttrium disilicate form after sintering. This work is noteworthy because the calcination time of 1 hour required for the formation of this ceramic at 1050°C is over an order of magnitude lower than the calcination times of over 100 hours required when calcined in the temperature range 900°C to 1150°C, as reported previously by other workers.
Order No.: JA811-016 **© 1998 MRS**

Helical etch channels in quartz
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Helical etch channels were found to form in α-quartz when treated with anhydrous HF vapor at 400°C. Both hydrogen and fluorine species were determined to play an important role in helix formation. Crystal orientation, quartz source, etch channel density, and surface pretreatments had no influence. Helix formation was altogether arrested when water was present in the etch vapor. The genesis of the helices remains unknown.
Order No.: JA811-017 **© 1998 MRS**

Growth mechanism of biaxially textured YSZ films deposited by ion-beam-assisted deposition
J. Wiesmann, J. Dzick, J. Hoffmann, K. Heinemann, H.C. Freyhardt
(Universität Göttingen)

Biaxially textured YSZ films have a large technical relevance for power or electronical applications of HTS films. The YSZ serves as a diffusion barrier and as a template for an epitaxial growth of the HTS. On polycrystalline substrates the biaxial alignment is achieved by using an ion-beam-assisted deposition method. The best obtained textures were characterized by a full width at half maximum of 7° in an <111> x-ray diffraction Φ scan. The FWHM decreases with increasing film thickness. The growth mechanism is investigated with respect to three important effects: nucleation, growth selection, and homoepitaxial growth. It could be shown that during nucleation at the beginning of deposition the angle between the assisting beam and the substrate normal has to be fixed at 55°, whereas during the growth selection this angle can be varied. Especially the homoepitaxial effects allow changes in the deposition conditions without destroying the already achieved texture quality.
Order No.: JA811-018 **© 1998 MRS**

On the fractal nature of crack branching in MgF_2
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*(*University of Florida, +Alexandria, Virginia)*

Nineteen disks of IR window grade, hot pressed magnesium fluoride (~0% porosity, grain size ~1 μm) previously loaded in ring-on-ring flexure tests were used to analyze the crack branching patterns. Fractal geometry was used to determine the crack branching fractal dimension which was named the crack branching coefficient or CBC. The failure stress was proportional to the CBC and the number of pieces generated during the fracture. Thus the number of pieces was proportional to the crack branching coefficient. The crack branching coefficient is distinct from the fractal dimension obtained from the onset of mist and hackle on the fracture sur-

face. The fractal dimension of the fracture surface is, in most cases for brittle materials, a constant and related to the crack tip stress field. The crack branching fractal dimension is a function of the stress at fracture and the far-field stress distribution, or in other words, related to both the type and magnitude of loading. The findings in this work have strong implications for many commercial processes such as comminution, attrition, grinding and basic studies in crack branching.

Order No.: JA811-019

Enhanced solid-state reaction kinetics of shock-compressed titanium and carbon powder mixtures

J-H. Lee, N.N. Thadhani
(Georgia Institute of Technology)

The effect of shock compression on the solid-state chemical reactivity of titanium and carbon powder mixtures was investigated with the objective of forming net-shaped TiC ceramics with a fine-grain microstructure. The combination of defect states and intimate interparticle contacts introduced during shock-compression results in significant enhancement of the otherwise-sluggish solid-state diffusion of Ti and C through the TiC_x boundary layer. The apparent activation energy for TiC_x formation was determined using solid-state reaction kinetics models, and was found to be reduced by four-to-six times that of diffusion of Ti into TiC_x and two-to-three times that of diffusion of C in TiC_x. As a result, net-shaped sections of shock-densified compacts (~85% dense) were reaction synthesized via solid-state diffusion, producing microstructures with grain size <6 μm and microhardness of ~2000 kg/mm^2, in contrast to statically pressed powder compacts which reacted by a combustion process resulting in a highly porous product.

