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COMMUNICATIONS

Precursor Pathway to Superconducting $HgBa_2(Ca_{0.86}Sr_{0.14})_2Cu_3O_{8+\delta}$ with a T_c of 132 K

N.H. Hur, N.H. Kim, Y.K. Park, J.C. Park
(Korea Research Institute of Standards and Science)

Polycrystalline samples of $HgBa_2(Ca_{0.86}Sr_{0.14})_2Cu_3O_{8+\delta}$ (denoted as Hg-1223) were prepared by a precursor route, which involves the reaction between HgO and two precursors: Ba_2CuO_{3+x} and $Ca_{0.86}Sr_{0.14}CuO_2$. X-ray powder diffraction analysis revealed that the Hg-1223 is isostructural with pristine $HgBa_2Ca_2Cu_3O_{8+\delta}$ and $TlBa_2Ca_2Cu_3O_{9-\delta}$. The Hg-1223 has tetragonal symmetry with space group *P4/mmm*, and lattice parameters a =3.8648(2) Å and c=16.0319(2) Å. The as-synthesized Hg 1223 sample has a T_c of about 126 K. After annealing in an oxygen atmosphere at 280°C for 10 h, the T_c increased to 132 K. Using this precursor pathway, Hg-1223 samples can be reproducibly synthesized.

Order No.: JA512-001

Microstructure and Diffusion in Nb/$NbSn_2$ Metal Bonding Structure

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This communication reports on the microstructure and interdiffusion observed in a new $NbSn_2$/Nb metallization structure on SiO_2, previously reported.[1] The as deposited $NbSn_2$ layer was found to be amorphous. After heating, the $NbSn_2$ becomes polycrystalline and heavily diffused with Au from the Au-Sn solder. The Nb layer remains pure and intact after heating. The microstructure, compositions and phases of the Au-Sn solder layer are also presented.

Order No.: JA512-002

Lattice Distortion Effects on Electrical Switching in Epitaxial Thin Film $NdNiO_3$

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Crystalline thin films of $NdNiO_3$ have been epitaxially grown on the (100) face of single crystal $LaAlO_3$ substrates. These films exhibit the characteristic reversible change in electrical conductivity with temperature previously observed in bulk polycrystalline material. The temperature of the electrical transition in the epitaxial thin films was lower than reported for the bulk polycrystalline ceramics. This effect is attributed to lattice strains associated with the film processing and interfacial lattice matching constraints.

Order No.: JA512-003

Patterning of Dielectric Oxide Thin Layers by Microcontact Printing of Self-Assembled Monolayers

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This communication describes a technique used to pattern oxide thin layers using microcontact printing (μCP) and sol-gel deposition. The technique involves μCP of self-assembled monolayers (SAMs) of alkylsiloxane on various substrates (SiO_2/Si, sapphire, indium tin oxide (ITO) and glass), followed by deposition of oxide thin layers from sol-gel precursors. Delamination of oxide layers from SAM-derivatized regions allows selective deposition of crystalline dielectric oxide layers on underivatized regions. To demonstrate the viability of this technique for integrated microelectronics and optics applications, patterned $(Pb,La)TiO_3$ (PLT) and $LiNbO_3$ layers were deposited on ITO and sapphire substrates, respectively. Use of lattice-matched substrates allows lithography-free deposition of patterned heteroepitaxial oxide layers. Strip waveguides of heteroepitaxial $LiNbO_3$ with 4 μm lateral dimensions were fabricated on sapphire. Dielectric measurements for patterned PLT thin layers on ITO are also reported.

Order No.: JA512-004

Synthesis of Functionally Graded Metal-Ceramic Microstructures by Chemical Vapor Deposition

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A composite microstructure consisting of small α-Al_2O_3 particles dispersed in a β-NiAl coating matrix was synthesized by chemical vapor deposition (CVD). While the surface of a pure Ni substrate was being reacted with $AlCl_3$ and H_2 to form β-NiAl at a temperature of 1050°C, the partial pressure of CO_2 in the reactor was controlled via pulsing to nucleate and disperse 50 to 500 nm α-Al_2O_3 particles in the β-NiAl matrix. The relative amount of the α-Al_2O_3 phase increased with coating thickness as the rate of the β-NiAl formation decreased with time. These experimental observations suggest that the synthesis of a graded composite microstructure by the CVD method is feasible.

