# JMR Abstracts

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# ABSTRACTS

## RAPID COMMUNICATIONS

### The effect of undercooling and Nd422 phase content on the nucleation of large Nd–Ba–Cu–O grains fabricated by top-seeded melt processing

N. Hari Babu, W. Lo, D.A. Cardwell, Y. Shi
*(University of Cambridge)*

The nucleation and growth of $BdBa_2Cu_3O_{7-\delta}$(Nd123)–$Nd_4Ba_2Cu_2O_{10}$ (Nd422) single-grain composites in a controlled 1% $O_2$ in $N_2$ atmosphere were investigated in detail as a function of solidification temperature and Nd422 phase content using a top-seeded melt growth technique. A schematic process phase diagram in the peritectic solidification region of Nd–Ba–Cu–O (NdBCO) was constructed primarily from constant isothermal growth experiments at various temperatures for several compositions and used to fabricate large single-grain material by both isothermal and continuous slow cooling over a limited temperature range. The nucleation at the seed surface and subsequent growth of uniform grains were observed to depend critically on the controlled rate of grain growth and the temperature range over which solidification occurred.

**Order No.: JA910-001** 

### A model for front evolution with a nonlocal growth rate

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In this paper we provide a new mathematical model for front propagation with a nonlocal growth law in any space dimension. Such a problem arises in composite fabrication using the vapor infiltration process and in other physical problems involving transport and reaction. Our model, based on the level set equation coupled with a boundary value problem of the Laplace equation, is a Eulerian formulation, which allows robust treatment for topological changes, such as merging and formation of pores without artificially tracking them. When applied to the fabrication of continuous filament ceramic matrix composites using chemical vapor infiltration, this model accurately predicts not only residual porosity, but also the precise locations and shapes of all pores.

**Order No.: JA910-002** 

### $BaRuO_3$ thin film electrode for ferroelectric lead zirconate titanate capacitors

S-M. Koo, L-R. Zheng, K.V. Rao
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The characteristics of a ferroelectric $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) capacitor on conductive $BaRuO_3$ thin films deposited by pulsed laser deposition (PLD) were investigated. The $BaRuO_3$ layer grown epitaxially on $LaAlO_3$(100) substrates at a substrate temperature of 700 °C was found to have a resistivity around 145 μΩ cm at 300 K. The subsequently deposited PZT film shows *c*-axis orientation perpendicular to the substrate, and the remnant polarization, $\Delta P$ (= $P^* - P^\wedge$) and coercive field, $E_C$ of the capacitor were 24.7 μC/cm² and 52 kV/cm, respectively. Fatigue characteristics of the PZT on $BaRuO_3$ electrodes are far better than those obtained with polycrystalline PZT with Pt structures and comparable to those on epitaxial $YBa_2Cu_3O_{7-x}$ electrodes. With the new metallic electrode, the PZT layer exhibits no serious degradation in fatigue endurance up to $10^{10}$ cycles.

**Order No.: JA910-003** 

### Internal friction of artificially multilayered Cu–Ni(100) membranes produced by electrodeposition

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The internal stress and internal friction of electrodeposited multilayered Cu–Ni(100) thin films were investigated as a function of temperature by a sensitive vibrating membrane technique. Each membrane was in a state of biaxial stress (approaching the yield strength) resulting from contributions of the growth stress in the as-deposited film and from the thermal stress as the membrane was heated. The measured internal friction of these stressed multilayered films was enhanced by over an order of magnitude, compared to the predicted value of classical damping related to the modulus defect when the effect of the internal stress was taken into account.

**Order No.: JA910-004** 

### High-temperature phases in ternary Zr–O–N systems

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Zirconium aerosol was ignited and burned in atmospheric pressure air in microgravity using a 2.2-s drop tower. Combustion products were collected and analyzed using electron microscopy. The elemental composition analyses indicated that combustion product compositions fell along two linear traces on a ternary Zr–O–N diagram. Currently, the equilibrium Zr–O–N phases are not characterized at temperatures above 2000 °C, typical of zirconium combustion in air, and it is suggested that the phases detected in zirconium combustion products can serve as a guide to further studies of the Zr–O–N system at high temperatures. It is also suggested that experimental metal combustion techniques can be adopted for studying high-temperature metal–gas phase equilibria.

**Order No.: JA910-005** 

## ARTICLES

### High-temperature phase relationships for $Y_xNd_{1-x}Ba_2Cu_3O_y$ ($0.7 \leq x \leq 1.0$) superconductors via containerless processing

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Drop-tube experiments have been performed on $Y_xNd_{1-x}Ba_2Cu_3O_y$ ($0.7 \leq x \leq 1.0$) to understand the effects of partial substitutions of Nd for Y on the phase relationships in these systems at elevated temperatures. Powders from 50 to 100 μm in diameter were processed in pure $O_2$ at furnace temperatures from 1575 to 1800 °C, every 25 °C. The resulting samples were examined microstructurally using scanning electron microscopy, energy dispersive spectroscopy, and optical microscopy. Powder x-ray diffraction was performed for phase identification. It was found that Nd substitution alters phase selection by introducing at least one new phase and by allowing for solidification of the superconducting composition directly from the melt via undercooling to below the peritectic transformation temperature. A decreasing trend in the overall melting temperature with increasing Nd was also identified.