Order No.: JA811-020

Size-controlled synthesis of nanocrystalline $BaTiO_3$ by a sol-gel type hydrolysis in microemulsion-provided nanoreactors

Ch. Beck, W. Härtl, R. Hempelmann
(Universität Saarbrücken)

Using the hydrolysis of appropriate alkoxide mixtures in water-in-oil microemulsions, nanocrystalline $BaTiO_3$ has been prepared in the form of non-aggregated cube-shaped crystals at room temperature without any sintering process as is demonstrated by means of x-ray diffractograms and transmission electron micrographs. By variation of the length of the hydrophilic part of the surfactant molecules, the diameter of the water droplets in the microemulsions could be tuned to values between 8 and 55 nm as determined by dynamic light scattering. The size of the resulting nano-$BaTiO_3$ (6 nm ≤ $<d>_{vol}$ ≤ 17 nm) was evaluated from the line broadening of x-ray reflections and correlates to the droplet size. The particle size distribution is very narrow, in some cases nearly monodisperse.

Order No.: JA811-021

Zirconolite transformation under reducing conditions

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The structural behavior of zirconolite ($CaZrTi_2O_7$) under reducing conditions at high temperature has been studied, mainly by scanning electron microscopy (SEM) and x-ray diffraction (XRD), but also with x-ray absorption spectroscopy, thermogravimetry, and electron paramagnetic resonance. The partial reduction of Ti^{4+} to Ti^{3+}, associated with a reducing atmosphere heat treatment, led to the initial formation of perovskite ($CaTiO_3$) as a second phase. As the concentration of Ti^{3+} in the zirconolite increased, so did the amount of perovskite until the zirconolite was totally transformed into a fluorite structured phase. Analysis of the reduced zirconolites showed them to be consistently deficient in Ca and enriched in Zr, in proportion to the concentration of Ti^{3+}. To determine how electroneutrality was preserved in these reduced zirconolites, a series of zirconolites were prepared in air using In^{3+} and Ga^{3+} as models for Ti^{3+}. These samples were then investigated by neutron and x-ray diffraction, SEM, solid state nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR). ^{71}Ga MAS NMR studies of the Ga substituted zirconolite exhibited a narrow resonance at ~13 ppm which was attributed to six-coordinate Ga incorporated in a trace perovskite phase. Broadline ^{71}Ga NMR and $^{69/71}Ga$ NQR were required to characterize the Ga incorporated in the zirconolite. The resultant quadrupolar parameters of C_Q = 30.0 ± 0.05 MHz and η =1.0 ± 0.03 indicate that the Ga site is in a highly distorted environment which would suggest that it is located on the five-coordinate Ti site within the zirconolite lattice. These results were complemented by Rietveld refinement of the neutron diffraction data from the In-doped zirconolite sample, which was optimal when all the In was located on the five-coordinate Ti site with the excess Zr located on the Ca site. It would therefore appear that charge compensation for the presence of Ti^{3+} in zirconolite is effected via the substitution of an appropriate amount of Zr on the Ca site. The Ti^{3+}-stabilized fluorite structure was readily oxidized back to a single phase zirconolite upon heating in air.

Order No.: JA811-022

Bonding between single-crystal manganese-zinc ferrites using electric field

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Bonding between single-crystal manganese-zinc ferrites using an electric field was investigated. For a given temperature, bonding was accelerated with the application of an electric field. Above 1100°C the effect of the electric field was not obvious due to thermally activated self motion of the atoms. Bonding improved with increased oxygen partial pressure. This was attributed to the higher diffusion coefficient of the cations at higher oxygen partial pressures.

Order No.: JA811-023

Phase transition energetics and thermodynamic properties of ferroelectric $PbTiO_3$

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The ferroelectric phase transition in polycrystalline $PbTiO_3$ was investigated using differential scanning calorimetry and high-resolution x-ray diffraction. The specimen studied was a highly crystalline powder sample carefully prepared by the solution-gelation synthesis technique. The behavior of the excess specific heat, excess enthalpy, excess entropy, and spontaneous tetragonal deformation near the $Pm3m \leftrightarrow P4mm$ transition was examined. The thermal evolution of the thermodynamic order parameter as obtained from the specific heat measurements was compared to that determined from the behavior of the spontaneous elastic strain. The coefficients of the relevant Landau potential for lead titanate were deduced from these data. The results provided additional information regarding the basic thermodynamic properties of lead titanate and confirmed that a simply formulated Landau-Devonshire polynomial, having temperature independent higher-order dielectric stiffness coefficients, affords a satisfactory and self-consistent description of the single-domain ferroelectric behavior.