Order No.: JA512-005

Grinding Force and Microcrack Density in Abrasive Machining of Silicon Nitride

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The relationship between grinding forces and the material's resistance to microfracture is investigated in abrasive machining of silicon nitride ceramics. Surface grinding is performed on two forms of silicon

nitride with different microstructures and the grinding forces are measured. In addition, single-point scratching is performed on polished surfaces to amplify the damage associated with the action of an individual abrasive particle in grinding. A thermal wave measurement technique is then used on the cross-sections to characterize the density of subsurface microcracks associated with scratching. Compared to a fine-grain silicon nitride, the density of microcracks in a coarse-grain silicon nitride is significantly larger, while the grinding force is smaller. The smaller grinding force for the coarse-grain silicon nitride is attributed to the ease of local intergranular microfracture and grain dislodgement during grinding.
Order No.: JA512-006

ARTICLES

NdBCO Melting and Solidification by a Zone Melting Method

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In a Nd-Ba-Cu-O system, a directional structure produced by a peritectic reaction has been observed. On heating, the sintered $Nd_1Ba_2Cu_3O_{6+\delta}$ (Nd123) precursor formed a rod-like directional structure of $Nd_4Ba_2Cu_2O_{10}$ (Nd422) phase. These Nd422 rods became thicker from the melting interface to the solidified interface. [100] direction of Nd422 crystal is parallel to the axis of Nd422 rod and the sample pulling direction. Moreover, Nd422 rod spacing was observed as a function of growth rate and decreased with an increase of growth rate. In addition, with an increase of growth rate, Nd123 solidified interface morphologies changed from planar, cellular to equiaxed.
Order No.: JA512-007

Thin Film Deposition and Interface Characterization of YBCO on $LiNbO_3$ Substrates

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High transition temperature superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) thin films have been epitaxially grown on YZ-cut $LiNbO_3$ (LNO) substrates by the pulsed laser deposition technique. The interface between YBCO and LNO has been systematically investigated by scanning electron microscopy, atomic force microscopy, Auger electron spectroscopy and x-ray photoelectron spectroscopy. Off-stoichiometry $LiNbO_x$ phases are found to segregate on the substrate surface because of lithium and oxygen vacancies formed during the high temperature YBCO growth. These submicro-meter particles are observed along the Z-axis on the X-Z plane of LNO with a height of ~30 nm above the LNO surface. This rough growth surface results in $YBa_2Cu_3O_{7-x}$ thin films grown on the LNO surface that have reduced J_c and T_c, possibly limiting the use of YBCO/LNO heterostructures for surface acoustic wave (SAW) devices.
Order No.: JA512-008

Preparation of $LaBa_2Cu_3O_y$ Thick Films in the La-Ba-Cu-O System by Partial Melting Techniques

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The preparation of thick films of the $LaBa_2Cu_3O_y$ (La-123) phase by using partial melting technique (PMT) of powders deposited on MgO substrates by drying alcoholic suspensions is reported. The effects of the starting composition, processing time (t) and temperature (T) on the superconducting properties of the $La_{1+x}Ba_2Cu_3O_y$ ($-0.25 \le x \le 0.5$) system were investigated. The presence of the $La_4Ba_2Cu_2O_y$ (La-422) phase was detected in the samples quenched in liquid N_2 after heating up to 1200°C. The crucial step of the processing is the cooling rate down to the crystallization temperature, T_p, determined by DTA analysis, in order to favor the formation of the La-123 phase from the reaction between the La-422 solid phase and the liquid. The superconducting properties, tested by magnetization measurements, showed a diamagnetic onset temperature ($T_{c,diam}$) as high as 89 K.
Order No.: JA512-009

New Method for Rapid Determination of Crystal Orientation via Kikuchi Patterns

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(Northwestern University)

