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COMMUNICATIONS

Experimental investigation of the Y_2BaCuO_5 surface free energy during peritectic solidification of YBCO
W. Lo, D.A. Cardwell, J.C.L. Chow, H-T. Leung
(University of Cambridge)

The characteristic inhomogeneous distribution of non-superconducting Y_2BaCuO_5 (211) inclusions in melt processed $YBa_2Cu_3O_{7-\delta}$ (123) grains has generally been attributed to 211 particle pushing by 123 growth fronts during peritectic solidification on the basis of reduced total surface free energy. Analysis of the morphology of the interfaces at the 211-211-123 and 211-211-liquid triple points in seeded melt processed samples invalidates this assumption for the pure YBCO system and has implications for the mechanism of 211 particle segregation.
Order No.: JA808-001

Precipitation of carbon nanoparticles encapsulating silicon carbide from molten oxide
M. Mitomo*, C-M. Wang+, H. Emoto#
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A kind of fullerenes, carbon nanoparticle encapsulating β-SiC grain, was precipitated during cooling Al_2O_3-Y_2O_3-CaO oxide melt containing SiC and C from 2023 K. The SiC grains with the diameter of 5–20 nm were covered with 2–4 graphitic carbon layers with the spacing of 0.34 nm as revealed by high resolution transmission electron microscopy. The result provides a new preparation method of carbon nanoparticles through a ceramic process, which contrasts with previous physical methods applying electric arc discharge or electron irradiation in vacuum.
Order No.: JA808-002

Protective AlZrN film for organic photoconductors
Y.C. Chan, X.S. Miao, E.Y.B. Pun
(City University of Hong Kong)

AlZrN protective film with high transmissivity was deposited onto organic photoconductor (OPC) surface, and the surface hardness was greatly increased by a factor of 1.5~3. The OPC surface protected by $(Al_{100-x}Zr_x)N$ ($x \leq 58.5\%$) film was significantly harder than that protected by AlN film. The electrophotographic properties of the OPC coated with $(Al_{100-x}Zr_x)N$ ($x \leq 37.7\%$) film were also better than those without coating or protected with AlN film, thus demonstrating the suitability of AlZrN film as a protective coating for enhancing the operating life of OPC.
Order No.: JA808-003

Theoretical assessment of systematic errors in volume fraction determinations by microscopy methods
E.D. Zanotto
(Federal University of Sao Carlos)

A set of equations were derived to estimate systematic errors in experimental determinations of volume fractions transformed by microscopy methods. For reactions that occur by continuous nucleation and growth, the experimental values of volume fractions transformed may

be subjected to significant errors when the largest grain size of the distribution is close to the microscope resolution limit. For transformations occurring from a fixed number of nuclei, the systematic errors are smaller than those observed in the continuous nucleation case, but can still be significant when reflection methods are used. Transmission methods lead to smaller errors than reflection techniques.
Order No.: JA808-004

ARTICLES

Growth morphology of large YBCO grains fabricated by seeded peritectic solidification: I. The seeding process

W. Lo, D.A. Cardwell, P.D. Hunneyball
(University of Cambridge)

The growth of large grain $YBa_2Cu_3O_{7-\delta}$ (YBCO) by peritectic solidification in the presence of a $(Sm,Y)Ba_2Cu_3O_{7-\delta}$ seed is characterized by the initial seeding process, development of a facet plane around the seed, and finally by continuous non-local growth away from the seed. A detailed investigation of the seeding process using electron microscopy, electron probe microanalysis, and thermal analysis techniques is reported here as the first in a series of studies of these key growth features. Results show that the seed partially melts below its nominal melting temperature due to a distribution of yttrium cations across the seed/YBCO interface. The formation of a $Sm/YBa_2Cu_3O_{7-\delta}$ solid solution, which occurs via a reaction between $(Sm,Y)_2BaCuO_5$ and liquid state $Ba_3Cu_5O_8$, has been observed across this interface at temperatures below the peritectic temperature (T_p) of the seed. The temperature window available for melting the YBCO phase while avoiding full peritectic decomposition of the $(Sm,Y)Ba_2Cu_3O_{7-\delta}$ seed is maximized for seeds of high Sm content and thickness in excess of 0.2 mm. Finally, the dwell time at temperatures above T_p should be as short as possible if the integrity of the seed is to be maintained throughout the YBCO growth process.
Order No.: JA808-005