Order No.: JA811-024

Elastic rebound between an indenter and a layered specimen: I Model

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A model approximates the compliance of elastic contact between an indenter and a layered specimen (isotropic and transversely isotropic layers) by averaging the displacements beneath a uniformly loaded area at the surface of an elastic half space. For a uniform, isotropic material the specimen compliance is $(1-\nu^2)/\beta ES$ where S is the square root of the projected contact area, E and ν are the Young's modulus and Poisson's ratio of the specimen, and β depends on indenter shape: β = 1.044, 1.057, or 1.086 for circular, square, and triangular-shaped indenters, respectively. An expression to replace $(1 - \nu^2) / E$ is provided in the treatment of a transversely isotropic solid.

Order No.: JA811-025

Elastic rebound between an indenter and a layered structure: II. Using contact stiffness to help ensure reliability of nanoindentation measurements

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Measurement of nanoindentation hardness and modulus relies on the determination of the projected area of the indent, A, usually done by

one of two methods: 1) indirectly, based on depth of indentation and calibrated indenter shape; or 2) directly, using a microscope image. In this article we introduce a new analysis to improve the reliability and precision of nanoindentation data. The analysis examines the specimen properties from perspective of the parameter $L_0^{1/2}C \approx H^{1/2}/E_{eff} + C_m L_0$ where C is the measured unloading compliance, C_m is the machine compliance, L_0 is the load, H is the hardness, and E_{eff} is the specimen-indenter contact modulus, which is a function of the size of the indent, and which can be calculated based on a theoretical model. We apply this analysis to the characterization of 1–2 μm-thick molybdenum films deposited on silicon.
Order No.: JA811-026

Substrate strain induced crystallographic texture in sputtered vanadium metal films
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The effects of varying surface strain of glass substrates on the crystallographic texture of vanadium metal thin films are reported. The strain on a soda glass surface can be varied as a function of duration of exchanging the Na ions with larger ions, K, Rb and Cs. The films which are oriented in the (110) direction on unstrained glasses pass through a region of completely random orientation as the strain on the substrates increases and regain the (110) orientation as substrate strain relaxation occurs. The magnitude of relaxation and, therefore, the preferred (110) orientation is ion-size dependent. This behavior is due to the change in total surface energy and provides experimental means for demonstrating the effects of surface energy on the crystalline evolution of thin films.
Order No.: JA811-027

Estimation of hardness by nanoindentation of rough surfaces
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The roughness of a surface influences the surface mechanical properties, estimated using nanoindentation data. Assuming a relation between the penetration depth normalized with respect to a roughness scale parameter, and the effective radius encountered by the indenter, a first order model of roughness dependency of hardness is proposed. The practical usefulness of this model is verified by the numerical simulation of nanoindentation on a fractal surface. As the roughness of a surface is increased, the hardness measured at depths comparable with the roughness scale deviates increasingly from the actual hardness. Given the constants related to indenter geometry, present work provides a rationale and a method for deconvoluting the effect of roughness in arriving at a real hardness characteristics of the near surface region of a material.
Order No.: JA811-028

Novel sol-gel processing for polycrystalline and epitaxial thin films of $La_{0.67}Ca_{0.33}MnO_3$ with colossal magnetoresistance
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(Stanford University)