Kikuchi electron diffraction patterns are used extensively to determine crystal orientations via transmission electron microscopy (TEM) or in the electron backscattering pattern (EBSP) mode of scanning electron microscopy (SEM). A new method is presented that is capable of finding crystal orientations, the camera length and the projection center from only one pattern per grain using a least-squares technique. This method eliminates the need to perform an alignment with a reference crystal in the backscattering mode. Application to a $\Sigma = 13a$ silicon bicrystal is presented for TEM patterns and EBSPs. A complete analysis of the propagation of random measurement errors into the disorientation axis/angle pair is carried out. The root mean square deviation from the nominal disorientation angle is found to be 0.3° in the case of TEM and 0.5° in the case of EBSP. The root mean square inclination between the nominal and measured disorientation axis is found to be 1° in the case of TEM and 0.5° in the case of EBSP.
Order No.: JA512-010

Morphology of Twinned Diamond Particles

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The morphology of twinned diamond particles grown by chemical vapor deposition was characterized by atomic force microscopy in both contact and tapping modes. Quantitative angle measurements using a surface normal algorithm were performed on untwinned crystals, penetration twins, re-entrant corners, and five-fold dimples. Tip-sample interaction is discussed. The morphology of the penetration twins and some of the re-entrant corners can be explained by low order $\Sigma 3$ twins and flat crystallographic surfaces. Abnormally shallow re-entrants with large vicinal faces are attributed to rapid nucleation of new layers at a point along the re-entrant intersection.
Order No.: JA512-011

Microstructural Evolution of Diamond/Si (100) Interfaces with Pretreatments in Chemical Vapor Deposition

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Diamond was deposited on Si(100) substrates by microwave plasma-assisted chemical vapor deposition method in three steps: carburization, biasing and growth. High-resolution transmission electron microscopy in cross-sectional view has been used to observe the evolution of microstructures around the interfacial region between diamond and Si in each processing step. The chemistry near the interface was characterized with elemental mapping using energy-filtered imaging technique with electron energy loss spectroscopy. An amorphous carbon layer, β-SiC and diamond particles, and graphite plates have been observed in the carburization stage. β-SiC can form in epitaxial orientation with Si in the following stage of biasing. Graphite and amorphous carbon were not observed after the bias was applied. Diamond grains were aligned in a strongly textured condition in the growth stage. It has been found that diamond, SiC and Si all have (111) planes in parallel. The relation of the evolution of microstructure with the processing conditions is also discussed.
Order No.: JA512-012

Investigation of Structurally Less Ordered Areas in the Nb Filaments of a Heavily Cold Rolled Cu-20wt.% Nb *In-Situ* Composite

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A fiber reinforced *in-situ* metal matrix composite (MMC) consisting of copper (Cu) and 20 mass% niobium (Nb) was produced by large strain cold rolling. The rolled MMC revealed a very high strength combined with good electrical conductivity. The microstructure of single Nb filaments was investigated employing transmission electron microscopy (TEM). In heavily rolled specimens (ε_{max}=99.4%) randomly arranged dislocations as well as dislocation cells were observed. Furthermore, structurally less ordered areas were discovered, the size of which frequently extended over the entire filament width. The shrinkage of these zones during heating was directly observed in the TEM. The impact of such structurally less ordered areas on the strength was assessed. The discovery of the degradation of structural regularity in the Nb filaments of heavily cold worked Cu-20wt% Nb shows that the underlying microstructural mechanisms responsible for the high strengths observed are far from being understood and that the strain hardening models for Cu-based *in-situ* composites currently discussed do not yet account for all relevant microstructural features.