**Order No.: JA910-006** 

### High-temperature phase relationships for $Y_xNd_{1-x}Ba_2Cu_3O_y$ ($0 \leq x \leq 0.5$) superconductors via containerless processing

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This paper presents the results of drop-tube experiments performed on $Y_xNd_{1-x}Ba_2Cu_3O_y$ ($0 \leq x \leq 0.5$) to understand some of the effects of partial substitutions of Nd for Y on the phase relationships in these systems at elevated temperatures. Powders from 50 to 100 μm in diameter were processed in pure $O_2$ at furnace temperatures from 1400 to 1800 °C, every 25 °C. The resulting samples were examined microstructurally using scanning electron microscopy, energy dispersive spectroscopy, and optical microscopy. Powder x-ray diffraction was performed for phase identification. It was verfied that Nd substitution alters phase selection by introducing at least one new phase and by allowing for solidification of the superconducting composition directly from the melt via undercooling to below the peritectic transformation temperature. In addition, solidification pathways are altered for samples processed at temperatures just below the liquidus temperature. Mictostructural and x-ray diffraction evidence was used to map the liquidus with increasing Nd substitution. It was found that a minimum in this liquidus occurs at or near the composition $Y_{0.1}Nd_{0.9}Ba_2Cu_3O_x$ and at a temperature of 1500 °C (± 25 °C).

**Order No.: JA910-007** 

### Creep of CdZnTe at high homologous temperatures

T.E. Stevens, J.C. Moosbrugger, F.M. Carlson
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The creep behavior of single-crystal Zn-doped CdTe was examined in the small strain regime. Specimens from two different sources, with tensile axes ⟨110⟩ and ⟨112⟩, were deformed at 1073 and 1173 K. Strain rates were of the order $10^{-6}$ to $10^{-7}$ $s^{-1}$. A laser interferometer was constructed to measure the small sample displacement. Cadmium overpressure was used to inhibit sublimation of test specimens at elevated temperature. Some tests showed a transition from secondary to tertiary creep at low levels of strain. An activation energy for steady-state creep was calculated as $Q_c$ = 1.4 eV, and the creep exponent was found to be approximately $n$ = 4.2. These results, coupled with reported activation energies for self-diffusion of Cd in Cd(Zn)Te, indicate a dislocation creep mechanism. Etch pit density was measured before and after deformation and approached a common level regardless of initial etch pit density.

**Order No.: JA910-008** 

### A solvothermal reaction route for the synthesis of $CuFeS_2$ ultrafine powder

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A 100-nm $CuFeS_2$ ultrafine powder was prepared through a solvothermal reaction at 200–250 °C. X-ray powder diffraction and transmission electron microscopy results revealed that chalcopyrite-phase $CuFeS_2$ was crystallized with single-crystalline nature and preferential orientation growth. Mössbauer spectrum exhibited a six-peak hyperfine magnetic spectrum and a single nonmagnetic peak. Elemental analysis gave the atomic ratio of Cu:Fe:S of 1:1.02:2.10. The influence factors on the formation of the $CuFeS_2$ ultrafine powder are discussed.

**Order No.: JA910-009** 

### Influence of solidification rate on precipitation and microstructure of directional solidification IN792 + Hf superalloy

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The effect of solidification rate on the precipitation and microstructure of directional solidification IN792 + Hf alloy was studied. The solidification sequence and the initial precipitation temperature of different phases were determined by the observation of the quenched microstructure combined with the differential thermal analysis measurement. The script carbide was turned into faceted carbide with the drop of solidification rate. It was concluded by microstructure analysis that the faceted carbide was pushed by the γ solid front before it was captured. The incorporation of γ phase into the faceted carbide was due to the dendrite growth of the carbide toward one point and the mergence of the dendrites. Some long carbide bars were formed along the grain boundaries by continual reaction of eutectic (γ + MC) at a solidification rate of 0.5 μm/s. Two zones, the γ′ forming elements enriched zone and depleted zone, were found in the residual liquid area. Eutectic γ/γ′ nucleated in the γ′ forming elements enriched zone. The η-phase precipitation was controlled by the ratio of (Ti + Hf +Ta + W)/Al in the residual liquid. The growth of eutectic γ/γ′ increased the ratio and induced the η-phase precipitation. A lower solidification rate decreased the ratio by sufficient diffusion and hence efficiently suppressed the η-phase precipitation.