Film/substrate interactions and superconducting properties of $Tl(Ba_{1-x}Sr_x)_2Ca_2Cu_3O_y$ thin films on (001) $SrTiO_3$ and $SrTiO_3$-buffered (001) MgO substrates

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We have developed a process for the fabrication of (001) oriented $SrTiO_3$ buffer layers onto (001) MgO substrates by rf magnetron sputtering followed by a post-deposition heat treatment in air. Precursor films with Tl:Ba:Ca:Cu ratio 2:2:2:3 were deposited by dc magnetron sputtering onto both these buffered substrates and directly onto (001) $SrTiO_3$ single crystal substrates, and thalliated at elevated temperatures. Due to Sr diffusion from the substrate/buffer layer, and its subsequent substitution for Ba in the superconducting film, the single Tl-O layer phase $Tl(Ba_{1-x}Sr_x)_2Ca_2Cu_3O_y$ was stabilized. Diffusion of Ba and Ca in the opposite direction led to the formation of a Ba-Ca-Tl-O compound at the interface. The $Tl(Ba_{1-x}Sr_x)_2Ca_2Cu_3O_y$ films typically have superconducting transition temperatures (T_cs) > 103 K and critical current densities (J_cs) > 2.9 x $10^5 Acm^{-2}$ at 77 K. R_s values measured on these films and scaled to 10 GHz were 3.0 mΩ at 80 K and <200 μΩ at 50 K for the film grown on $SrTiO_3$ buffered MgO, and 2.0 mΩ and 1.0 mΩ at 50 K for the film grown directly onto the (001) $SrTiO_3$ substrate. Films fabricated on (001) $SrTiO_3$ using an *in-situ* deposition technique with a substrate temperature around 100°C lower than the *ex-situ* thalliation temperature showed no evidence of an interfacial reaction layer.
Order No.: JA808-006

The effect of molding pressure on the structural and electrical properties of $Y_1Ba_2Cu_3O_{7-\delta}$ superconductors

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Measurements of structural and electrical properties as a function of the molding pressure in $Y_1Ba_2Cu_3O_{7-\delta}$ superconductors have been performed to investigate the texturing behavior. The magnitudes of the molding pressure were 0.5 x 10^3 N/cm^2, 1 x 10^3 N/cm^2, 2 x 10^3 N/cm^2, and 4 x 10^3 N/cm^2. As the molding pressure increases, the anisotropy of the crystal structure decreases and the crystal grows preferentially along the c-axis. As the molding pressure increases, since the size of the grain becomes larger due to the decreased porosity, denser textures are formed. This result indicates that the critical current density is improved, resulting in increased thermal stability at higher molding pressure. While the molding pressure does not affect the oxygen mole fraction below 500°C, increases in the molding pressure have a remarkable effect on the formation of textures and on the onset temperature for the superconducting transition in $Y_1Ba_2Cu_3O_{7-\delta}$. These results indicate that structural and electrical properties in $Y_1Ba_2Cu_3O_{7-\delta}$ superconductors are affected by the molding pressure during growth.
Order No.: JA808-007

Depth-sensing indentation measurements with Vickers and Berkovich indenters

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Depth-sensing indentation measurements are performed with two different Vickers indenters and one Berkovich indenter. The sample materials were mirror polished Ag, Al, Au, Ni and Ti samples. From the load-indentation depth data, the conventional hardness plots as well as the first derivative are calculated. The latter procedure yields a specific volume related density of deformation energy in the probed material. That specific energy density is shown to be a constant material parameter for extended indentation depths and for different Vickers indenters. Vickers and Berkovich indenters delivered within the error margin the same results.
Order No.: JA808-008

Role of bonding and coordination in the atomic structure and energy of diamond and silicon grain boundaries