Order No.: JA512-013

Structural Properties and Thermal Stability of Fe/Al_2O_3 Multilayers

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Iron/alumina multilayers have been deposited on sapphire wafers using RF magnetron sputtering. To study the interdiffusion, the multilayers were annealed in a tubular furnace under a 10^{-7} mbar vacuum, and the samples examined by using a combination of classical diffractometry ($\Theta/2\Theta$) and grazing incidence scattering (GIS) for the phase determination, and small angle x-ray scattering (SAXS) for the superstructure of the multilayers. In all cases, in the as-deposited state the alumina is amorphous and the iron is crystalline in the bcc phase. Thermal anneals at temperatures between 573 and 873 K give evidence for segregation to the interfaces. At higher temperatures, interdiffusion occurs leading to the formation of different phases. The Fe-Al_2O_3 interdiffusion coefficient has been evaluated in the temperature range from 873 to 1273 K.

Order No.: JA512-014

Novel Thin Films of Titanium Dioxide Particles Synthesized by a Sol-Gel Process

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Novel thin films of ultra-fine titanium dioxide particles dispersed in a matrix of hydroxypropylcellulose (HPC) polymer have been made on quartz and silicon substrates. The titanium dioxide particles were made by the hydrolysis and condensation of titanium tetraethoxide (TEOT) in solutions of HPC in a mixture of ethanol and water. HPC controlled the particle size by adsorbing at the particle surface during the growth process and generating repulsive steric forces. The TiO_2/HPC composite films were transparent in the visible region and completely blocked ultra violet radiation at 300 nm. These films were crack-free and uniform in composition and thickness. Transparent films of amorphous TiO_2 were made by burning out the HPC at 500°C. These films were highly uniform and had no macroscopic cracks. X-ray diffraction revealed a transition to the anatase form upon sintering at 600°C. A film sintered at 700°C had a porosity of 38%. The crystalline films remained transparent until they densified at 800°C.

Order No.: JA512-015

Sputtered Amorphous Carbon Nitride Films

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The recent announcement of the synthesis of C_3N_4 has increased interest in this unique material. Carbon nitride may have several useful applications as wear and corrosion resistant coatings, electrical insulators, and optical coatings. We have produced amorphous carbon nitride coatings containing up to 40% nitrogen using planar magnetron RF sputtering with and without an ion beam in a nitrogen atmosphere. Both WDX and XPS indicate this composition. Coatings up to 2 μm thick were produced on alumina, silicon, SiO_2, and glass substrates using a graphite target. Films with transparency greater than 95% in the visible wavelengths and harder than silicon have been produced. The properties of these films are correlated with composition, fabrication, conditions, and subsequent heat treatments. STM and TEM were used to characterize the morphology of the films. XPS studies confirm the stability of a carbon nitrogen phase up to 600°C. Compositional variations were determined with SIMS depth profiling and the Raman spectra are compared with those of carbon and carbon nitride films prepared by other methods.

Order No.: JA512-016

A Transmission Electron Microscopy Study on the Decomposition of Synthetic Hillebrandite ($Ca_2SiO_4 \cdot H_2O$)

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The decomposition mechanism of hillebrandite ($Ca_2SiO_4 \cdot H_2O$) to larnite (β-Ca_2SiO_4) was studied by conventional and *in-situ* hot-stage transmission electron microscopy (TEM) methods. The hillebrandite structure is suggested to be a composition of parawollastonite ($CaSiO_3$) and portlandite ($Ca(OH)_2$) adjoining on {001} planes. The larnite fibers showed occasional bending and kinking as well as internal defects such as dislocations and domains. No transformation-related microstructures such as twinning were observed. The preferred orientations in the larnite fibers were not distinct. The decomposition mechanism of hillebrandite in air and in a vacuum may be different. In air, the CaO from the decomposed portlandite layer directly participates in the process of SiO_4 chain breaking to form larnite. In the TEM this CaO is removed and apparently reprecipitated, so that hillebrandite converts directly to parawollastonite. A possible lattice correspondence between hillebrandite (C_2SH) and larnite (β-C_2S), based on crystallographic considerations, is proposed to be: $\underline{b}_{C2SH} // \underline{b}_{\beta\text{-}C2S}$, $\underline{a}_{C2SH} // \approx [102]_{\beta\text{-}C2S}$, and $\underline{c}_{C2SH} // \approx [401]_{\beta\text{-}C2S}$.