A novel sol-gel processing method has been developed to fabricate homogeneous powder, polycrystalline and epitaxial thin film of $La_{1-x}Ca_xMnO_3$. Homogeneous powders of single phase $La_{1-x}Ca_xMnO_3$ were synthesized at below 400°C Polycrystalline thin films were fabricated on Si(100) with thermally oxidized SiO_2 layer, while epitaxial films were grown on $LaAlO_3$(100) and MgO(100) single crystal substrates The films were composed of uniformly distributed spherical grains with diameters in the range of 100 ~ 1000 Å depending on annealing temperature. The surface rms roughness were 60 ~ 80 Å. All films displayed a typical behavior of colossal magnetoresistance oxides: semiconductor-metal transitions accompanied by magnetic transitions were observed, and peak MR ratio occurred near the transition temperatures. The peak MR ratio, $(R_0-R_H)/R_H$, ranged from 30% to 90% at a field of H = 9000 Gauss, depending on the annealing temperature. The optimized MR performance was obtained in the thin films deposited on $LaAlO_3$(100) and annealed at 900°C in O_2. It is proposed that a higher MR ratio is associated with larger grains.
Order No.: JA811-029

Effects of annealing temperature on the microstructure and initial permeability of nanocrystalline alloy $Fe_{73.5}Cu_1Mo_3Si_{13.5}B_9$
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The effects of annealing temperature on the microstructure and initial permeability of nanocrystalline alloy $Fe_{73.5}Cu_1Mo_3Si_{13.5}B_9$ have been investigated using x-ray diffraction (XRD) and transmission election microscopy (TEM) in this paper. In the annealing temperature range of 460–540°C, the crystalline phase in the nanocrystalline alloy $Fe_{73.5}Cu_1Mo_3Si_{13.5}B_9$ is the α-Fe(Si) with a DO_3 superstructure, and it has a grain size of ~14 nm. The volume fraction, Si content, and degree of order of the α-Fe(Si) phase increase with increasing the annealing temperature. The DO_3 ordered region in the α-Fe(Si) grain is approximately spherical, its size increases as the annealing temperature increases. There is an obvious change in the microstructure of the residual amorphous phase with the annealing temperature. Both the microstructure of the α-Fe(Si) phase and that of the residual amorphous phase have effects on the initial permeability of nanocrystalline alloy $Fe_{73.5}Cu_1Mo_3Si_{13.5}B_9$.
Order No.: JA811-030

Morphology and kinetics of the interaction between $Ni_{90}Ti_{10}$ alloy thin film and 6H-SiC single crystal
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Morphology and kinetics of phase formation were investigated in $Ni_{90}Ti_{10}$ alloy thin film evaporated on a 6H-SiC single crystal. The study was carried out by Auger electron spectroscopy, x-ray diffraction, and analytical transmission electron microscopy. The interaction was found to begin at 450°C with the formation of the Ni-rich silicide, $Ni_{31}Si_{12}$, on the interface. The silicide exhibited highly oriented growth. After annealing at 800°C for 1/2 hr, three layers were observed in the reaction zone. In the first layer the presence of Ni-rich silicide, Ni_2Si, and of C precipitates, was revealed. The second layer was composed mainly of TiC, the third of Ni_2Si. Kinetics of the $Ni_{90}Ti_{10}$/6H-SiC interaction were investigated in the temperature range, 450–500°C. The $Ni_{31}Si_{12}$ silicide was found to grow by a parabolic law with an activation energy ~1.3 eV/at. The growth process was assumed to be controlled by Ni diffusion through the silicide. An "incubation time" was found to exist when the interaction occurs at temperatures lower than 500°C.
Order No.: JA811-031

Thermal cycling fatigue and deformation mechanism in aluminum alloy thin films on silicon
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Thermal cycling was performed between room temperature and 723 K in a sputter deposited thin film of Al-1mol%Si alloy on a silicon substrate. After given numbers of cycling, residual stress was determined at room temperature by measuring the film curvature using a laser deflection apparatus. Residual stress was found to increase with increasing the cycle number up to the 4th cycle, followed by a continuous decrease by further cycling. Based on the microstructure observation, the initial increase of residual stress was caused by the increase of lattice dislocations and their tangling. The following decrease of residual stress was caused by crack formation and delamination. Stress relaxation experiments were also performed during isothermal annealing at various temperatures. Analysis of the relaxation curves indicated three temperature regions representing different deformation mechanisms. The boundaries between the neighboring regions were found to agree with the boundaries in a deformation mechanism map calculated for an Al thin film. Based on the obtained knowledge of the deformation mechanisms, the origin of the microstructure changes and the structural failure by thermal cycling were discussed.
Order No.: JA811-032

