# JMR Abstracts

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# ABSTRACTS

## COMMUNICATIONS

### Characterization of GaN grown on SiC on Si/$SiO_2$/Si by metalorganic chemical vapor deposition

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SiC (3C–SiC) was grown on the top Si layer of SIMOX (Si/$SiO_2$/Si) by carbonization followed by chemical vapor deposition (CVD). Subsequently, GaN was deposited on the SiC by metalorganic (MO)CVD to produce a GaN/SiC/Si/$SiO_2$/Si multilayer structure. This multilayer film was investigated by conventional transmission electron microscopy (TEM) and high-resolution (HR)TEM from cross-sectional view. The GaN layer was found to consist of predominately hexagonal gallium nitride (*h*-GaN), and a small fraction of cubic GaN (*c*-GaN) crystallites. The orientation relationship between most of the *h*-GaN grains and SiC (3C–SiC) was found to be $(000\bar{1})_{GaN}$ //$(111)_{SiC}$; $[11\bar{2}0]_{GaN}$//$[1\bar{1}0]_{SiC}$, while most of the *c*-GaN grains had an orientation relationship $(001)_{GaN}$//$(001)_{SiC}$; $[1\bar{1}0]_{GaN}$//$[1\bar{1}0]_{SiC}$ with respect to 3C–SiC substrate. The hexagonal grains of GaN were found to grow as two variants. The defects in both *h*-GaN and *c*-GaN are also discussed.

**Order No.: JA9904-01** 

### *Nanostructure of GaN and SiC nanowires based on carbon nanotubes*

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The nanostructure of GaN and SiC nanowires produced by carbon nanotube confined reaction has been studied by means of high-resolution electron microscopy, microanalysis, and microdiffraction. The GaN nanowire is a single crystal with fewer defects and the SiC nanowire is a β–SiC crystal with heavy layer sequence faults. Considering experimental results a possible reaction path for making GaN is suggested.

**Order No.: JA9904-02** 

### Intercalation of ε-caprolactam ions into inorganic hosts

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The intercalation reaction of ε-caprolactam anion (ε–$CL^-$) into hydrotalcite heated up to 500 °C to expel $CO_3^{2-}$ in its double hydroxide gallery and also that of ε-caprolactam cation (ε–$CL^+$) into mica were successfully performed in their aqueous solutions. The intercalation reaction of ε–$CL^-$ into 500 °C-heated hydrotalcite was completed within 1 h at 60 °C, and the resultant intercalation compound had the interlayer spacing of 0.77 nm. The intercalation of ε–$CL^+$ into mica, on the other hand, proceeded rather slowly in two steps, which was due to the presence of two species, $Na^+$ and hydrated $Na^+$, in the mica gallery, and gave the intercalation compound with the interlayer spacing of 1.47 nm.

**Order No.: JA9904-03** 

### Enthalpy of formation of rare-earth silicates ($Y_2SiO_5$ and $Yb_2SiO_5$) and N-containing silicate [$Y_{10}(SiO_4)_6N_2$]

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The enthalpies of formation of two rare-earth silicates ($Y_2SiO_5$ and $Yb_2SiO_5$) and a N-containing rare-earth silicate $Y_{10}(SiO_4)_6N_2$ have been determined using high-temperature drop solution calorimetry. Alkali borate (52 wt% $LiBO_2$–48 wt% $NaBO_2$) solvent was used at 800 °C, and oxygen gas was bubbled through the melt. The nitrogen-containing silicate was oxidized during dissolution. The standard enthalpies of formation are for $Y_2SiO_5$, $Yb_2SiO_5$, and $Y_{10}(SiO_4)_6N_2$, respectively, -2868.54 ± 5.34, -2774.75 ± 8.21, and -14145.20 ± 16.48 kJ/mol from elements, and -52.53 ± 4.83, -49.45 ± 8.35, and -94.53 ± 11.66 kJ/mol from oxides ($Y_2O_3$ or $Yb_2O_3$, $SiO_2$) and nitride ($Si_3N_4$). The silicates and N-containing silicate are energetically stable with respect to binary oxides and $Si_3N_4$, but the N-containing silicate may be metastable with respect to assemblages containing $Y_2SiO_5$, $Si_3N_4$, and $SiO_2$. A linear relationship was found between the enthalpy of formation of a series of $M_2SiO_5$ silicates from binary oxides and the ionic potential (*z*/*r*) of the metal cation.

**Order No.: JA9904-04** 

### Two- and three-dimensional arrays of magnetic microspheres

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A novel fabrication approach for two- and three-dimensional arrays of magnetic microspheres is presented in this paper. The magnetic microsphere is made from 47 μm size $Al_2O_3$ spheres onto which a 2–3 μm thick nickel layer is coated through electroless plating. After proper anneal, the outer nickel layer is converted to exhibit a crystalline structure. As an example for utilizing such magnetic microspheres, a two-dimensional, anisotropically conductive matrix is made by transferring the magnetic microsphere array from a template to a transparent adhesive tape using a magnetic attractive force. In addition, a three-dimensional array has also successfully been constructed on a metal plate. The two-dimensional conductor array may be useful for high-density circuit packaging applications in the semiconductor industry, and the three-dimensional array may open up a possibility for constructing three-dimensional photonic crystals.

**Order No.: JA9904-05** 

### Microstructural and ferroelectric properties of a chemical solution deposited epitaxial $PbZr_{0.5}Ti_{0.5}O_3$ thin film on a $SrRuO_3$/$SrTiO_3$ substrate

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Epitaxial $PbZr_{0.5}Ti_{0.5}O_3$ (PZT) thin films were grown on top of a $SrRuO_3$ epitaxial electrode layer on a (100) $SrTiO_3$ substrate by the chemical solution deposition method at 600 °C. The microstructure of the PZT thin film was investigated by x-ray diffraction and transmission electron microscopy, and the ferroelectric properties were measured using the Ag/PZT/SRO capacitor structure. The PZT thin film has the epitaxial orientational relationship of $(001)[010]_{PZT}$‖$(001)[010]_{SRO}$‖$(001)[010]_{STO}$ with the substrate. The remnant ($P_r$) and saturation polarization ($P_s$) density were measured to be $P_r$~51.4 μC/cm² and $P_5$ ~62.1 μC/cm² at 5V, respectively. Ferroelectric fatigue measurements show that the net switching polarization begins to drop (to 98% of its initial value) after $7 \times 10^8$ cycles.

**Order No.: JA9904-06** 

### Epitaxial growth of patterned $SrBi_2Ta_2O_9$ lines by channel stamping

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Patterned epitaxial $SrBi_2Ta_2O_9$ (SBT) lines with (00*l*) out-of-plane orientation were grown on a (001) $SrTiO_3$ substrate by the novel "channel stamping" method. Parallel channels in a poly(dimethylsiloxane) stamp were filled with a metalorganic precursor solution by spin coating. After solvent evaporation, the solid precursor within the channels was transferred to the substrate by stamping. Stamped precursor lines were pyrolyzed at 350 °C/1 h and then heated to 850 °C/1 h. It was shown by x-ray diffraction and scanning electron microscopy that patterned SBT lines were epitaxial, had a smooth surface with *c*-axis out-of-plane orientation, and had a single in-plane orientation.

**Order No.: JA9904-07** 

### Thin film microstructure control using glancing angle deposition by sputtering

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Thin films with microstructures controlled on a nanometer scale have been fabricated using a recently developed process called glancing angle deposition (GLAD) which combines oblique angle evaporation with controlled substrate motion. Critical to the production of GLAD thin films is the requirement for a narrow angular flux distribution centered at an oblique incidence angle. We report here recent work with low-pressure, long-throw sputter deposition with which we have succeeded in fabricating porous titanium thin films possessing "zig-zag," helical, and "pillar" microstructures, demonstrating microstructural control on a level consistent with evaporated GLAD. The use of sputtering for GLAD simplifies process control and should enable deposition of a broader range of thin film materials.