Order No.: JA512-017

Memory Effect of ZrO_2 Matrix on Surface Co_3O_4-CoO Transition

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Cobalt oxide system Co_3O_4-CoO has been studied on the ZrO_2 matrix surfaces with FTIR and XPS. The tetragonal and monoclinic ZrO_2 matrix materials have been synthesized from Zr-n-propoxide-acetylacetone-water-isopropanol system. The study shows that the ZrO_2 matrix is able to retain the relative Co_3O_4:CoO population at elevated temperatures. The thermodynamically stable oxide population (Co_3O_4:CoO) at room temperature for ZrO_2-supported Co_3O_4-CoO is about 50:50 (Co^{2+}:Co^{3+} = 2:1), which is markedly different from the 100:0 case (Co^{2+}:Co^{3+} = 1:2) for an unsupported Co_3O_4-CoO surface oxide system. The relative Co_3O_4:CoO ratio in the surface region of the ZrO_2 is temperature dependent but matrix-polymorph independent. The composition of an oxide solid solution formed by the Co_3O_4-CoO and matrices of ZrO_2 is determined to have a cobalt molar percentage of 4.5%. Diffusion thermody-

namic quantities are investigated and the measured diffusion activation energy for a cobalt ion in the ZrO_2 matrices is 0.21 eV. The mechanism of the ZrO_2 memory effect on surface Co_3O_4-CoO transition will also be addressed.

Order No.: JA512-018

Preparation of Well-Defined Colloidal Barium Titanate Crystals by the Controlled Double-Jet Precipitation

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A new method for the preparation of well-defined colloidal barium titanate ($BaTiO_3$) crystals by the controlled double-jet precipitation (CDJP) technique is described. The process is extremely fast and requires a low temperature (<100 °C). The reactants, barium and titanium salts, can be used in high concentrations and the yield is quantitative. The stoichiometry of the $BaTiO_3$ particles can be controlled precisely and reproducibly. The effects of the composition of reactant solutions, flow rates, reaction time, and the addition of polymers on the precipitation process were investigated. The $BaTiO_3$ powders, produced by the CDJP technique, sinter to high density at a temperature as low as 1200°C and exhibit a relative dielectric constant of 5000 at 20°C, which is the highest value reported in the literature. The grain sizes of the sintered samples are small and uniform, ranging between 1 and 2 μm.

Order No.: JA512-019

Determination of Diamond [100] and [111] Growth Rate and Formation of Highly Oriented Diamond Film by Microwave Plasma-Assisted Chemical Vapor Deposition

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A novel method was proposed for measuring epitaxial growth rate of diamond by microwave plasma-assisted chemical vapor deposition (MPCVD). Cubo-octahedral crystals were formed on an Si (100) wafer and were used as the substrate in the homoepitaxial growth. Growth rates of the {100} and {111} were simultaneously measured from the change in the top view size of crystals. Thus, the relative growth rate of {100} to {111} was obtained without any limitation of its value. The homoepitaxial growth rate was strongly affected by the type of diamond faces, CH_4 concentration in the gas phase and deposition temperature. The growth rate of {100} was more dependent on CH_4 concentration than that of {111}, while the activation energy for the [100] growth was about half that for the [111] growth. These tendencies were in accordance with growth mechanisms proposed for each diamond plane. Reaction conditions were optimized based on the relative growth rate of (100) to (111) planes, and a highly oriented (100) diamond film with a quite smooth surface was formed on an Si (100) wafer.

Order No.: JA512-020

Analysis of Nitride Films on Silicon Substrates by Ion Beam Methods

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The simultaneous determination of light element contamination levels and accurate nitrogen-to-metal ratios in nitride thin films deposited on silicon substrates is demonstrated by using α-particle beam energies in the range 3-4 MeV. In this energy range, significant light element sensitivity enhancements are observed, while the heavy elements show classical Rutherford behavior. The use of resonance scattering at different resonance energies is shown to be the method of choice for analyzing BN films on silicon. Also, a technique is suggested for analyzing very thin films in which an aluminum foil substrate and buffer layer are used to enhance sensitivities.