Mechanism of TiN barrier-metal oxidation in a ferroelectric RAM
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In the stacked structure of $PbZr_{1-x}Ti_xO_3$(PZT)/Pt/TiN/poly-Si for a ferroelectric RAM, the mechanism of TiN barrier-metal oxidation was investigated by transmission electron microscopy (TEM). In the cross-sectional TEM images of PZT/Pt/TiN/Si, titanium oxide was observed beneath the Pt grain boundary. The oxygen was diffused through the Pt grain boundary during the heat treatment in an oxygen atmosphere for crystallization of PZT films. The annealing of the TiN film in ammonia resulted in the suppression of the oxidation during the crystallization annealing of PZT. The minimum required Pt film thickness to protect TiN from oxidation can be reduced from 200 nm to 100 nm.
Order No.: JA811-033

Can there be a second kind of entropy catastrophe in the melting of metastable solids?
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We explore here the thermodynamic possibility of the superheating of alloys and the existence of a second order melting transition in metastable alloys subject to concentration fluctuations. Towards this purpose, a novel approach has been adopted which involves simultaneous consideration of the free energy and entropy changes associated with the melting of the fluctuated region. Similar to the well-known Kauzmann paradox in freezing, in principle, there exists an entropy catastrophe in the nucleation of melting in metastable solids, too. However, it would be experimentally difficult to realize the melting of metastable solids because of the tendency to equilibrate at elevated temperatures.
Order No.: JA811-034

Damping of fluid infiltrated nanoporous media: Part I. Loss tangent
Z. Chen, F. Jiang, J.C.M. Li
(University of Rochester)

Mechanical damping behavior of Corning Vycor porous glass, code 7930, fully and partially saturated with water, was studied. This porous glass had 28% volume porosity, 2.3 nm average pore radius and 207 m^2/gram internal surface area. The relaxation strength appears consistent with the damping mechanism in which the infiltrated water flows from the compressive region to the tensile region inside the glass specimen undergoing a three-point bending vibration. The effect of water content in partially saturated specimens suggests that only about 40% of the absorbed water is free to flow under pressure gradients and the rest (60%) of the absorbed water or about three monomolecular layers were adsorbed on the internal surfaces. Such adsorbed water does not seem to contribute to the relaxation strength but appears to increase the damping background. The behavior of the loss tangent of the porous glass partially saturated with water implied that some pores are full and others are empty except for the adsorbed layer.
Order No.: JA811-035

Damping of fluid infiltrated nanoporous media: Part II. Relaxation time
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For water confined in a nanoporous glass, the damping behavior is studied further. Specifically, this paper reports how the water transport process depends on temperature, specimen thickness, pore size and water content. The experimental results seem to agree wtih the predictions of the preceding paper.
Order No.: JA811-036

Structural study of iron borate glasses containing NiO and ZnO
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Iron-borate glasses with NiO and ZnO having composition yNiO-yZnO-xFe_2O_3-(100-x-2y)B_2O_3, x = 7–20 and y = 4–10 mol% were prepared by melt quench route. The structure of the glasses and the structural changes with compositions were investigated by x-ray diffraction, SEM, DTA, IR, and Mössbauer measurements. IR study of these glasses shows that there is no trace of six fold boroxol rings, and the glass network is formed by the randomly connected BO_4 and BO_3 units. The Mössbauer data show that two states of tetrahedrally co-ordinated iron (Fe^{3+} and Fe^{2+}) are present in these glasses.
Order No.: JA811-037