**Order No.: JA910-010** 

### Time evolution of the structural short-range order during the mechanical milling of Fe–Co–Cu nanocrystalline alloys

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The local order around Fe, Co, and Cu atoms was investigated by extended x-ray absorption fine structure spectroscopy in Fe–Co–Cu nanocrystaline alloys prepared by mechanical alloying. In order to study the time evolution of the alloying process, $Fe_{30}Co_{20}Cu_{50}$ samples were studied after several processing times. The analysis of the data shows that, in a first step, a binary Co–Cu alloy is formed, but iron remains separately in the form of nanocrystals with a high defect concentration. Afterward, in a second step, the final ternary Fe–Co–Cu alloy with the face-centered-cubic structure is obtained.

**Order No.: JA910-011** 

### Anomalous wetting of Ti–48 at.% Al–2 at.% Cr–2 at.% Nb substrates by liquid copper

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Conventionally, the wetting of metallic substrates by liquid metals involves undermining of the substrate–oxide layer by the liquid. In this paper, evidence is presented for an alternative wetting process involving spreading of liquid copper along the exterior of the oxide layer on Ti–48 at.% Al–2 at.% Cr–2 at.% Nb substrates. A mechanism is presented involving compositional changes in the liquid, which in turn allow a wetting-promoting reaction between the (initially unreactive) liquid and the exterior layer of the substrate–oxide.

**Order No.: JA910-012** 

### High-temperature lead-free SnSb solders: Wetting reactions on Cu foils and phased-in Cu–Cr thin films

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We report the soldering behaviors of the high-temperature (300 °C) lead-free SnSb alloys on Cu foils and phased-in Cu–Cr thin films. With the increase of the Sb content from 5 to 15 wt%, the solder surface became rougher, and the wetting angle decreased from 50° to 20° on the Cu foils. Interfacial compounds were found to be $Cu_6Sn_5$ and $Cu_3Sn$. The $Cu_6Sn_5$ showed a scallop-type morphology, whereas the $Cu_3Sn$ had a layer-type morphology. The growth of the latter was found to be diffusion-limited. On phased-in Cu–Cr thin films, the solders showed much lower wetting angles than on the Cu foils, but the dewetting phenomenon was observed after 1 min of reflow time in the 85Sn15Sb alloy. In comparison, we found no dewetting of the high-temperature 95Pb5Sn solder.

**Order No.: JA910-013** 

### Effects of the porosity on the thermal properties of a 380-aluminum alloy

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Effective values of the thermal diffusivity, specific heat, and thermal conductivity of a porous 380-aluminum alloy prepared by melting in a gas-fired furnace were determined as a function of the volume fraction of porosity. For that, photoacoustic, differential calorimetric, density, and image analyzer measurements were done. Thermal conductivity and specific heat capacity decrease with the increase of porosity, whereas the thermal diffusivity shows less dependence. Among the effective models for the analysis of the thermal conductivity of a two-phase system, the Maxwell model best fits the experimental data, implying a homogeneous distribution of the pores in the aluminum-alloy matrix.

**Order No.: JA910-014** 

### Interface modification for increased fracture toughness in reaction-formed yttrium aluminum garnet/alumina eutectic composites

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The validity of controlling interfacial toughness in reaction-formed composites was explored using solid-state reaction processing and microanalysis techniques. A variety of rare-earth oxides were added to a yttrium aluminum garnet (YAG)/alumina powder mixture and then melted in air. Some melts retained the crystallography and microstructure of the pure, binary YAG–alumina eutectic. Using scanning transmission electron microscopy in conjunction with energy dispersive x-ray spectroscopy, rare-earth ions were observed both to segregate to the YAG/alumina interface and to form a third phase. Some evidence of increased crack deflection at these interfaces was observed via indentation fracture.

**Order No.: JA910-015** 

### The preparation of metal–polymer composite materials using ultrasound radiation: Part II. Differences in physical properties of cobalt–polymer and iron–polymer composites

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Composite materials containing amorphous iron embedded in poly(methylacrylate) or poly(methlymethacrylate) and amorphous cobalt embedded in poly(methylacrylate) were formed using a sonochemical method. The physical and thermal properties of the composite materials were probed. A significant difference in the solubility of the iron–poly(methylacrylate) and cobalt–poly(methylacrylate) in various solvents was observed. This difference is accounted for by the stronger interaction existing between the cobalt and the surrounding polymer. For iron–poly(methylacrylate) this interaction is weakened due to the formation of an iron complex.

**Order No.: JA910-016** 

### The effect of phase separation in metal carboxylate gels on perovskite lead magnesium niobate crystallization

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Phase separation during the synthesis and decomposition of lead magnesium niobate (PMN)–ethylene diamine tetra-acetic acid (EDTA) and PMN–citrate gels strongly affects perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ phase formation. The PMN–EDTA gel was synthesized from a solution containing Pb–EDTA, Mg–EDTA, and peroxo–citrato–niobium complexes at pH 8. Pb–EDTA precipitation was avoided by using Pb:EDTA in the mole ratio >1:2.5 and flash pyrolyzing the PMN–EDTA solution at 225 °C. Consequently, the PMN yield increased from 80 to 98 wt%. The sequential decomposition of Pb–EDTA, Mg–EDTA, and peroxo–citrato–Nb in the PMN–EDTA precursor in 1 vol% $O_2$ leads to phase separation of Pb and PbO, and this lowers the PMN yield to 92 wt%. At $P_{O_2} > 2.5$ vol% the Pb, Mg, and Nb complexes co-thermalyze to form ≥97% perovskite PMN. The presence of a heterometallic citrato–Pb–Mg–Nb complex in PMN–citrate leads to oxygen partial pressure independent co-decomposition of the Pb, Mg, and Nb complexes. Accordingly, PMN yields of ≥96 wt% were obtained from the PMN–citrate precursor for oxygen partial pressures between 1 and 5 vol%.