Order No.: JA512-021

Self-Propagating High-Temperature Synthesis of TiC and NbC by Mechanical Alloying

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Titanium and niobium carbides have been synthesized through self-propagating high-temperature reaction by mechanically alloying the elemental powder mixtures. It is found that this reaction is very similar to the conventional self-propagating high-temperature synthesis (SHS) process, but the ignition of the reaction is identified to be the mechanical collisions instead of heating the materials. Analysis of the products reveals that the final products of Ti-C system are in good agreement with the equilibrium phase diagram, showing less relation with the alloying process. The decrease of the C content shortens the milling time prior to the SHS reaction of TiC by promoting the intimate mixing of the components, but lowers the heat release of the reaction and makes the propagation of the reaction more slowly. The SHS reaction during the mechanical alloying of the Nb-C system shows little difference, but the decrease of the C content can hardly influence the milling time prior to the reaction. By lowering the heat release of the SHS reaction of NbC, it lowers the reaction propagating rate. Mechanical alloying $Nb_{50}C_{50}$ and $Nb_{55}C_{45}$ results in the formation of NbC, while mechanical alloying $Nb_{60}C_{40}$ results in NbC + Nb instead of NbC + Nb_2C according to phase diagram. This contributes to the rapid SHS reaction favoring the formation of NbC, but hindering the occurrence of Nb_2C phase through slow diffusion between NbC and the residual Nb. The measurement of the lattice parameters of TiC and NbC for different compositions affirms the observed results. The particle sizes of obtained TiC and NbC are very fine around, or even less than, 1 μm.

Order No.: JA512-022

Structural Characterization of Ti-Implanted AlN

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Sintered AlN ceramics were implanted by $1x10^{17}$ Ti/cm^2 at an energy of 70 keV in order to investigate the role of the chemical properties of the implanted species on the phase formed during the implantation process. The implanted ions were found in a depth profile corresponding to the calculated distribution of the vacancies produced during the implantation process instead of the predicted ion profile. Identification of the local environment of Ti and of the resulting phase led us to conclude that Ti is surrounded by N after the collision cascade and forms TiN after post-implantation annealing. The TiN nucleus is formed by substitution of Al by Ti. Therefore, the heat of formation, which is more negative for TiN than for AlN, is found to be a key parameter to predict the final system.

Order No.: JA512-023

A Phase Transformation Study in $BaO.Al_2O_3.2SiO_2$(BAS)-Si_3N_4 System

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A phase transformation study was carried out with barium aluminosilicate (BAS) forming powders ($BaCO_3$, Al_2O_3 and SiO_2) in a BAS-Si_3N_4 system. Powders were heat treated in air at one atmospheric pressure at different temperatures from 600° to 1150°C at an interval of 50°C to study the phase transformations during the formation of BAS. The phase transformations of α to β-Si_3N_4 is studied by heat treating the powders at 1600°C for different sintering times in a nitrogen environment at one atmospheric pressure. Formation of different phases were identified by using powder x-ray diffraction. Formation of different forms of barium silicates occur as an intermediate step between 650° to 950°C and hexagonal BAS forms between 900° and 950°C. The hexagonal form of BAS always forms first and persists as a metastable phase in the composites with no evidence of the monoclinic phase. An attempt made to

fully transform hexagonal BAS to monoclinic BAS by using LiF as a mineralizer proved to be successful. The hexagonal form of BAS forms first when heat treated at 1000°C and is fully transformed to monoclinic BAS when heat treated at 1100°C.
Order No.: JA512-024