**Order No.: JA9904-08** 

# ARTICLES

## Thermoelectric properties and power factor of $YBa_2Cu_3O_{6+x}$ with rare-earth dopants

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Both the thermoelectric power and the resistivity of the oxygen deficient $YBa_2Cu_3O_{6+x}$ samples were measured. The rare-earth-doped samples, such as Sm and Dy, whose magnetic moments in the +3 valence state are different, were studied. Then the power factor of the thermoelectric ability was calculated. The power factor of the Dy-doped samples is smaller than those of the other samples, especially at high temperature. This smallness of the power factor is the main reason why the Dy-doped samples have larger resistivity. We try to analyze the data by the theoretical expression under the variable range hopping conduction model. The expression of the thermoelectric power could be fit for the non-doped and Sm-doped samples, except at low temperature. In this situation, the thermoelectric power increases as temperature increases, and this temperature dependence is good for the thermoelectric materials at high temperature where the resistivity decreases with temperature increasing.

**Order No.: JA9904-09** 

## Speeding up film deposition rate: Its effects on microstructures of $YBa_2Cu_3O_y$ superconducting thick films

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Two very different pulsed laser deposition rates, 192 Å/s and 6 Å/s were used to produce 1 μm thick superconducting $YBa_2Cu_3O_x$ (YBCO) films on (001) $SrTiO_3$ single crystal substrates at 790 °C. Transmission electron microscopy (TEM) was used to characterize and compare microstructures between the two films. It has been found that the high deposition rate led to a slight deviation from the expected epitaxial orientations, and extra stress was induced in the films by increased lattice mismatch between the films and the substrates. In addition, misoriented YBCO grains were formed in the high-rate films after a thickness of about 150 nm. Postannealing in oxygen had no visible influence on these defects, although superconducting properties were improved significantly. In contrast to the high-rate films, overall epitaxial orientations have been formed in the low-rate films, and no misoriented YBCO grains were found. However, variations in lattice parameters and columnar voids were observed, although their existence apparently does not have considerable influence on superconducting current density ($J_c$). Cation disorder was observed in both films. A two-step film growth mechanism is concluded which is responsible for the formation of some defects in the high-deposition rate films.

**Order No.: JA9904-10** 

## Effects of the heating rate on conversion of the precursor powders used for melt processes into $YBa_2Cu_3O_{7-y}$

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Effects of the heating rate (100–6000 °C/h) to a peritectic temperature ($T_p$ = 1015 °C) on conversion of $Y_2O_3$–$BaCuO_2$–CuO and $Y_2BaCuO_5$–$BaCuO_2$–CuO precursor powders into $YBa_2Cu_3O_{7-y}$ (Y123) were studied. Both precursor powders were rapidly converted into the Y123 phase. A volume fraction of the Y123 phase was more than 50%, even at a relatively fast heating rate of 3000 °C/h. At about 100–200 °C/h, which correspond to the rates of the first heating cycles of practical melt processes, almost 100% of the precursor powders were converted into a Y123 phase. Microstructures were studied in respect to $Y_2BaCuO_5$ (Y211) particle size, and distribution, gas evolution, and nucleation mechanism of Y211 particles were discussed.

**Order No.: JA9904-11** 

## Electrochemical synthesis and characterization of $La_2CuO_{4+\delta}$ single crystals

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An electrochemical oxidation technique was used to obtain bulk oxidized $La_2CuO_{4+\delta}$ single crystals from the as-grown crystals. Samples were prepared by galvanostatic oxidation with currents in the range 5–10 μA and with different charging times. Some samples were annealed at 110 °C in flowing oxygen. Small high quality crystals were obtained from electrochemically oxidized larger crystals that contained microcracks. Transmission x-ray Laue photography and rocking curve measurements for several fundamental diffraction peaks were used to confirm the crystal quality. The $T_c$ and bulk magnetic properties of samples at different stages in the oxidation process are reported. After annealing at 110 °C, a 15 K transition was observed

**Order No.: JA9904-12** 

## Photoluminescence spectral lines identification in $Ho^{3+}$-, $Er^{3+}$- and $Tm^{3+}$-doped $Mg_xZn_{1-x}Sc$ single crystals

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$Mg_xZn_{1-x}Se : Ho^{3+}$, $Mg_xZn_{1-x}Se : Er^{3+}$, and $Mg_xZn_{1-x}Se : Tm^{3+}$ single crystals were grown by the closed-tube sublimation method. The single crystals crystallized into a zincblende structure at the composition $x = 0.11$ and a wurtzite structure at the composition $x = 0.25$, 0.32, and 0.41. The trivalent ions ($Ho^{3+}$, $Er^{3+}$, and $Tm^{3+}$) of the rare-earth elements Ho, Er, and Tm site in $T_d$ and $C_{3v}$ symmetries in the single crystals with zincblende and wurtzite structures, respectively. Sharp emission peaks appeared in the photoluminescence spectra of the single crystals. These emission peaks are identified to originate from the radiation recombination between the energy levels of the trivalent ions sited in $T_d$ and $C_{3v}$ symmetries.

**Order No.: JA9904-13** 

## Local and electronic structure of siloxene

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Silicon $L_{2,3}$ x-ray emission spectra (XES) of siloxene powder samples prepared according to Wöhler and Kautsky (Wöhler and Kautsky siloxene) are presented. The results are compared with the Si $L_{2,3}$ spectra of the reference compounds a-Si, c-Si, $SiO_2$ and $SiO_x$. A close similarity of the electronic structure of Wöhler siloxene to that of a-$SiO_{0.43}$ : H and of Kautsky siloxene to that of a-$SiO_{0.87}$ : H is found. We determine the number of oxygen atoms per Si atom as ~ 0.5 in Wöhler siloxene and ~ 0.8 in Kautsky siloxene. The relative concentrations are in a good agreement with the results of infrared absorption measurements on the same samples.

**Order No.: JA9904-14** 

## Atmospheric pressure chemical vapor deposition growth window for undoped gallium antimonide

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Metal organic chemical vapor deposition (MOCVD) GaSb growth using trimethylgallium and trimethylantimony as a function of substrate temperature and V/III ratio was examined. These parameters were found to have a significant effect on the growth rate and surface morphology of the GaSb films. A phase diagram is used to interpret the effect of these growth parameters on the GaSb film growth. The region of single phase growth was found to be narrow, falling between 540–560 °C. The optimum growth conditions for the MOCVD growth of GaSb have been determined for a TMGa flow rate of 20 sccm and a carrier gas flow of 8 l/min. The optimum substrate temperature and V/III ratio were found to be 540 °C and 0.72, respectively. In these conditions the lowest hole concentration of $5 \times 10^{16}$ $cm^{-3}$ and the highest room temperature mobility of 500 $cm^2$ $V^{-1}$ $s^{-1}$ were achieved, accompanied by a steep, well-resolved band-edge at 0.72 eV.

**Order No.: JA9904-15** 

## Stress relaxation in Al–Cu and Al–Si–Cu thin films

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Substrate curvature measurements were used to study stress changes during thermal cycling and isothermal tensile stress relaxation in 800 nm Al–0.5 wt% Cu and Al–1 wt% Si–0.5 wt% Cu films. For both compositions dislocation glide can describe the relaxation data well for temperatures up to 120 °C for Al–Si–Cu and up to 100 °C for Al–Cu. The average activation energy for Al–Si–Cu and Al–Cu is 1.7 ± 0.2 eV and 3.0 ± 0.3 eV, respectively. The athermal flow stress is the same for both and equal to 600 ± 200 MPa. This result is consistent with the obstacles for glide being $Al_2Cu$ precipitates, which, in the case of Al–Si–Cu, are fine and can be cut by the dislocations, and, in the case of Al–Cu, are strong and provide Orowan strengthening. Also, the stress changes during thermal cycling in the Al–Cu films are different from those in the Al–Si–Cu films. For Al–Cu films, the room temperature stress decreases after each thermal cycle, while for Al–Si–Cu stress changes during thermal

cycling are stable from the second cycle on. These observations are supported by thorough transmission electron microscopy (TEM) studies.
**Order No.: JA9904-16** 

### Changes in preferred orientation of Pt thin films deposited by dc magnetron sputtering using $Ar/O_2$ gas mixtures

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(200)-oriented Pt thin films were deposited on $SiO_2$/Si substrates by a dc magnetron sputtering using $Ar/O_2$ gas mixtures. Oxygen incorporation into Pt films changed deposition rate, resistivity, stress, and preferred orientation of the films. Increase in film resistivity and decrease in tensile stress were presumed to be the result of the incorporated oxygen into grain boundaries, while the change of preferred orientation resulted from the oxygen incorporation into the Pt lattice. The preferential growth of (200) planes with less total strain energy from the incorporated oxygen resulted in strong (200) preferred orientation in Pt films.
**Order No.: JA9904-17** 