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The high-temperature equilibrated atomic structures and energies of large-unit-cell grain boundaries (GBs) in diamond and silicon are determined by means of Monte-Carlo simulations using Tersoff's potentials for the two materials. Silicon provides a relatively simple basis for understanding GB structural disorder in a purely sp^3 bonded material against which the greater bond stiffness in diamond combined with its ability to change hybridization in a defected environment from sp^3 to sp^2 can be elucidated. We find that due to the purely sp^3-type bonding in Si, even in highly disordered, high-energy GBs at least 80% of the atoms are four-fold coordinated in a rather dense confined amorphous structure. By contrast, in diamond even relatively small bond distortions exact a considerable price in energy that favors a change to sp^2-type local bonding; these competing effects translate into considerably more ordered diamond GBs, however at the price of as many as 80% of the atoms being only three-fold coordinated. Structural disorder in the Si GBs is therefore partially replaced by coordination disorder in the diamond GBs. In spite of these large fractions of three-coordinated GB carbon atoms, however, the three-coordinated atoms are rather poorly connected amongst themselves, thus likely preventing any type of graphite-like electrical conduction through the GBs.
Order No.: JA808-009

Precipitates in GaN epilayers grown on sapphire substrates

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Precipitates in GaN epilayers grown on sapphire substrates were investigated by atomic number contrast (ANC), wavelength-dispersive x-ray spectrometry (WDS), energy-dispersive spectrometry (EDS), and cathodoluminescence (CL) techniques. The results showed that the precipitates are mainly composed of gallium and oxygen elements and distribute more sparsely and inhomogeneously in <1120> directions in the sample grown on substrate nitridated for a longer period. Yellow luminescence intensity was imaged to be stronger in the precipitates. The results suggest that the precipitates are formed on dislocations and grain boundaries by

substituting oxygen onto nitrogen site, and result in the formations of deep levels nearby.
Order No.: JA808-010

Microstructural control of amorphous silicon films crystallized using an excimer laser
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A technique for microstructural control of excimer laser-annealed silicon thin films on SiO_2 substrates has been developed. By using single-crystal photolithographically-etched silicon seed wafers in intimate contact with the silicon films, we have shown that it is possible to spatially control nucleation. Transmission electron micrographs show the resultant microstructure to consist of large (~1 μm) grain structures in the area surrounding the seed contact, with distinct organization not previously observed. A theoretical discussion is presented to explain the observed phenomena. Also, results from a numerical simulation are given which outline the effects of the seed wafer on the resultant microstructure of the laser-annealed film, as compared to non-seeded areas.
Order No.: JA808-011

Investigation of the solidus boundaries and microstructure in the ZnO-$PrO_{1.5}$-CoO system
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ZnO ceramics used as varistors are prepared with cobalt oxide as an essential additive to improve nonohmic properties. Because some of its effects during the liquid-phase sintering remain unexplained, we characterize the liquid-phase formation temperatures and phase reactions in the system ZnO-$PrO_{1.5}$- CoO. Using differential thermal analysis (DTA) during sintering, we detect new thermal phenomena. An addition of cobalt oxide to ZnO-$PrO_{1.5}$ mixtures (ZnO-5 mol% $PrO_{1.5}$-10 mol% CoO) significantly decreases the liquid-phase formation temperature to 1272 ± 5°C, which is about 110°C lower compared to those in ZnO-$PrO_{1.5}$ system. Characterization of ceramics quenched during sintering allows us to describe an isoplethal section with $PrO_{1.5}$ contents of 5 mol% and solubility limit of Co in ZnO.
Order No.: JA808-012

Influence of nitrogen implantation on the properties of Ti and substoichiometric TiN_x films deposited on high speed steel
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Ti and TiN_x ($x < 1$) thin films have been deposited on high speed steel (HSS) substrates by reactive sputtering and then N^+ implanted. The increase of the N/Ti ratio of the films during deposition is related to a decrease in their roughness, and N^+ implantation produces another additional slight decrease of the roughness. The hardness of samples increases with the nitrogen content in the as-deposited samples; nevertheless, N^+-implanted Ti coatings show lower values of hardness than reactive sputtered TiN_x films. α-Ti, ε-Ti_2N and δ-TiN phases were identified by grazing x-ray diffraction.
Order No.: JA808-013