**Order No.: JA910-017** 

### Effects of cationic dopants on the phase transition temperature of titania prepared by the sol-gel method

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The effect of different cations in the anatase–rutile phase transition temperatures for titania prepared by the sol-gel method was studied. The metal dopants were chosen from different periods and groups of the periodic table to see the role played by the electronic configuration, the oxidizing state, the atomic size, etc. on these temperature modifications. Linear relationships between the anatase–rutile phase transition temperatures and the ionic radii for alkali, alkaline earth, and groups 3 and 13 elements were obtained. For elements of the period 4, there was not such a defined tendency; for most of them the modification of the phase transition temperature was too small. The cations were $Li^{+1}$, $Na^{+1}$, $K^{+1}$, $Mg^{+2}$, $Ca^{+2}$, $Sr^{+2}$, $Ba^{+2}$, $Al^{+3}$, $Y^{+3}$, $La^{+3}$, $Er^{+3}$, $Ti^{+4}$, $Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Zn^{+2}$. In all cases the dopant's concentration was 2 mol% with respect to titanium, and the same anion (nitrate) was used for all salts. A variation of more than 330 °C in the anatase–rutile phase transition temperatures was obtained by using these dopants. The transition temperatures from amorphous to anatase and from anatase to rutile phases were obtained from the x-ray diffractograms.

**Order No.: JA910-018** 

### Preparation of nanocrystalline titania powder via aerosol pyrolysis of titanium tetrabutoxide

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Nanocrystalline titanium dioxide was prepared via aerosol pyrolysis of titanium alkoxide precursor at 200–580 °C in air and in nitrogen atmospheres. Powders were characterized by x-ray diffraction, thermogravimetric analysis, Brunauer–Emmett–Teller analysis, scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy, x-ray fluorescence, Raman and infrared spectroscopy, and Berner-type low-pressure impact. The anatase phase transition was initiated at 500 °C in nitrogen and at 580 °C in air. In other conditions amorphous powders were observed and transformed to nanocrystalline $TiO_2$ via thermal postannealing. In air, smooth and spherical particles with 2–4-μm diameter were formed with an as-expected tendency to convert to rutile in the thermal postannealings. In nitrogen, a fraction of the titanium tetrabutoxide precursor evaporated and formed ultrafine particles via the gas-to-particle conversion. At 500 °C thermally stable anatase phase was formed in nitrogen. A specific surface area as high as 280 $m^2\ g^{-1}$ was observed for an as-prepared powder.

**Order No.: JA910-019** 

### Reaction synthesis of mullite–silicon carbide–yttria-stabilized zirconia composites

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SiC/mullite/zirconia composites were fabricated by controlling the oxidation of powder compacts of SiC, alumina, and 3 mol% yttria-stabilized zirconia. The powder compacts were first oxidized in air at 1100 °C for various times to obtain proper amounts of amorphous silica. Subsequent reaction sintering at 1500 °C for 2 h combined the amorphous silica with alumina to form mullite with planned amounts. The incorporation of 3 mol% yttria-stabilized zirconia promoted mullite formation and enhanced the densification of the samples. With ≥10 vol% of 3 mol% ytrria-stabilized zirconia in the samples, the mullite formation temperature was lowered from 1400 to 1300 °C, and mullitization was near completion after sintering at 1500 °C for 2 h. The densification of the samples depended on the contents of SiC and 3 mol% yttria-stabilized zirconia. Samples with 20 vol% SiC and 10–20 vol% 3 mol% yttria-stabilized zirconia could be sintered to reach approximately 97% of theoretical density after sintering at 1500 °C for 2 h.

**Order No.: JA910-020** 

### Nanocrystalline $MnFe_2O_4$ produced by niobium doping

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Nano-sized $MnFe_2O_4$ phase with diameters in the range of 13.7 to 100 nm were produced by calcination and sintering treatments in the system $zNb_2O_5 \cdot (50 - z)MnO \cdot 50Fe_2O_3$ with $z$ having values between 0 and 20. $Nb^{5+}$ ions are believed to give rise to the vacancies in the $Mn^{2+}$ sites, which break up the coupling of ferrimagnetically active oxygen polyhedra. The Curie temperature decreases as the size of $MnFe_2O_4$ phase is reduced. This is explained on the basis of a decrease in the number of exchange pairs of the type $Mn^{2+}$–$Fe^{3+}$. The coercivity increases with a decrease in the size of the ferrimagnetic phase. This is believed to arise due to a decrease in saturation magnetization as the size of the $MnFeO_4$ phase is reduced.