### The role of Ni in the formation of low resistance Ni–Ge–Au ohmic contacts to *n*+ GaAs heterostructures

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Nickel is a commonly used wetting agent in alloyed Au–Ge ohmic contacts to *n*-GaAs, resulting in uniformity improvements to the morphology and contact resistance. In order to study the role of Ni in Ni–Ge–Au alloys, we have fabricated samples with varying Ni-content and characterized them using electron microbeam techniques. Our data indicate the amount of Ni in the alloy affects the microstructure and composition, the morphology of the metal/GaAs interface, and the amount of GaAs consumed during the alloy reaction. Also, the dopant distribution into the GaAs is heterogeneous depending on the alloy microstructure.
**Order No.: JA9904-18** 

### Nanoscale heterogeneities in amorphous semiconductor$_x$metal$_{1-x}$ alloys: A small-angle x-ray scattering study

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A series of small-angle x-ray scattering (SAXS) experiments has been conducted in order to probe further the x-ray absorption fine structure (EXAFS)-derived nanoscale structure of amorphous hydrogenated silicon$_x$tin$_{1-x}$, hydrogenated silicon$_x$nickel$_{1-x}$, and germanium$_x$gold$_{1-x}$ materials as a function of metal content. The SAXS results reveal information on cluster formation within these reactively radio-frequency–sputtered amorphous thin films. The data are considered within the context of EXAFS data and lend support to a model in which the degree and nature of the heterogeneities depend primarily on the metal species, with the level of metal content inducing additional effects. In particular, the results support a percolation model for the metal : non-metal transition in amorphous semiconductor$_x$transition metal$_{1-x}$ alloys, the conducting volume elements comprising metal, or metal compound-rich regions within the amorphous tetrahedral host network.
**Order No.: JA9904-19** 

### Effect of Ti substitution on the microstructure and properties of Zr–Mn–V–Ni $AB_2$-type hydride electrode alloys

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The electrochemical capacity, hydrogen absorbed/desorbed activation properties of alloy $Zr(Mn_{0.1}V_{0.3}Ni_{0.6})_2$ were improved after Ti substitution for the Zr. The microstructure of $Zr_{1-x}Ti_x(Mn_{0.1}V_{0.3}Ni_{0.6})_2$ ($x = 0, 0.5$) alloys was analyzed by x-ray diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive spectrum (EDS) analysis. A systematic structural analysis shows that there are two phases in the Ti-substituted alloy of $Zr_{0.5}Ti_{0.5}(Mn_{0.1}V_{0.3}Ni_{0.6})_2$, C14 Laves phase, and Ti containing "premartensite" R-phase of $Ti_{0.8}Zr_{0.2}Ni$. The improvement of electrochemical properties of alloy $Zr(Mn_{0.1}V_{0.3}Ni_{0.6})_2$ after Ti substitution can be attributed to the Ti substitution for Zr sites in C14 laves phase, the formation of $Ti_{0.8}Zr_{0.2}Ni$ R-phase and disappearance of Zr–Ni binaries.
**Order No.: JA9904-20** 

### Mechanical stress, grain-boundary relaxation, and oxidation of sputtered CuNi(Mn) films

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This paper focuses on understanding stress development in CuNi42Mn1 thin films during annealing in Ar. Besides stress-temperature measurements, also resistance-temperature investigations and chemical and microstructural characterization by Auger electron spectroscopy, scanning and transmission electron microscopy, x-ray diffraction, and atomic force microscopy were carried out. The films are polycrystalline with a grain size of 20 nm up to 450 °C. To explain the stress evolution above 120 °C, atomic rearrangement (excess-vacancy annihilation, grain-boundary relaxation, and shrinkage of grain-boundary voids), and oxidation were considered. Grain-boundary relaxation was found to be the dominating process up to 250–300 °C. A sharp transition from compressive to tensile stress between 300 and 380 °C is explained by the formation of a NiO surface layer due to reaction with the remaining oxygen in the Ar atmosphere. This oxidation is masking the inherent structural relaxation above 300 °C.
**Order No.: JA9904-21** 

### Ultrasonic linear and nonlinear behavior of fatigued Ti–6A1–4V

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The change in ultrasonic nonlinear property of a titanium alloy subjected to cyclic loading has been studied, with an objective to develop a new characterization methodology for quantifying the level of damage in the material undergoing fatigue. In order to determine the degree of nonlinearity, the ultrasonic second harmonic generation technique has been used. The second harmonic signal was monitored during the fatigue process and a substantial increase in the second harmonic amplitude (180% increase in nonlinear factor) was observed. This indicates that the second harmonic signal is very sensitive to the microstructural changes in the material caused by fatigue.
**Order No.: JA9904-22** 

### Some physicochemical studies on organic eutectics and molecular complex: Urea–p-nitrophenol system

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The phase diagram of urea–p-nitrophenol system, in the form of a temperature-composition curve, shows the formation of 1 : 1 molecular complex surrounded by two eutectics containing 0.216 and 0.777 mole fraction of p-nitrophenol. Data on growth velocity ($v$), obtained by measuring the rate of movement of the interface at different undercoatings ($\Delta T$), suggest that they obey the Hillig–Turnbull equation, i.e., $v = u\,(\Delta T)^n$, where $u$ and $n$ are constants depending on the nature of materials involved. From the heat of fusion values, determined by the differential scanning calorimetry (DSC) method, heat of mixing, entropy of fusion, roughness parameter, interfacial energy, radius of the critical nucleus, and the excess thermodynamic functions were calculated. While the x-ray diffraction data show that the eutectics are not mechanical mixtures of the components under investigation, the microstructural investigations give their characteristic features.
**Order No.: JA9904-23** 

### Constrained cavitation and fast fracture at metal-ceramic interfaces at elevated temperatures

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Processes that constrain or promote cavity growth and fast fracture at elevated temperatures are examined. Solutions are given for the stress caused by inhomogeneous deposition of matter in metal-ceramic and alumina grain boundaries and for the tensile stress near the top of a hemispherical pore during pore growth. Velocities of dislocation climb that could promote fast fracture are calculated for elastic stresses acting upon dislocations arising from both a crack tip and interface repulsion. The rates for the atomic diffusive processes and the magnitudes of stresses resulting from them are found to agree well with experimental rate of pore growth, and new data on pore growth and fracture at an aluminum-sapphire interface are presented.
**Order No.: JA9904-24** 

### Crack-bridging processes and fracture resistance of a discontinuous fiber-reinforced brittle matrix composite

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A simple bridging model is proposed for the toughening of a discontinuous fiber reinforced brittle matrix composite, in which the frictional bridging of fibers during, as well as after, the interfacial debonding is considered. The *R*-curve behavior and the work-of-fracture of the composite can be theoretically predicted by the computation of the bridging model applying material parameters, such as fiber volume fraction, size and shape of fibers, fiber tensile strength, elastic moduli of fibers and matrix, fracture toughness and work-of-fracture of matrix, and frictional shear stress at interface. The experimental result obtained from a SiC-whisker-reinforced $Al_2O_3$ composite confirms the theoretical predictions of the present bridging model. Through the model calculation, the *R*-curve, crack profile, and bridging stresses of the composite can be estimated correspondingly to the bridging processes.

**Order No.: JA9904-25** 

### Chemical and morphological analysis of sol-derived $KCa_2Nb_3O_{10}$

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The chemical and morphological properties of a sol-derived layered perovskite compound, $KCa_2Nb_3O_{10}$ (KCN), are presented. Development of this compound is motivated by its use as an interphase fiber coating material for ceramic matrix composites (CMC's). In such systems, this material is to be placed between the fiber and matrix to control crack propagation in the vicinity of the fiber, thereby enhancing toughness. Comparative analyses are performed between known bulk specimens of KCN and the sol-derived product using transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). The suitability of the sol-derived KCN for CMC applications is demonstrated through microstructure and chemical composition similar to that of the known bulk KCN samples.