Plasticity in ion-irradiated austenitic stainless steels
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In an attempt to take advantage of charged particle irradiation for studying the effects of irradiation on the mechanical properties of metals, we developed an experimental procedure based on the combination of transmission electron microscopy (TEM) and submicron indentation of ion-implanted layers. We applied this technique to industrial 316L steel, irradiated with krypton ions up to 10 dpa at 873 K. A domain where the penetration range of the ions and the indentation depth are compatible has been identified. The indentation tests then yielded a good estimate of hardness and bulk modulus, while the TEM observations provide microstructural information in the plastic regime. It is shown that the combination of the two techniques is necessary for rationalizing the observed results.
Order No.: JA808-014

Extended x-ray absorption fine structure study on amorphous Nd-Fe-B alloys
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The local structure and crystallization behavior of $Nd_{15}Fe_{77}B_x$ (x = 2–14) melt-spun alloys were studied by Nd L_3 extended x-ray absorption fine structure (EXAFS). The conventional x-ray powder diffractometry studies showed that the Nd-Fe-B melt-spun ribbons had the amorphous structure regardless of the boron content. EXAFS studies of the local structure around the Nd atom confirmed that the Nd-Fe-B melt-spun alloys had the amorphous structure and virtually the same nearest neighbor distance from the Nd atom. The amorphous alloys were heated by a differential scanning calorimetry in order to investigate the variation in the local structure during the crystallization process by EXAFS measurements. Although no appreciable difference was found in the nearest neighbor distance of the Nd atom between the amorphous alloys and the crystallized alloys, the small variation in the nearest neighbor distance during the crystallization process was detected by EXAFS measurements.
Order No.: JA808-015

Formation of graphite encapsulated ferromagnetic particles and a mechanism for their growth
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Graphite encapsulated nanoparticles have numerous possible applications due to their novel properties and their ability to survive rugged environments. Evaporation of Fe, Ni, or Co with graphite in a hydrogen atmosphere results in graphite encapsulated nanoparticles found on the chamber walls. Similar experiments in helium lead to nanoparticles embedded in an amorphous carbon/fullerene matrix. Comparing the experimental results in helium and hydrogen, we propose a mechanism for the formation of encapsulated nanoparticles. The hydrogen arc produces polycyclic aromatic hydrocarbon (PAH) molecules, which can act as a precursor to the graphitic layers around the nanoparticles. Direct evidence for this mechanism is given by using pyrene ($C_{16}H_{10}$), a PAH molecule, as the only carbon source to form encapsulated nanoparticles.
Order No.: JA808-016

Chemical interaction between nitrogen and iron in silica glasses via sequential ion-implantation
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Silica glass plates (Corning 7940 excimer grade) were implanted sequentially with N^+ at 52 keV to different doses, ranging from 0 to 1.2 x 10^{17} ions cm^{-2}, and then with Fe^+ at 160 keV to 6 x 10^{16} ions cm^{-2} at room temperature and 4 μA cm^{-2}. The intensity of ferromagnetic magnetic resonance (FMR) absorption and the magnetization calculated by the angular dependence of the FMR field reach maxima at an N/Fe atomic ratio ~0.2. Two peaks due to Fe $2p_{3/2}$ electron are observed at 707.2 ± 0.2 and 710.9 ± 0.2 eV in the x-ray photoelectron spectra. The intensity of the former relative to the latter decreases with increasing the N dose. The conversion electron Mössbauer spectrum reveals the formation of superparamagnetic iron nitride as well as the existence of Fe^{2+} and Fe^{3+} in silica when implanting N^+ to 7.5 x 10^{15} ions cm^{-2} and then $^{57}Fe^+$ to 6 x 10^{16} ions cm^{-2} at N/Fe = 0.125. These results suggest that sequential ion-implantation of N^+ and Fe^+ produces iron nitride in silica glasses.
Order No.: JA808-017

Durability of cement-based materials in simulated radioactive liquid waste: Effect of phosphate, sulphate and chloride ions
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The durability of a specific backfilling pozolanic cement mortar, which is employed in Spain, in concrete containers for the storage of low

and medium level wastes (LLW) (MLW), has been studied by means of the Köch-Steinegger test at the temperature of 40°C during a period of 365 days. Mortar samples were immersed in a simulated radioactive liquid waste very rich in sulphate (0.68M), phosphate (0.89M) and chloride (0.51M) ions. The changes of the microstructure were followed by x-ray diffraction (XRD), mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM). Pore solution was extracted at different periods in order to see the changes of the chemical composition caused by the diffusion of those ions inside the microstructure.