**Order No.: JA910-021** 

### Mechanical, tribological, and stress analyses of ion-beam-deposited boron-rich boron nitride films with increasing N content

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Boron (B) films and B-rich $BN_x$ films with different N contents (4.1–40.3 at.%) were deposited by dual ion-beam deposition. The films consist of a B-rich phase constructed of icosahedreal atomic clusters and a graphitelike boron nitride phase. The films with N content ≤20.3 at.% are dominated by the B-rich phase. Their hardness rises with increasing N content to reach the maximum value of 18.8 GPa. The hardness-to-elastic modulus ratio (*H/E*) and the critical load of the films also increase, showing stronger wear resistance of the films. These results can be explained if some N–B–N chains are formed at the interstitial sites in the network of the B-rich phase, which cross-link different icosahedral atomic clusters in the B-rich phase and strengthen the rigidity of the structure. For the films with higher N contents, the volume fraction of the graphitelike boron nitride phase becomes higher, and the hardness drops as a consequence. However, the change in the *H/E* ratio is rather mild. This implies that the wear resistance of the films is not altered and explains why the critical load of the films remains almost unchanged. In addition, the friction coefficient $\mu$ of all the films depends on the normal load $L$ in the form of $\mu = aL^y$, where $a$ and $y$ are numerical parameters and are insensitive to the change in the N content. Furthermore, compressive stress was found to increase from about 0.12 to 1.7 GPa when the N content rises from 4.1 to 40.3 at.%.

**Order No.: JA910-022** 

### Atomic force microscopy study of nanoindentation deformation and indentation size effect in MgO crystals

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The dependences of various nanoindentation parameters, such as depth of penetration $d$, indentation diameter $a$, deformation zone radius $R$, and height $h$ of hills piled up around indents on applied load were investigated for the initial (unrecovered) stage of indentation of the (100) cleavage faces of MgO crystals by square pyramidal Si tips for loads up to 10 μN using atomic force microscopy. The experimental data are analyzed using theories of elastic and plastic deformation. The results revealed that (i) $a$, $R$, and $h$ linearly increase with $d$; (ii) the development of indentation size and deformation zone and the formation of hills are two different processes; (iii) the load-dependence of nanohardness shows the normal indentation size effect (i.e., the hardness increases with a decrease in load); and (iv) there is an absence of plastic deformation involving the formation of slip lines around the indentations. It is found that Johnson's cavity model of elastic–plastic boundary satisfactorily explains the experimental data. The formation of hills around indentations is also consistent with a new model (i.e., indentation crater model) based on the concept of piling up of material of indentation cavity as hills.

**Order No.: JA910-023** 

### Oriented calcium metaphosphase glass-ceramics

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Highly oriented calcium metaphosphate glass-ceramics were obtained directly from the corresponding melt. On the interface between the $Ca(PO_3)_2$ melt and an $Al_2O_3$ rod, the nucleation could easily be induced. The dependence of the crystal growth rate on the crystallization temperatures was determined. The crystal growth rates observed were up to 71 μm/s. The $c$ axes of most crystals were oriented in the direction perpendicular to the surface of the $Al_2O_3$ rod as illustrated by scanning electron microscope and pole figures. The degree of crystal orientation increased with increasing crystallization temperature. At higher temperatures (e.g., at 892 °C), even single-crystal-like dendrites were formed.

**Order No.: JA910-024** 

### Chemical vapor deposition of barium strontium titanate thin films using direct liquid injection of a single cocktail solution with $Ba(methd)_2$, $Sr(methd)_2$, and $Ti(MPD)(tmhd)_2$

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Deposition characteristics of (Ba,Sr)$TiO_3$ (BST) thin films by metalorganic chemical vapor deposition using a mixture solution were investigated. $Ba(methd)_2$ (methd = methoxyethoxytetramethylheptanedionate), $Sr(methd)_2$, and $Ti(MPD)_2(tmhd)_2$ (MPD = methylpentanedioxy, tmhd = tetramethlyheptanedionate) were dissolved together in methanol solvent. Mass spectrometry showed that $Ba(methd)_2$ was less aggregated that $Ba(tmhd)_2$-tetraglyme adduct (tetraglyme = tetraethylene glycol dimethyl ether) in the gas phase. Similar results were obtained from Sr precursors. Step coverage and electrical properties of the BST films were investigated as a function of deposition temperature from 350 to 600 °C. With the increase of the deposition temperature up to 500 °C, Ti composition in the films increased, but Ba and Sr remained almost constant, and the step coverage became poor. Also, leakage current density and $SiO_2$ equivalent oxide thickness were reduced as the deposition temperature increased. The poor incorporation of Ti below the deposition temperature of 500 °C was observed.