**Order No.: JA9904-26** 

### Structural properties of yttria-stabilized zirconia thin films grown by pulsed laser deposition

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Yttria-stabilized zirconia (YSZ) thin films grown by the pulsed laser deposition method on (0001) sapphire substrates have been studied by x-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and scanning electron microscopy (SEM). It was found that the crystal orientation of the YSZ films changes as a function of oxygen pressure during deposition. At low oxygen pressure (50 mTorr), well-defined (111) oriented YSZ films are grown. High oxygen pressure favors the nucleation of (001) oriented YSZ grains. A model to explain the preferred growth direction of (001) YSZ is presented. Utilizing the experimental data, we have developed a two-step process to epitaxially grow high-quality (001) oriented YSZ on (0001) sapphire substrate.

**Order No.: JA9904-27** 

### Processing magnetoresistive thin films via chemical solution deposition

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A chemical solution deposition (CSD) Procedure was used to prepare epitaxial lanthanum calcium manganese oxide (LCMO) thin films on (100) $SrTiO_3$ single-crystal substrates. The colossal magnetoresistance (CMR) properties of the films were found to be comparable to those processed with vacuum deposition techniques and to bulk samples. The (200) LCMO d-spacing and metal-insulator-transition temperature ($T_{IM}$) were measured for films heat-treated at different temperatures, partial pressures of $O_2$, and different times. The variations observed suggest a direct link between lattice parameter and $T_{IM}$, as can be understood through their mutual dependence on the $Mn^{4+}/Mn^{3+}$ ratio. The measurements also suggest that film and powder samples crystallize $Mn^{4+}$-rich with respect to the Ca-substitution level, consistent with the larger lattice parameter and higher $T_{IM}$ observed following short heat treatments at high temperatures or long treatments at lower temperatures. Films refired in reducing conditions had the largest (200) d-spacing and slightly lower $T_{IM}$, as expected from the 30% Ca-substitution level and consistent with the LCMO electronic/magnetic phase diagram constructed for bulk samples.

**Order No.: JA9904-28** 

### Structure and thermal stability of nanostructured iron-doped zirconia prepared by high-energy ball milling

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Fully-stabilized cubic zirconia doped with iron oxide has been synthesized by high-energy ball milling from powder mixtures of monoclinic zirconia and hematite. It is found that the iron ions dissolved in cubic $ZrO_2$ are in substitutional positions with a maximum solubility of approximately 18.5 mol% $\alpha$–$Fe_2O_3$. The unit-cell volume of the cubic $ZrO_2$ phase decreases with increasing iron content. During heating the cubic-to-tetragonal transition occurs at approximately 827 °C and the tetragonal-to-monoclinic transition seems to be absent at temperatures below 950 °C. During cooling the tetragonal-to-monoclinic transition occurs at 900–1100 °C.

**Order No.: JA9904-29** 

### Synthesis and properties of chemically modified polycarbosilane containing organofluoric groups

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The chemically modified polycarbosilane (PC) containing organofluoric groups, PCOCF, was synthesized through chemical reaction of PC and fluoric alcohol. Pyrolysis of the polymer precursor occurred in three stages under 1000 °C. Weight loss due to evaporation of low molecular compounds was observed at the first stage below 300 °C, followed by the largest weight loss from 300 to 600 °C at the second stage. At this stage, side chains formed during the chemical reaction were removed. Finally, side chains such as $Si–CH_3$ decomposed at the third stage above 600 °C. At 1000 °C, the chemical modification of PC resulted in high yield of solid product. After coating PCOCF on silicon carbide (SiC) powders, the conversion yield of pyrolyzed PCOCF was further improved due to the interaction between PCOCF and SiC powders. Coating of PCOCF on SiC powders was found to be effective in increasing the green density of uniaxially pressed bodies.

**Order No.: JA9904-30** 

### Effects of borosilicate glass on densification and properties of borosilicate glass + $TiO_2$ ceramics

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Effects of borosilicate glass (BSG) on densification and dielectric and thermal expansion properties of a binary composite of BSG + $TiO_2$ ceramics have been investigated. Two different phases of $TiO_2$ including anatase and rutile are used. A much greater densification is observed with anatase because it has a much better wetting with BSG than rutile. With increasing BSG content, the densification of BSG + $TiO_2$ increased. Activation analysis shows that the densification is controlled by viscous flow of BSG. Both dielectric constant and coefficient of thermal expansion of the binary composite of BSG + $TiO_2$ increase with decreasing BSG content and increasing the degree of anatase-to-rutile transformation, as well.

**Order No.: JA9904-31** 

### Phase evolution and dielectric characterization of lead nickel niobate-lead zirconate ceramics prepared from the hydrothermally derived precursors

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The perovskite compounds with the composition of $(1\text{-}x)Pb(Ni_{1/3}Nb_{2/3})O_3$–$xPbZrO_3$ have been successfully prepared from hydrothermally treated precursors. During calcination, the primary intermediate compound is pyrochlore phase in the $Pb(Ni_{1/3}Nb_{2/3})O_3$-rich composition, while it is $PbZrO_3$ on the $PbZrO_3$-rich side. On calcination at 800 °C, all precursors convert into perovskite phases. In the formed solid solutions, increasing $PbZrO_3$ content results in a rise in the apparent Curie temperature as well as the maximum dielectric permittivity. The $Pb(Ni_{1/3}Nb_{2/3})O_3$-rich perovskites ($x < 0.8$) possess the characteristics of relaxor ferroelectrics. With increasing $PbZrO_3$ content, the dielectric response gradually becomes less diffuse and dispersive, reflecting a reduction in the relaxor characteristics of the formed perovskites.

**Order No.: JA9904-32** 

### Imprint and fatigue properties of chemical solution derived $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ thin films

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We have investigated the effect of oxygen vacancies on imprint and fatigue behavior of the PLZT thin films. It is found that the compensation of oxygen vacancies with various dopant concentrations and electrode structures is an important process parameter in determining the tendency to imprint and fatigue. In the case of PLZT thin films, the voltage shifts related to imprint are attributed to the trapping of electrons at ionic defect sites such as oxygen vacancies near the film/electrode interface, the magnitude of polarization, and concentration of defect-dipole complexes involving oxygen vacancies such as $V''_{Pb}$ - $V''_O$. The strong dependence of fatigue rate on electrode material for PLZT thin films is due to the effect of the ferroelectric/electrode interaction on the pinning and/or unpinning rate involving the accumulation of oxygen vacancies near the film/electrode interface during fatigue cycling. By using $RuO_2$ as the top and/or bottom electrode instead of Pt, improved fatigue properties are obtained compared to Pt/PLZT/Pt capacitors. This is because a reduced accumulation of oxygen vacancies near the interface by the oxide electrode such as $RuO_2$ may reduce the electronic charge trapping and, consequently, lead to less domain wall pinning.

**Order No.: JA9904-33** 

### Relations between coarsening and densification and mass transport path in solid-state sintering of ceramics: Model analysis

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The correlations between coarsening (including grain and pore growth) and densification, and the effects of mass transport on particle coarsening and densification were discussed based on the simple particle array models and for real particle compacts. Grain boundary motion could cause particle coarsening only under a certain particle size distribution but not densification; mass transport is reasoned to contribute to both grain growth (particle coarsening) and shrinkage for one- dimensional particle arrays. Under a certain limitation for the change of the particle size aspect ratio during sintering, very limited effects of grain growth by itself on the shrinkage of particle arrays through reinitiating the sintering could been found. For a real powder compact system, mass transport between the particles, which surround a pore, contributes to the particle coarsening and densification when the pore is thermodynamically unstable and only to particle coarsening when the pore is thermodynamically stable. The mass transport mechanism for both particle coarsening and densification would be the same, which cannot exclude, at least on thermodynamics, the contribution from surface diffusion in the intermediate stage of sintering.

**Order No.: JA9904-34** 

### Relation between coarsening and densificaton in solid-state sintering of ceramics: Experimental test on superfine zieconia powder compacts

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Coarsening (including grain growth and pore growth) and densification behavior of superfine Y-TZP and YSZ powder compacts in the intermediate stage were investigated. It has been found that grain growth in the compacts is basically not affected by the compaction properties, and pore growth is driven by both grain growth and densification. Grain growth alone leads to size-proportional pore growth, and densification results in pore shrinkage. The relation between grain size and density is analyzed to be linear when grain growth and densification are believed to be driven by different stresses under an identical diffusion process. Both theoretical and experimental results show that compaction properties and the heating rate do not alter this linear relation between grain size and density but influence the slope of the linear relation. Larger dihedral angle, higher green density, and narrower particle and pore size distributions are found favorable for the achievement of the grain size density trajectory with promoted densification and minimized grain growth.