Phase Transformations in Rapid Thermal Processed Lead Zirconate Titanate (PZT)
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The crystallization kinetics of the pyrochlore to perovskite phase transformation in PZT thin films have been analyzed using rapid thermal processing (RTP). Sol-gel PZT thin films, fabricated on platinum electrodes, were annealed at 550°C to 650°C with hold times ranging from 1 sec to 5 min. Glancing angle x-ray diffraction (XRD) was used for depth profiling to identify the location of phases in the films. Transmission electron microscopy (TEM) provided information on grain structure, nucleation and growth. The phase information was correlated to the ferroelectric and dielectric properties. The perovskite phase nucleated in the pyrochlore phase throughout the film thickness, and at 650°C the transformation was complete in 15 sec. Fast growing (100) PZT nucleated at the platinum and consumed a small grained matrix until a columnar structure was obtained. A ramp rate of 100°C/s was sufficiently fast to prevent transformation during heating and allowed the direct application of an Avrami model for transformation kinetics. An activation energy of 610 kJ/mol was determined.
Order No.: JA512-025

A Model for Microwave Processing of Compositionally Changing Ceramic Systems
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A finite-difference model was used to simulate the temperature and composition distributions produced inside a specimen heated with microwave energy during a process involving a change in composition. The dielectric properties of the specimen change with composition, resulting in non-uniform microwave power absorption and steady state temperature gradients. When the specimen becomes less lossy as it reacts, or if the changes in the microwave heating properties are gradual, the reaction proceeds relatively uniformly and the volumetric microwave heating creates an inside out reaction profile leading to increased conversions for processes such as reaction bonding and chemical vapor infiltration (CVI). If the specimen becomes more lossy as it reacts, then the reaction proceeds non-uniformly with rapid reaction rates in the hottest parts of the specimen and little or no reaction in the cooler areas. The process may then occur as a reaction front which moves along the specimen, as with combustion synthesis. This type of processing has potential advantages and disadvantages depending on the system.
Order No.: JA512-026

Phase Characterization and Burning Rate in the Self-Propagating High Temperature Synthesis (SHS) of Titanium Borides
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Combustion synthesis of titanium borides from Ti and B binary powder mixtures having molar ratios B/Ti of 1.9 to 2.4 resulted in the formation of TiB_2 as the primary phase and TiB as the secondary phase. The amount of TiB decreased when the particle size of the Ti in the powder mixtures became small and when the B content was increased. The results are discussed in terms of the homogeneity of reactant powder mixtures and the degree of boron saturation of the Ti-B melt. The burning rate increased from 11 to 15 mm/s as the titanium particle size decreased from -100 to -325 mesh with the same boron particle size of -325 mesh.
Order No.: JA512-027

Dielectric and Piezoelectric Properties of Thermally Annealed $Pb(Zn,Mg)_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ System Across Rhombohedral/Tetragonal Morphotropic Phase Boundary
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Effects of thermal annealing on the dielectric/piezoelectric properties of $Pb(Zn,Mg)_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ ceramics (PZMN-PT with Zn/Mg = 6/4) were examined across the rhombohedral/tetragonal morphotropic phase boundary (MPB). Examination of the lattice parameters and the rhombohedral angle indicated that the MPB is in the vicinity of 24 mol% $PbTiO_3$. Both the relative dielectric permittivity (ε_r) and the piezoelectric constant (d_{33})/electromechanical coupling constant (k_p) were increased by thermal annealing (800°~900°C) after sintering at 1150°C for 1 h. The observed improvements in the dielectric and piezoelectric properties were attributed to the elimination of PbO-rich amorphous intergranular layers (about 1 nm thickness) induced by thermal annealing. Both the dielectric analysis using the series mixing model and the microscopic examination by transmission electron microscopy supported this conclusion.
Order No.: JA512-028