**Order No.: JA910-025** 

### Formation of patterned microstructures of polycrystalline ceramics from precursor polymers using micromolding in capillaries

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Micromolding in capillaries has been used to generate patterned microstructures of $ZrO_2$ or $SnO_2$ from its polymeric precursor. After patterning, the amorphous precursor was converted into the desired polycrystalline ceramic material by calcination in air at 460 °C. The final phase for each ceramic material was determined by powder x-ray diffraction. The shrinkage of the precursor material during pyrolysis was investigated by scanning electron microscopy and atomic force microscopy. These ceramic microstructures could be either supported on solid substrates or released as freestanding fibers and membranes. Their lateral dimensions could be as small as approximately 500 nm.

**Order No.: JA910-026** 

### Epitaxial growth of $PbZr_{0.5}Ti_{0.5}O_3$ thin films on (001) $LaAlO_3$ using the chemical solution deposition method

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Epitaxial $PbZr_{0.5}Ti_{0.5}O_3$ (PZT) thin films were grown on (001) $LaAlO_3$ (LAO) substrates (~6.1% lattice mismatch) by the chemical solution deposition method. The sequence of epitaxy during heating between 375 and 700 °C/h

was characterized by x-ray diffraction and transmission electron microscopy. At about 375 °C/h, a nanocrystalline metastable fluorite phase of PZT was formed from the pyrolyzed amorphous precursor. At higher temperatures (400–425 °C/h), thermodynamically stable PZT crystallites were first observed at the interface; with increasing higher temperatures, these nuclei grew across the interface and through the film toward the surface by consuming the metastable nanocrystalline fluorite grains. PZT thin films annealed above approximately 500 °C/h were observed to be dense with an epitaxial orientation relationship of $[100](001)_{PZT}\|[100](001)_{LAO}$. The metastable nanocrystalline fluorite to the stable single-crystal perovskite transformation gives an extra driving force by providing an additional decrease in free energy in addition to a driving force from the elimination of grain boundary area for epitaxy.

**Order No.: JA910-027** 

## The role of Ni and Zr doping on the electrical, optical, magnetic, and structural properties of barium zinc tantalate ceramics

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Properties of Ni- and Zr-doped $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics are reported. The nickel ion has an effective paramagnetic moment of 3.22 ± 0.05. Optical spectra of Ni-doped $Ba(Zn_{1/3}Ta_{2/3})O_3$ are dominated by discrete internal transitions between $Ni^{2+}$ 3*d*-orbitals. Absorption from the $^3\Gamma_2(F)$ ground state to $^4\Gamma_3(F)$, $^3\Gamma_1(D)$, $^5\Gamma_1(D)$, $^4\Gamma_3(P)$ excited states occurs at approximately 1.55, 1.75, 2.50, and 2.80 eV, respectively. The ligand field strength of neighboring oxygen ions ranges from about 7300 $cm^{-1}$ (0.25% Ni) to about 7700 $cm^{-1}$ (1.0% Ni). A significant increase in the visible continuum background is correlated with increased tan δ. This effect is attributed to point defects in the Ni environment, suggesting that point defects play an important role in microwave loss in practical dielectric material.

**Order No.: JA910-028** 

## Temperature effect on nonhydrolytic foaming process

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This paper describes the effect of temperature on the formation of nonhydrolytic alumina foams. The foams are generated by the heat treatment of crystals of the aluminum chloride isopropyl ether complex $[AlCl_3(Pr^i_2O)]$, with the release of isopropyl chloride ($Pr^iCl$). The chlorine content in the foams was determined by titration while their weight loss during sintering was measured by thermogravimetric and differential thermal analysis. Based on these measurements, the condensation degree (CD) in the foams was modeled. The foaming time ranged from several minutes at 70 °C to several seconds at 160 °C. It was found that the chlorine-to-aluminum ratio of the foam (Cl/Al) decreased form 1.79 at 70 °C to 1.56 at 160 °C. Thermogravimetric analysis data confirm that the smaller Cl content gives rise to a smaller weight loss during thermal decomposition, consistent with a higher CD in the foams created at higher temperatures. Finally, about 80% of the $Pr^iCl$ produced during the complex decomposition and subsequent –Al–O–Al– condensation reactions is lost during foaming.

**Order No.: JA910-029** 

## Measurement and improvemenet of the adhesion of copper to polyimide

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A contact angle measurement technique has been used to obtain an estimate of the interfacial energy and thermodynamic adhesive strength between copper and polyimide (PMDA-ODA and BPD-PDA). Values of the strength of adhesion from these contact angle measurements are in reasonable agreement with values calculated using the Girifalco–Good–Fowkes nonpolar interfacial adhesion theory. Based on the surface energy, the prediction that small copper clusters would embed into the polymer matrix if heated under ultrahigh vacuum conditions at temperatures near $T_g$ of the polymer was experimentally observed. Controlled embedding of nanometer clusters was utilized to produce a textured interface, where the partially embedded clusters acted as "nano-nails" to anchor a metal overlayer to the underlying polyimide substrate. These nano-nails greatly increased the bonding between the copper overlayer and the polyimide, as demonstrated by mechanical debonding studies.