**Order No.: JA9904-35** 

### Thermodynamics and densification kinetics in solid-state sintering of ceramics

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Based on the stability analysis of the closed pores in two dimension which was determined mathematically with their particle coordination number and dihedral angle, the stability of those in three dimension was determined with a spherical pore model. The model is set up by first excluding the effect of interface tension, so the pore was supposed to be spherical, and then the tensile stress arisen from the interface tension was supposed to act on this hypothesized spherical pore. On the basis of the spherical pore model, microstructure models based on pores, not grains, for the real powder compacts were first established. Densification kinetics were then determined from the models by the densification rate equations, which were derived by relating density to pore size to grain size ratio for the intermediate and final stages of sintering. The criteria for pore shrinkage were discussed quantitatively. The derived equations can be used to simulate the relation between densification rate and density during heating with a constant rate, and for the explanation of the effects of pore size distribution, agglomerates, and green density on sintering

**Order No.: JA9904-36** 

### Effective sintering aids for low-temperature sintering of AlN ceramics

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A disappearing sintering aid was used to promote densification during the initial and middle stages of sintering and to be removed in gaseous form from the specimens during the final stage of sintering. From thermodynamic consideration such as assessment of Gibbs free energy change of formation of $Al_2O_3$ compounds including metal-oxide and evaluation of the vapor pressure of metal-oxide, $Li_2O$ is expected to become a disappearing sintering aid for AlN sintering. Doping with $Li_2O$ resulted in densification of AlN ceramics with $Y_2O_3$ and CaO additives by sintering at a firing temperature of 1600 °C. The amount of $Li_2O$ in the specimens decreased by volatilization at temperatures higher than 1300 °C, and its amount was at a level of several ppm after firing at 1600 °C for 6 h. Low-temperature densification of AlN specimens by addition of $Li_2O$ also caused the improvement of thermal conductivity and mechanical strength of sintered specimens. Present results indicate that a $Li_2O$ addition is effective for AlN sintering. Furthermore, $LiYO_2$ was also used as a new sintering aid instead of $Li_2O$ and $Y_2O_3$, and the results of thermal conductivity and mechanical strength were shown.

**Order No.: JA9904-37** 

### Atomistic structure of sodium and calcium silicate intergranular films in alumina

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Sodium silicate intergranular films (IGF) in contact with the [0001] basal plane of α-alumina were studied using the molecular dynamics computer simulation technique. The results were compared to previous simulations of calcium silicate and sol-gel silica IGFs in contact with alumina. An ordered, cage-like structure was observed at the interface. Sodium ions segregated to the cages at the interfaces. Calcium and hydrogen ions were also observed to segregate to the cages in the previous simulations. The modifier ions were surrounded by more oxygen ions in the cages at the interface than in the bulk of the IGF. This explains the segregation of modifiers at the interface. Interface energy decreased as the sodium content of the IGF increased. Interface energy decreased faster as a function of $Na_2O$ content than as a function of CaO content. However, interface energy decreased slower as a function of $Na^+$ content than as a function of $Ca^{2+}$ content.

**Order No.: JA9904-38** 

### Initiation of dislocation systems in alumina under single-point scratching

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This paper aims to investigate the initiation and distribution of dislocations and twins in the subsurface of alumina subjected to single-point scratching and to gain a deeper understanding of the mechanisms of ductile-regime grinding of alumina. It found that there generally exist three regions of dislocation and twin systems in the scratched alumina. The first region contains five independent slip systems so that macroscopic plastic flow is possible there. In the second and third regions, not all the systems can be activated and then microcracking in subsurface may occur easily. The distribution of these regions varies with the grain size of alumina. In the 25 μm-grained alumina all the three regions appear. Thus in this case, microcracking is difficult to avoid. In the 1 μm grained alumina, however, only the first region appears, indicating that the material may be scratched under a real ductile mode without micro-

cracking. A comparison shows that theoretical predictions are in good agreement with experimental observations.
**Order No.: JA9904-39** 

### Preparation and microstructure characterization of anodic spark deposited barium titanate conversion layers

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Anodic spark deposition (ASD) is an advanced plasma-electrochemical coating process to prepare polycrystalline, ceramic-like conversion coatings on metal surfaces. As an example, polycrystalline barium titanate ($BaTiO_3$) phases have been prepared by the anodic conversion of metal substrate and the metal ions in the electrolyte. By a combination of various characterization techniques the configuration of the coating was elucidated. On the metal substrate a thin (~50 nm) passivating amorphous film of titania ($TiO_2$) first forms, which subsequently changes to anatase and rutile structures. With increasing anodic potentials, a plasma-chemical conversion reaction starts, leading to the heterogeneous formation of $BaTiO_3$ layers of 2–10 μm thickness. The results of this study lead to the formulation of a model describing a polycrystalline and inhomogeneous layer configuration.
**Order No.: JA9904-40** 

### Characterization of porosity over many length scales: Application to colloidal gels

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Processing-microstructure relationships in a silica gel system, based on mixtures of colloidal sol and soluble potassium silicate, have been studied. Quantitative microstructural information regarding colloidal cluster sizes, size distributions, surface areas, and pore-size distributions from the nanopore range to the macropore range were determined via small-angle scattering and transmission electron microscopy. The colloid cluster size distribution varies systematically, with gels fabricated with the least colloidal fraction possessing the most polydisperse microstructure. It is shown that the porosity over the entire range can be tailored by selecting the appropriate starting chemistry; under the same pH conditions, the ratio of the two silicate ingredients controls the average size, the polydispersity of sizes, and the connectivity of the pores. A population of fine (2 nm) uniformly-dispersed nanopores, which result from leaching, is responsible for large increases in surface area. The leaching process can be controlled by the surrounding macropore void size, which determines alkali transport. The product material consists of 85% large, open pores, with fine pores within the gel skeleton, making this gel an ideal candidate for controlled-porosity applications such as catalyst supports and magnetic composites.
**Order No.: JA9904-41** 

### Hydrothermal coarsening of $CeO_2$ particles

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The effects of reaction temperature (150–300 °C), chemical composition of the starting cerium salt (cerium nitrate and cerium chloride) and doping with trivalent cations ($Sc^{3+}$ and $Y^{3+}$) on the coarsening of $CeO_2$ particles in dilute suspensions under hydrothermal conditions were investigated. The particle size was measured by x-ray line broadening and by transmission electron microscopy. The particle coarsening kinetics followed a parabolic law, indicating that the interfacial reaction (dissolution) was the rate-controlling step. Furthermore, the particle size distribution data can be well-described by the Lifshitz–Slyozov–Wagner theory of Ostwald ripening controlled by the interfacial reaction. Doping with 6 at.% $Y^{3+}$ produced a significant reduction in the coarsening rate but almost no change in the activation energy. At the same concentration, $Sc^{3+}$ was more effective than $Y^{3+}$ in reducing the coarsening rate. Particles synthesized from a starting solution of cerium (III) chloride coarsened at a markedly slower rate than that for particles synthesized from cerium (III) nitrate. The mechanisms controlling the coarsening of the particles are discussed.
**Order No.: JA9904-42** 

### Effects of phase equilibrium on the oxidation behavior of rare-earth-doped α-sialon ceramics

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A series of rare-earth (RE)-doped α-sialons ($RE_xSi_{12-4.5x}Al_{4.5x}O_{1.5x}N_{16-1.5x}$, with $x = 0.40$ for RE = Nd, Sm, Yb, and $x = 0.48$ for RE = Y) were prepared and heat-treated in air at 1350 °C for 66 h to 727 h (3 days to 30 days), and the variations in composition and structure with time of the formed oxide scales and matrix materials were investigated. In the oxide scales of the Nd-, Sm-, and Y-containing samples a liquid was formed, apparently in (quasi-)equilibrium with the crystalline phases cristobalite and mullite, while only crystalline $Yb_2Si_2O_7$, cristobalite, and mullite were observed in the Yb sample. Apparently, the liquid plays an important role in the oxidation process. In the depleted zone, located between the scale and the matrix, the liquid attacks the matrix phases, and a process takes place where the originally formed phases dissolve and reprecipitate as more oxygen-rich phases. In the Nd- and Sm-doped systems, where the α-sialon phase is inherently metastable at 1350 °C, an extensive α → β-sialon transformation takes place, creating still more liquid. As a consequence, the oxidation resistance of α-sialons containing Nd and Sm is much lower than those containing Y and, in particular, Yb.
**Order No.: JA9904-43** 