Kinetic manipulation of the composition of electroprecipitated poly(vinylferrocene) films
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The electroprecipitation of poly(vinylferrocene) as the perchlorate salt from dichloromethane solutions is limited by the diffusion of neutral polymer to the electrode surface. The composition of the film depends on the deposition potential. Gravimetric and coulometric data suggest that deposition at low potentials leads to dense films whose composition is close to $P(VF^+ClO_4^-)$, i.e., containing little or no solvent or electrolyte. At higher potentials, the gravimetric data indicate the incorporation of appreciable amounts of solvent and/or electrolyte. Variation of deposition potential offers the opportunity to manipulate film composition.
Order No.: JA811-038

On the prediction of the shear stress of electrorheological suspensions
C.W. Wu, H. Conrad
(North Carolina State University)

Several common methods used for calculating the shear stress and shear modulus of electrorheological (ER) suspensions are reviewed. It is found that when the mismatch ratio of the particle dielectric constant to that of the host liquid in an ac electric field or the ratio of the particle conductivity to that of the host fluid in a dc electric field is >300, no significant difference exists between the predictions of the various methods employed to date. However, when $\Gamma<300$ the several methods give different estimates for the shear yield stress and shear modulus. Empirical equations are given for a simple estimate of the shear yield stress and the shear modulus when $\Gamma<300$.
Order No.: JA811-039

Intercalation of non-linear amines into γ-titanium phosphate
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The intercalation of amines (aniline, benzylamine, cyclohexylamine, piperidine, pyridine, pyrazine, piperazine, naphthylamine, and indoline) into γ-titanium phosphate, $Ti(H_2PO_4)(PO_4)\cdot 2H_2O$, has been investigated by the batch method and by exposing the host to the amines vapor. The changes in the interlayer distance of the solid during the intercalation process were followed by x-ray powder diffraction. The new intercalates were characterized by chemical and thermal analysis and IR spectroscopy. Materials with a monolaminar and/or bilaminar arrangement of amine molecules in the phosphate interlayer region are obtained as a function of the amine nature. The thermal decomposition of the intercalates (nitrogen atmosphere) takes place in three stages: dehydration, amine removal, and phosphate to pyrophosphate condensation.
Order No.: JA811-040

On the nature of microwave deposited hard silicon-carbon films
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Hydrogenated silicon-carbon films have been deposited from argon tetramethylsilane mixtures at 873 or 673 K, with or without hydrogen dilution and at 673 K with silane addition, by using microwave assisted CVD. Except from the case where silane was added, the Si/C atomic ratio is almost constant: $0.6 < Si/C < 0.8$. These films whose mechanical properties vary largely can be regarded as constituted by SiC microcrystallites embedded in an amorphous carbon phase which furthermore contains silicon when prepared at 873 K. The concentration of C-C homonuclear bonds is reduced by increasing the temperature and by hydrogen dilution. Addition of silane increases the contributions of Si-Si and Si-H bonds.
Order No.: JA811-041

Luminescence probing of various sol-gel hosts with a Ru(II) complex and the practical ramifications for oxygen-sensing applications

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Organically-modified silicate (ORMOSIL) sol-gel matrices doped with oxygen-sensitive fluorescence indicators have shown great potential for optical sensing applications. In this work, the luminescence decay behavior of ruthenium(II)-tris-4,7 diphenyl-1,10-phenanthroline perchlorate dissolved in different ORMOSIL matrices was studied. This was done in order to investigate the effect of organic modification on the oxygen sensing properties of the doped sol-gel materials. Bulk xerogels were synthesized from an organically-modified precursor, methyltrimethoxysilane (MTMS), tetraethyl orthosilicate (TEOS), and an equimolar mixture of the two. Systematic changes in composition were conducted to examine the structural properties of sol-gel silicates for possible oxygen supports. Luminescence quenching behavior was analyzed as a function of varying sol-gel composition and oxygen partial pressure. The Stern-Volmer quenching ratio was found to increase with increasing MTMS content. In addition, phase fluorimetric analysis was conducted on all doped sol-gel samples to examine the accuracy of the luminescence decay times.

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