**Order No.: JA910-030** 

## Dislocations emission and crack extension at atomistic crack tip in body-centered-cubic metal Mo

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The behaviors of a crack in body-centered-cubic metal Mo under different loading modes were studied using the molecular dynamics method. Dislocation emission was observed near the crack tip in response to mode II loading with $\theta = 0°$ in which $\theta$ is the inclination angle of the slip plane with respect to the crack plane, and two full dislocations were observed at the stress level of $K_{II}$ = 1.17 M $Pam^{1/2}$ without any evidence of crack extension. Within the range of $0° \leq \theta \leq 45°$, crack extension was observed in response to mode I loading, and the effect of crystal orientation on the crack propagation was studied. The crack propagated along the [111] slip direction without any evidence of dislocations emission.

**Order No.: JA910-031** 

## Influence of stacking fault energy on microstructural development in equal-channel angular pressing

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Equal-channel angular (ECA) pressing is a procedure having the capability of introducing an ultrafine grain size into a material. Experiments were conducted to examine the effect of the low stacking fault energy in pure Cu on microstructural development during ECA pressing at room temperature. The results show that the low stacking fault energy and the consequent low rate of recovery lead to a very slow evolution of the microstructure during pressing. Ultimately, a stable grain size of ~0.27 μm was established in pure Cu, but the microstructure was not fully homogeneous even after pressing to a total strain of ~10. It is shown by static annealing that the as-pressed grains are stable up to ~400 K, but at higher temperatures there is grain growth. These results lead to the conclusion that a low stacking fault energy is especially favorable for the introduction of an exceptionally small grain size using the ECA pressing procedure.

**Order No.: JA910-032** 

## Aluminum metallization for flat-panel displays using ion-beam-assisted physical vapor deposition

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Failures in aluminum interconnects in display control devices are often caused by the formation of hillocks during postdeposition annealing. Ion-beam-assisted deposition was used to create a (110) out-of-plane texture in aluminum films to suppress hillocking. X-ray diffraction was used to quantify the (110)/(111) out-of-plane texture ratio, and scanning electron microscopy and atomic force microscopy were used to characterize the surface topology. Results show that no hillocks were observed on (110)-textured aluminum films following annealing for 30 min at 450 °C. Following annealing, the resistivity of the films made by ion-beam-assisted deposition recovered to within a factor of 2 of the physical-vapor-deposition films. Results showed that ion-bean-assisted deposition can effectively modify the aluminum out-of-plane texture in such a way that hillock suppression can be achieved without significant change in resistivity.

**Order No.: JA910-033** 

## Reduction of copper oxide with graphite by mechanical alloying

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The reduction of CuO with different amounts of C (CuO:C = 2:1, 2:1.5, and 2:2 in molar ratio) driven by mechanical alloying was examined by x-ray diffraction and transmission electron microscopy. It was found that reduction behaviors are closely related to the carbon content. The reduction of CuO for the mixture with 1 mol carbon follows a two-step process, i.e., $CuO \rightarrow Cu \rightarrow Cu_2O$. However, the CuO can be completely converted to Cu for the mixtures with higher carbon content. A tentative model in terms of solid-state reactions at the interfaces is propsed to explain the effect of carbon content. Additionally, the thermal responses of the premilled mixtures were investigated by thermogravity and differential thermal analysis followed by x-ray identification. Contrary to mechanical alloying, reduction of CuO during thermal treatment follows a transition sequence of $CuO \rightarrow Cu_2O \rightarrow Cu$. The preferential formation of $Cu_2O$ at the early annealing stage is probably due to the involvement of gaseous reduction.

**Order No.: JA910-034** 

### Nonstoichiometry and lattice parameter of $(Mg_{0.22}Mn_{0.07}Fe_{0.71})_{3-\delta}O_4$ ferrite

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$(Mg_{0.22}Mn_{0.07}Fe_{0.71})_{3-\delta}O_4$ ferrites with different oxygen nonstoichiometry ($\delta$) were prepared in the range of $-0.006 \leq \delta \leq 0.0050$ by a solid-state electrochemical technique, and their lattice parameter–nonstoichiometry correlation was examined. It was found that the lattice parameter decreases with increasing deviation ($|\delta|$) from the stoichiometric composition ($\delta = 0$). The electrochemical technique is detailed and the correlation is discussed in the light of defect structure of the ferrite.

**Order No.: JA910-035** 

### The pyramidal indentation load–depth curve of viscoelastic materials

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The indentation load $P$ versus depth $h$ curves are examined to investigate the time-dependent surface deformation of viscoelastic materials. The viscoelastic $P$–$h$ curves significantly depend on the temperature of measurement and the penetration rate of indentation. The Sneddon's elastic solution of a conical indentation is extended to a viscoelastic one for a conical or a pyramidal indentation in terms of the hereditary integral. Several types of viscoelastic problems are discussed in relation to the test techniques and analyses for determining the relaxation modulus $E(t)$ and the creep compliance $D(t)$. The superposition rules of time–temperature, penetration depth–temperature, and penetration depth–penetration rate are examined. The viscoelastic indentation rests (constant rate penetration test and constant load creep test) of amorphous Se are conducted at temperatures from 10 to 42 °C. The theoretical considerations and the test results encourage pyramidal indentation as an efficient microprobe for the viscoelastic characterization, in particular, of extremely small-size test specimens, and ceramic, metal, and polymer thin films coated on substrate.