### The indentation load-depth curve of ceramics

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The pyramidal indentation-induced surface deformation of brittle ceramics is examined on the basis of extensive test results for indentation load (*P*)-depth (*h*) curves during loading/unloading cycle. A mechanically stiff test system is essential for obtaining *P-h* curves acceptable and reliable for subsequent analyses. Both the loading and unloading *P-h* curves are expressed by quadratic functions within experimental variations for all the indenters used (Vickers, Berkovichi, and Knoop). The loading curve is then related to the Meyer hardness and the unloading curve to the Young's modulus by the use of semi-empirical equations which enable to estimate these moduli from the observed loading/unloading parameters. An elastoplastic constitutive equation for indentation surface deformation is theoretically derived. This equation not only predicts well the experimental observations but also gains an important physical insight into the Meyer hardness. The Meyer hardness of brittle materials is not a measure for plasticity, but an elastic/plastic parameter which significantly depends on the geometry of indenter. The concept and experimental determination of "true" hardness as a characteristic material measure for plasticity is proposed.
**Order No.: JA9904-44** 

### Novel ceramic foams from crystals of $AlCl_3(Pr^i_2O)$ complex

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In this paper we report a novel process for the production of ultralight cellular ceramics. The foams are generated by the heat treatment of crystals of the aluminum chloride isopropyl ether complex ($AlCl_3(Pr^i_2O)$). The crystals, which are the only foam precursor, are obtained from concentrated solutions of $AlCl_3$, $Pr^i_2O$, and $CH_2Cl_2$. The foams consist of an arrangement of closed cells, 50–300 μm in diameter, having cell walls approximately 1–2 μm thick. An exceptionally high porosity is obtained ranging from 94 to 99 %, and the cellular structure is retained during heating at 1500 °C. The foaming mechanism involves two consecutive nonhydrolytic sol-gel chemical reactions and physical processes including crystal dissociation, solvation, phase separation, and foaming. While other foaming mechanisms cited in the literature utilize one or more of the processes above, no analog mechanism exists in the organic, ceramic, or metal foam production processes. The effectiveness of the process originates from an initial precursor which contains all the necessary foaming components in such a way that the application of mild heating accelerates its transformation to a solid, dry, ultralight foamed material.
**Order No.: JA9904-45** 

### Synthesis of $Sr_2KNb_5O_{15}$ thin films by chemical solution deposition method

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Crack-free and transparent $Sr_2KNb_5O_{15}$ (SKN) thin films have been synthesized by the chemical solution deposition method. A homogeneous and stable precursor solution was prepared via controlling the reaction of metal alkoxides. SKN precursor was found to be the complex alkoxide between $Sr[Nb(OEt)_6]_2$ and $KNb(OEt)_6$ with high structural symmetry. SKN powders and thin films on fused silica substrates directly crystallized to the polycrystalline tetragonal tungsten bronze phase at 600 °C. Highly oriented SKN thin films with the tetragonal tungsten bronze phase were fabricated on MgO(100) and Pt(100)/MgO(100) substrates. Two crystal lattice planes of SKN were intergrown at an orientation of 18.5° on MgO(100). The dielectric constant of SKN thin films on Pt(100)/MgO(100) was about 590 at 20 °C at 1 kHz.
**Order No.: JA9904-46** 

### Lead zirconate titanate via reaction sintering of hydroxide precursors

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Lead zirconate Titanate (PZT) has been successfully fabricated via a unique one-step sintering processing route, which is simpler than the traditional precursor-calcination-milling-pelleting-sintering route and is able to deliver an enhanced sintered density at a much reduced sintering temperature. The hydroxide precursor was prepared by coprecipitation from a mixed nitrate solution containing $Pb^{2+}$, $Zr^{4+}$, and $Ti^{4+}$ ions, and it was then compacted into pellets without being calcined at a low temperature. The precursor pellets were dehydrated at 400, 500, and 600 °C for 4 h, respectively, followed by an isostatic pressing at 350 MPa, prior to being sintered at a high temperature. Dehydration temperature has a large impact on the sintering behavior of these hydroxide-derived PZT ceramics. The PZT dehydrated at 400 °C was seriously cracked when sintered at temperatures ranging from 950 to 1150 °C, due to the incomplete dehydration. A sintered density of 99.2% theoretical density was obtained at 1050 °C for 2 h for the powder pellet dehydrated at 500 °C for 4 h. It exhibits a dielectric constant of 1024 and a dielectric loss of 2.1% at a frequency of 1 kHz at room temperature. A calcination at a too-high temperature, e.g. 600 °C, results in a reduction in the sinterability of the precipitate-derived PZT ceramic.

**Order No.: JA9904-47** 

### Sol-gel lithium borophosphates

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In this paper we present sol-gel synthesis, and thermal and structural characterization of some lithium borophosphates. The as-prepared samples are mostly partially crystalline, and densification heat treatments at 500 °C cause samples to crystallize. In the phosphorus-rich part of the composition triangle we have lithium excess with respect to the nominal composition, which is likely due to the low reactivity of the phosphorus precursor. On the boron-rich side, in contrast, lithium losses are found which probably occur during syneresis.

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### Effect of gravity on titanium carbide foams by self-propagation high-temperature synthesis

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Titanium carbide foams are synthesized by a self-propagation high-temperature synthesis technique using carbon black which generates gases during the synthesis. The synthesis is performed under terrestrial and microgravity conditions. The effects of gravity on the synthesis are evaluated in this study. The foaming is mainly caused by $H_2O$ and CO gases from the carbon black. The elongation of the products increases with decreasing environmental pressure and increasing amount of generated gases. Since the gas flows out along the direction of the combustion wave propagation, the products expand only along this direction. The propagation velocity of the combustion wave increases with increasing amount of generated gases and environmental pressure, which is due to the amount of molten Ti transporting into the reaction/pre-heat zone. Under higher environmental pressures, thermal convection of the environmental gases mainly affects the propagation velocity. However, at lower pressures, the behavior of the molten Ti has a great effect compared with the gases surrounding the specimens

**Order No.: JA9904-49** 

### Nanostructured yttria powders via gel combustion

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Nanostructured yttria powders were prepared by a gel combustion technique. The technique involves exothermic decomposition of an aqueous citrate-nitrate gel. The decomposition is based on a thermally-induced anionic oxidation-reduction reaction. A variety of yttria powders with different agglomerate structures can be made by altering the citrate-nitrate ratio $\gamma$. The gel with $\gamma = 0.098$ *in situ* yields nanostructured yttria powder at 258 °C that is porous and agglomerated with an average of 25 nm primary particles. Its specific surface area is 55 $m^2/g$. The decomposition of the gels was investigated by simultaneous thermogravimetry analysis (TGA) and differential thermal analysis (DTA) experiments. The produced ashes and calcined powders are characterized by x-ray diffraction (XRD), ir spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Brunauer, Emmett, and Teller analyses (BET).

**Order No.: JA9904-50** 

### The synthesis of ZnO acicular particles by hydrothermal discharging-gas method

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In this paper, a new hydrothermal method—hydrothermal discharging-gas method—is introduced. ZnO acicular particles with the ratio of length and diameter 16 : 1 are synthesized by hydrothermal discharging-gas method using mixed solution of $Zn(CH_3COO)_2$ with $NaNO_2$ as precursor at 190 °C for 1 h. The effects of reaction temperature and precursor concentration on formation of acicular particles are investigated. The results showed that the main factor for formation of acicular particles prepared by hydrothermal discharging-gas method is the extent of crystallinity of ZnO powders before releasing gas.

**Order No.: JA9904-51** 

### Hot isostatic pressing to increase thermal conductivity of $Si_3N_4$ ceramics

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Highly anisotropic $Si_3N_4$ ceramics were successfully fabricated by tape-casting of raw $\alpha$–$Si_3N_4$ powders with $\beta$–$Si_3N_4$ single-crystal particles as seed particles and $Y_2O_3$ as an effective sintering aid, followed by hot isostatic pressing at a temperature of 2773 K for 2 h under a nitrogen gas pressure of 200 MPa. The microstructure consists of very large elongated grains (diameter ~ 10 μm; length of ~ 200 μm), highly oriented in the tape-casting direction. The thermal conductivity along this direction reaches 155 $W\ m^{-1}\ K^{-1}$ at room temperature, but varies significantly between room temperature and 1273 K. This thermal conductivity is closely related to (1) formation of extremely large elongated $\beta$–$Si_3N_4$ grains with a reduced amount of crystal defects due to the high-temperature firing and to (2) orientation of $\beta$–$Si_3N_4$ grains due to addition of seed particles and to tape-casting.