Microstructural Effects on Dielectric and Piezoelectric Behavior of Calcium-Modified Lead Titanate Ceramics
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This work presents an analysis on the main microstructural parameters that affect the dielectric and piezoelectric behavior of ceramics of calcium-modified lead titanate with Ca/Pb = 26/74. To this aim, ceramics were prepared under different sintering conditions to get a series of materials with different microstructures. Compositional and microstructural characterization were achieved by x-ray diffraction, energy dispersion spectroscopy and optical microscopy. Computerized image analysis was carried out on the micrographs to determine grain and pore size distributions. These distributions were thoroughly analyzed using probability plots. Electromechanical coupling factors and piezoelectric coefficients were measured by the resonance method on thickness poled thin disks and rectangular bars. A similar combined effect of the grain size and the percentage of porosity on the inverse of the permittivity, the coupling factors at room temperature and the temperature behavior of the electromechanical coupling factor k_{31}, is found.
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Preparation of $La_{1-z}Sr_zCo_{1-y}Fe_yO_{3-x}$ Thin Films, Membranes, and Coatings on Dense and Porous Substrates
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A modified Pechini process has been successfully developed for preparation of thin films of $La_{1-z}Sr_zCo_{1-y}Fe_yO_{3-x}$ (LSCF) on both dense and porous substrates. Results indicate that the most important processing parameter is the ratio of the polymerization/complexation agent to metal ions. Ceramic films derived from solutions with a relatively low ratio of citric acid to metal ions are usually cracked, while films derived from solutions with a relatively high ratio are crack-free and uniform. The use of ethylenediamine as an additional chelating agent further improves film quality, especially the adhesion and uniformity of the films. A single coating of solution typically yields a ceramic film of thickness about 0.4 micron, and thicker films can be prepared by application of successive coatings. For deposition of thin-film membranes on a porous substrate,

however, it is necessary to modify the surface of the porous substrate in order to prevent solution from infiltrating into the pores due to capillary force, and to prevent oxide films from cracking due to surface roughness. The application of an intermediate polymer film to the surfaces of porous substrates has effectively overcome the problems and has resulted in uniform, non-porous membranes of LSCF on porous substrates. Successful deposition of thin-film ceramic membranes on porous substrates is important to fabrication of various ionic and micro ionic devices based on ceramic thin films.

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Characterization of Single Layer PZT(53/47) Films Prepared from an Air Stable Sol-Gel Route

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Single layer $Pb(Zr_{0.53}Ti_{0.47})O_3$ films up to 0.7 μm thick have been prepared from air-stable titanium and zirconium precursors using a diol based sol-gel route. Information on film crystallization, surface microstructure and electrical properties under different firing temperatures and three different heating rates including rapid thermal annealing are presented. Films exhibited (111) preferred orientation, the extent of which reduced with increasing firing temperature or heating rate. It is possible that a $PbPt_x$ interfacial reaction product was formed during the prefiring step at 350°C and this, together with the influence of the 111 bottom platinum electrode, contributed to (111) orientation in the PZT films. Surface microstructure was also influenced by firing temperature and heating rate as well as by film thickness. The 0.4 μm thick films used for electrical measurement had a grain size of ≤0.1 μm, whereas 0.7 μm thick films made from concentrated sols exhibited "rosette" microstructures with grain sizes up to 0.5 μm. Among three firing schedules studied, directly inserting the gel coatings in a furnace preset at 700°C produced films with the most favorable electrical properties. A 0.4 μm thick film gave rise to a remanent polarization, P_r, of 33 μC cm^{-2}; coercive field, E_c, of 46 kV cm^{-1}; relative permittivity, ε_r, of 1100 and dissipation factor, D, of 0.05. For a 0.7 μm single layer film, the respective values were 21 μC cm^{-2}; 36 kV cm^{-1}; 1300 and 0.05.

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High-Temperature Oxidation Behavior of Reaction-Formed Silicon Carbide Ceramics

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The oxidation behavior of reaction-formed silicon carbide (RFSC) ceramics was investigated in the temperature range of 1100 to 1400°C. The oxidation weight change was recorded by TGA; the oxidized materials were examined by light and electron microscopy, and the oxidation product by x-ray diffraction analysis (XRD). The materials exhibited initial weight loss, followed by passive weight gain (with enhanced parabolic rates, k_p), and ending with a negative (logarithmic) deviation from the parabolic law. The weight loss arose from the oxidation of residual carbon, the enhanced k_p values from internal oxidation and the oxidation of residual silicon, while the logarithmic kinetics is thought to have resulted from crystallization of the oxide. The presence of a small amount of $MoSi_2$ in the RFSC material caused a further increase in the oxidation rate. The only solid oxidation product for all temperatures studied was silica.

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