**Order No.: JA910-036** 

### Initial hillock formation and changes in overall stress in Al–Cu films and pure Al films during heating

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The effect of adding a few percent (3 at.%) Cu to Al films on the initial hillock formation and the changes in overall film stress were studied. Al films were evaporated by an electron-beam gun onto Si wafers in an ultrahigh vacuum deposition system, and Al–Cu films were coevaporated using a thermally heated source for the Cu. The as-deposited samples were radiatively heated at 3 °C/s in air environment. During heating, measurements of the initial hillocking and the changes in overall stress were performed simultaneously and in real time with a specially designed optical instrument. The measurement principle of this instrument is based on laser beam deflection, caused by wafer bending due to film stress, and collection of the laser light scattered off from the hillocks appearing on the film surface. The experimental results show that Cu alloying has a strengthening effect on Al films resulting in a delayed and considerably reduced hillock formation. Prior to heating, the as-deposited Al–Cu samples were investigated by total integrated scattering and atomic force microscopy. These investigations showed that Al–Cu films are considerably smoother and have smaller grains than Al films of similar (340 nm) thickness. It was found that the small grains of Al–Cu films contribute to increasing the tensile stress–temperature slope. In addition, Al–Cu films can withstand higher compressive stresses than Al films.

**Order No.: JA910-037** 

### Czochralski growth and spectroscopic investigations of $Yb^{3+}$, $La^{3+}$:$Na_2SO_4$(I) and $Nd^{3+}$:$Na_2SO_4$(I)

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$Ln^{3+}$-stabilized $Na_2SO_4$ (phase I) single crystals were grown by the Czochralski method. Differential thermal analysis revealed the influence of the ionic radius of $Ln^{3+}$ on the stabilization of $Na_2SO_4$(I). Distribution coefficients were measured by the inductively coupled plasma optical emission spectroscopy method and x-ray fluorescence spectroscopy. Spectroscopic investigations yielded absorption cross sections of $0.6 \times 10^{-20}$ cm$^2$ ($\pi$-polarized, 928.5 nm) and $1.5 \times 10^{-20}$ cm$^2$ ($\pi$-polarized, 797.3 nm) for $Yb^{3+}$, $La^{3+}$:$Na_2SO_4$ and $Nd^{3+}$:$Na_2SO_4$, respectively. Crystal growth of $Gd^{3+}$ stabilized $Na_2SO_4$(I) provides an interesting new material for stimulated Raman scattering experiments.

**Order No.: JA910-038** 

### A novel bulk sol-gel process to prepare monolithic silica materials

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A bulk sol-gel process has been developed to prepare transparent and monolithic silica materials at room temperature. The process involves an acid-catalyzed hydrolysis of tetraethyl orthosilicate in tertahydrofuran containing aqueous HCl catalyst, followed by neutralization with carbonate salts, extraction with aliphatic nonpolar solvents, molding, gelation, and drying. This method shortens the processing time from weeks for the conventional sol-gel process to several days. The silica objects prepared from the process are transparent, crack-free, and of relatively low volume shrinkage (e.g., 52%) and high silica content (e.g., 82%).

**Order No.: JA910-039** 

### Strain gradient plasticity effect in indentation hardness of polymers

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Plasticity in material is typically described as a function of strain, but recent observations form torsion and indentation experiments in metals suggested that plasticity is also dependent on strain gradient. The effects of strain gradient on plastic deformation in thermosetting epoxy and polycarbonate thermoplastic were experimentally investigated using nanoindentation and atomic fore microscopy in this study. Both thermosetting and thermoplastic polymers exhibited hardening as a result of imposed strain gradients. Strain gradient plasticity theory developed on the basis of a molecular kinking mechanism has predicted strain gradient hardening in polymers. Comparisons made between indentation data and theoretical predictions correlated well. This suggests that strain gradient plasticity in glassy polymers is determined by molecular kinking mechanisms.

**Order No.: JA910-040** 

### Solvent-induced stresses in glassy polymer: Elastic model

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The solvent-induced stresses in glassy polymers were investigated. The mass transport accounts for case I, case II, and anomalous transport. Case I transport is attributed to the concentration gradient, whereas case II transport is attributed to the stress relaxation. Anomalous transport is the mixture of case I and case II. Both one-side and two-side mass transports with the boundary condition of constant surface concentration are considered. The stresses and longitudinal displacement arising from the mass transport are formulated based on the linear elasticity theory The maximum stress is always located at the surface at the initial time. The stresses are a function of the partial molal volume, Young's modulus, and Poisson's ratio. From the longitudinal displacement data, the partial molal volume was determined.

**Order No.: JA910-041** 