**Order No.: JA9904-52** 

### Control of cobalt nanoparticle size by the germ-growth method in inverse micelle system: Size-dependent magnetic properties

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Control of Co particle size was achieved by a germ-growth method during inverse micelle synthesis. Magnetic coercivity and blocking were both a function of the particle size, which ranged from 38 to 88Å. Interparticle dipolar interaction was proven to be important in order to interpret the magnetic properties for large-size particles.

**Order No.: JA9904-53** 

### Repeated loading, residual stresses, shakedown, and tribology

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Protective residual stresses may be developed in the near surface layers of tribological contacts which enable loads sufficiently large to cause initial plastic deformation to be accommodated purely elastically in the longer term. This is the process of shakedown and, although the underlying principles can be demonstrated by reference to relatively simple stress systems, the situation is complex under a moving Hertzian pressure distribution. Bounding theorems can be used to generate appropriate load or shakedown limits not only for uniform half-spaces but also those with plastic and/or elastic properties which vary with depth. In this way, shakedown maps, which delineate the boundaries between potentially safe and unsafe operating conditions, can be generated for both hardened and coated surfaces.

**Order No.: JA9904-54** 

### Growth and characterization of epitaxial NiMnSb/PtMnSb $Cl_b$ Heusler alloy superlattices

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We have sputter deposited NiMnSb/PtMnSb Heusler alloy superlattices with bilayer periods from 9–160 Å. X-ray diffraction and cross-sectional transmission electron microscopy (TEM) measurements indicate that even for short bilayer periods, the superlattices are compositionally modulated, epitaxial, and maintain the Heusler alloy $Cl_b$ structure. Low- and high-angle diffraction profiles are in agreement with simulations of the superlattice peaks. TEM images reveal defects, including stacking faults, which help relieve lattice mismatch strain. Energy minimization calculations of the stacking fault density are within

a factor of 3 of the density observed by TEM. The saturation magnetization of the superlattices is close to bulk PtMnSb and NiMnSb, with a tendency for perpendicular magnetization at short bilayer periods.
**Order No.: JA9904-55** 

### Characterization of nanocrystalline γ–$Fe_2O_3$ prepared by wet chemical method

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Homogeneous maghemite (γ–$Fe_2O_3$) nanoparticles with an average crystal size around 5 nm were synthesized by successive hydrolysis, oxidation, and dehydration of tetrapyridinoferrous chloride. Morphological, thermal, and structural properties were investigated by trasmission electron microscopy (TEM), differential scanning calorimetry (DSC), and x-ray diffraction (XRD) techniques. Rietveld refinement indicated a cubic cell. The superstructure reflections, related to the ordering of cation lattice vacancies, were not detected in the diffraction pattern. Kinetics of the solid-state phase transition of nanocrystalline maghemite to hematite (α–$Fe_2O_3$), investigated by energy dispersive x-ray diffraction (EDXRD), indicated that direct transformation from nanocrystalline maghemite to microcrystalline hematite takes place during isothermal treatment at 385 °C. This temperature is lower than that observed both for microcrystalline maghemite and for nanocrystalline maghemite supported on silica.
**Order No.: JA9904-56** 

### Perovskite $NdTiO_3$ in Sr- and Ca-doped BaO–$Nd_2O_3$–$TiO_2$ microwave dielectric ceramics

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$Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ (BNT) is a useful dielectric resonator at microwave frequencies. Recent work has shown that the major secondary phase in this system can be indexed as $Nd_4Ti_9O_{24}$ (JCPDS 33-943). The present study has revealed that when half of the stoichiometric $Ba^{+2}$ is replaced with $Ca^{+2}$ or $Sr^{+2}$, a third, tilted perovskite-structured phase, $NdTiO_3$, is also present. It forms as coherent intragranular regions within BNT grains and always contains some of the divalent dopant species. The orientational relationship between $NdTiO_3$ and BNT has been established.
**Order No.: JA9904-57** 

### Al–Ta bilayer as an oxidation resistant barrier for electrode structures in high dielectric constant capacitors

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Aluminum-tantalum bilayers have been investigated for their potential to serve as conductive barriers to oxygen diffusion when annealed at conditions corresponding to crystallization of perovskite dielectrics such as lead lanthanum titanate (PLT). Ta (50 nm)/Al (15 nm) structures have been deposited on Si substrates and annealed in oxygen at 650 and 700 °C for various amounts of time. The as-deposited and annealed structures have been characterized by x-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), and Auger electron spectroscopy (AES) analysis and by four-point probe electrical measurements. It has been found that the Al–Ta structures can withstand complete oxidation when exposed to oxygen at 650 °C for 30 min or 700 °C for 1 min and the oxide layer formed at the surface of the structure acts as a barrier to further oxygen diffusion. When a PLT film was deposited directly on the Al–Ta structures intermixing took place. It was therefore necessary to insert a Pt layer between the Al–Ta barrier and PLT layer. In such a case the PLT showed electrical properties similar to those obtained when deposited on $SiO_2$/Pt, however, the Al–Ta structure did interact with Pt during the perovskite formation anneal. It has been found that this interaction can be prevented by preannealing the Al–Ta, in oxygen, prior to the deposition of Pt.
**Order No.: JA9904-58** 

### Deposition of epitaxial titanium carbide films on MgO(001) and 6H–SiC(0001) by coevaporation of Ti and $C_{60}$

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Epitaxial films of $TiC_{1-x}$ ($0.15 < x < 0.50$) were deposited on MgO(001) and 6H–SiC(0001) at 250 and 400 °C by coevaporation of $C_{60}$ and Ti. Films deposited on MgO(00l) were single-crystalline down to deposition temperatures of at least 250 °C as determined by x-ray diffraction (XRD), low energy electron diffraction (LEED), and transmission electron microscopy (TEM). Films deposited on 6H–SiC(0001) were also epitaxial at 250 °C, but TEM showed a columnar microstructure due to the occurence of twinned domains in the [111] growth direction normal to the substrate.
**Order No.: JA9904-59** 

### Interface characterization of AlN/TiN/MgO(001) prepared by molecular beam epitaxy

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The AlN/TiN/MgO(001) interfaces, prepared by molecular beam epitaxy, have been characterized by cross-sectional high-resolution electron microscopy (HREM). The thin TiN buffer layer, with the thickness of 40 nm, is epitaxially grown on the MgO(001) substrate. Owing to the same structure-type as well as the small mismatch of their lattice parameters, the growth is governed by the parallel orientation relationship of (001)TiN//(001)MgO, (010)TiN//(010)MgO, and (111)TiN//(111)MgO. Two kinds of processes of the hexagonal AlN epitaxial growth on the as-received TiN(001), differed by the (0001)AlN plane parallel to, and the $(10\bar{1}2)$ plane *approximately* parallel to the MgO substrate surface, respectively, are identified, and within them, several cases are classified which are based on the consideration of crystallographic symmetry. Theoretical calculations based on the geometrical model that was recently proposed and applied to a number of epitaxial systems have been carried out to rationalize these observations.
**Order No.: JA9904-60** 

### Layered TaSiN as an oxidation resistant electrically conductive barrier

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TaSiN films deposited as layered TaN–SiN structures of various compositions have been examined for their oxidation resistant properties during annealing in oxygen at annealing conditions commonly used to prepare perovskite dielectrics. The films have been characterized by Rutherford backscattering analysis (RBS), x-ray diffraction (XRD), and electrical resistivity measurements. Films with less then 15 at.% Si showed some resistance to oxidation after annealing for 1 min at 650 °C but became fully oxidized after longer anneals. Increasing the Si content up to 28 at.% increasingly improved the oxidation resistance of the alloys to the point where the films resisted complete oxidation for up to 5 min at 700 °C. For alloys with greater than 28 at.% Si no oxidation could be detected by RBS or electrical measurements for anneals up to 5 min at 700 °C. Furthermore, these high Si content alloys were still conductive with resistivities of near 1000 μΩ cm. It was also found that TaSiN and lead lanthanum titanate (PLT) interact strongly during annealing and another nonoxidizing barrier metal, such as Pt. is required between the two materials if TaSiN is to be used as an electrode/barrier with lead-based perovskites.
**Order No.: JA9904-61** 

### Sol-gel processing and characterization of alkaline earth and rare-earth fluoride thin films

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Alkaline earth and rare-earth fluoride thin films were prepared on silica glass substrates by a sol-gel process using trifluoroacetic acid (TFA) as a fluorine source. Homogeneous solutions were obtained by stirring a mixture of alkaline earth or rare-earth metal acetates, TFA and $H_2O$ dissolved in isopropanol. The solutions were spin-coated and heated at 300–800 °C. The fluoride thin films were obtained by heat-treatment around 400 °C in air. The crystallization behavior, the surface morphology, and the optical properties of the films depended on the heating temperature as well as the chemical species of the metal ions.
**Order No.: JA9904-62** 

### Characterization and optical investigation of diamondlike carbon prepared by electron cyclotron resonance plasma

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Diamondlike carbon (DLC) films have been prepared on radio-frequency (rf) biased substrates maintained at low temperature (~60 °C) using electron cyclotron resonance $CH_4$–Ar plasma. The structures of the resultant films were characterized by Fourier transform infrared (FTIR), Raman, and ultraviolet/visible (UV/VIS) spectrometry. The studies revealed that the deposited structures were DLC films with $sp^3/sp^2$ bond hybridization, extremely high hardness (> 3000 kgf/mm$^2$), and high electrical resistivity (up to $10^{14}$ Ω cm). The DLC films deposited on colorless

(transparent) polymer plastics were examined to determine visible light transparencies and optical band gaps. The results indicate that electron cyclotron resonance (ECR) plasma processing with low negative rf bias, low deposition temperature and suitable $CH_4$/Ar gas composition can form optically visible light transparent and hard protective DLC films on polymer plastic surfaces.
**Order No.: JA9904-63** 

## Seeded epitaxial growth of $PbTiO_3$ thin films on (001) $LaAlO_3$ using the chemical solution deposition method

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Epitaxial $PbTiO_3$ (PTO) thin films were grown on (001) $LaAlO_3$ (LAO) substrates by a preseeded, two-step process via spin-coating a Pb–Ti double-alkoxide precursor solution. In the first step, a substrate was preseeded with epitaxial islands of PTO by coating the substrate with a very thin layer of the precursor solution and heat treating to 800 °C for 1 h. The isolated islands had an epitaxial orientation relationship of $[100](001)_{PTO}\|[100](001)_{LAO}$. In the second step, another PTO thin film was deposited by spin coating to produce an epitaxial film via grain growth from the seeded islands. The sequence of epitaxy during heating between 400 and 800 °C was characterized by x-ray diffraction, scanning electron microscopy, atomic force microscopy, and transmission electron microscopy (TEM). This sequence was compared to the case where the LAO substrate was not seeded. Regardless of whether the substrate was seeded or not, perovskite PTO grains nucleated and grew within the pyrolyzed, amorphous film. Films grown on the unseeded substrates were, at best, only highly textured, polycrystalline films. TEM observations showed that only a low number of epitaxial nuclei formed at the substrate/film interface due, apparently, to the large strain energy associated with the large lattice mismatch (~4%) between PTO and LAO. Other, unoriented, PTO grains that nucleated within the amorphous film were not consumed as the epitaxial grains grew larger with increasing temperature. On the other hand, good epitaxial films could be produced when the number density of epitaxial nuclei was increased by first forming a seeded substrate.
**Order No.: JA9904-64** 

## A novel organic complex thin film for rewritable optical storage

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Erasable optical storage on an organic complex thin film m-nitrobenzal malononitrile and diamine benzene (m-NBMN/DAB) has been demonstrated. High contrast pattern can be produced by 780 nm laser pulses and can be erased by heating. The static optical recording characteristics were studied by the homemade static characterizer and the structural properties of the thin films were investigated by the high-resolution scanning electron microscope (HRSEM) and transmission electron microscope (TEM).
**Order No.: JA9904-65** 

## The effect of heat treatment on the corrosion behavior of amorphous Mg–Ni–Nd alloys

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The effect of heat treatment on the corrosion behavior of seven amorphous melt-spun Mg–Ni–Nd alloys containing 10–20 at.% Ni and 5–15 at.% Nd has been studied. Hydrogen evolution testing was used to determine the dissolution rate of the heat-treated specimens immersed in a 3% NaCl solution saturated with $Mg(OH)_2$. The dissolution rates of the partially crystallized specimens were found to be lower than those of the untreated specimens, while the fully crystallized specimens exhibited marked deterioration of corrosion resistance. X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies on the heat-treated specimens revealed precipitation of $Mg_3Nd$, $Mg_{12}Nd$, and $Mg_2Ni$ phases during the crystallization. TEM results show that the partially crystallized structure consists of uniform dispersion of either $Mg_3Nd$ or $Mg_2Ni$ in the amorphous matrix. In contrast, multiple phases precipitate in the fully crystallized specimen.
**Order No.: JA9904-66** 

## Crystalline morphologies of polychloroprene thin films as revealed by transmission electron microscopy observation

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Thin films of polychloroprene (CR; Neoprene-W) were made by casting its solution (2.0 wt%) in benzene onto the water surface, and some of them were stretched by a desired amount of strain ε in their molten state. The specimens thus prepared were then crystallized and examined by transmission electron microscopy. Morphological observations in bright- and dark-field imaging modes and selected-area electron diffraction analysis revealed directly that filamentous entities observed in the bright-field image are the edge-on lamellar crystals. It was, therefore, confirmed that the morphological results obtained from the thin specimens of CR without any electron staining are basically in accord with those reported so far for the $O_sO_4$-stained thin films of CR.
**Order No.: JA9904-67** 

## Oxygen gettering effect during the reactive evaporation of manganese oxide films

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Manganese oxide films for lithium secondary batteries were prepared using a reactive evaporation method. Mn was evaporated from a molybdenum boat by resistive heating and deposited on a glass slide under oxygen atomosphere. These films were examined with x-ray photoelectron spectroscopy (XPS) and x-ray diffraction. The Mn oxide films with a wide valency of Mn were prepared in this study. A rapid change of the back pressure was found as the deposition of Mn was started. This implies that Mn atoms start to react with $O_2$. This means that *in situ* detection of reactive evaporation process can be utilized.
**Order No.: JA9904-68** 

## Amorphous, silicide, and crystalline Fe films grown on Si(001) by radio-frequency magnetron sputtering

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The microstructure of the amorphous, silicide, and crystalline Fe films grown on Si(001) substrates by a radio-frequency (rf) magnetron sputtering was studied in synchrotron x-ray scattering experiments. During the growth, iron-silicide interlayers were always formed. The silicide interlayer became crystalline β–$FeSi_2$ at high rf power (≥20 W/cm$^2$) and at the substrate temperature of 100 °C. The formation of the β–$FeSi_2$ was also promoted by postannealing to 300 °C. The Fe films grown on top of the silicide interlayer were amorphous at low substrate temperatures (≤100 °C). It became crystalline only at high substrate temperature (300 °C) with the low rf power of 2 W/cm$^2$. The crystalline Fe film was nonepitaxial but had the [111] preferred orientation.
**Order No.: JA9904-69** 

## Effect of temperature and vapor-phase encapsulation on particle growth and morphology

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The effect of *in situ* vapor phase salt-encapsulation on particle size and morphology was systematically investigated in a sodium co-flow/furnace reactor. The temperature of the furnace was varied and the primary particle size and degree of agglomeration of the resulting silicon and germanium particles were determined from transmission electron micrograph images of particles sampled *in situ*. Particle size increased with increasing temperature, a trend expected from our understanding of particle formation in a high-temperature process in the absence of an encapsulant. Germanium, which coalesces faster than silicon, formed larger particles than silicon at the same temperatures, also in agreement with observations of particle growth in more traditional aerosol processes. At the highest temperatures, unagglomerated particles were formed, while at low temperatures, agglomerated particles were formed, with agglomerate shape following the shape of the salt coating.
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