Order No.: JA808-018

Transmission electron microscopy and x-ray structural investigation of $La_{0.7}Ca_{0.3}MnO_3$ thin films

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The structural changes and magnetoresistance (MR) properties of as-grown and post-annealed $La_{0.7}Ca_{0.3}MnO_3$ films were investigated by transmission electron microscopy (TEM) and x-ray diffraction (XRD). The data for the films was compared to that for bulk $La_{0.7}Ca_{0.3}MnO_3$ post-annealed under the same conditions. The main structure of the as-grown films was face centered pseudo-cubic with a doubled perovskite unit cell, of size ~$2a_p$x~$2a_p$x~$2a_p$, where a_p is the single perovskite parameter. The phase showed a cube-on-cube epitaxy with the underlying $LaAlO_3$ substrate. Upon annealing to a saturation point, a minor primitive pseudo-tetragonal structure evolved, of cell parameters ~$\sqrt{2}a_p$x~$\sqrt{2}a_p$x~$2a_p$. A total of four possible orientations of the two structures was observed by TEM, comprised of one orientation of the ~$2a_p$x~$2a_p$x~$2a_p$ cell, i.e. the cube-on-cube epitaxy, giving rise to (001) peaks in x-ray, and three orientations of the ~$\sqrt{2}a_p$x~$\sqrt{2}a_p$x~$2a_p$ cell, giving rise to a single (001)/(hk0) peak in x-ray. The bulk $La_{0.7}Ca_{0.3}MnO_3$ sample also contains the $\sqrt{2}a_p$x~$\sqrt{2}a_p$x~$2a_p$ structure. The difference between the bulk and the film and the effects of annealing on films can be ascribed to the influence of strain between the film and substrate, induced by lattice mismatch.

Order No.: JA808-019

Kinetics of formation of the pyrochlore and perovskite phases in sol-gel derived lead zirconate titanate powder

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Lead zirconate titanate (PZT) powder is prepared by the sol-gel method. The formation of pyrochlore and perovskite phases is investigated by high temperature XRD and thermal analysis techniques. The pyrochlore phase first appears in x-ray amorphous form, and then gets converted to crystalline state on annealing in air. We show that vacuum-annealing of the pyrolyzed amorphous PZT gel suppresses the formation of the crystalline pyrochlore phase. This, in turn, enhances the kinetics of conversion of pyrochlore to perovskite, such that a pyrochlore-free perovskite phase can be obtained by annealing at about 500°C. On the other hand, if annealing is carried out in air, a crystalline pyrochlore phase is formed, which requires annealing temperatures higher than 600°C for transformation to the perovskite phase. These observations are explained tentatively in terms of the oxygen stoichiometry of the two phases.

Order No.: JA808-020

Metastability of tetragonal ZrO_2 derived from Zr-*n*-propoxide-acetylacetone-water-isopropyl alcohol

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ZrO_2 nanopowders derived from zirconium *n*-propoxide $Zr(OC_3H_7)_4$]-acetylacetone-water-isopropanol have been investigated with respect to their tetragonal metastability on heating-cooling processes. The transformation temperature of metastable tetragonal to monoclinic (t'→m) phase is found to be governed by ultimate firing temperature, time and atmospheres employed. Crystallite growth is fastened with increase in calcination temperatures over 1000-1400°C, and the t'→m transformation temperature is correlated linearly with crystallite size in the studied range of 12-20 nm. Heating in an oxygen environment increases the size of the final crystallites and hence the rate of the t'→m transformation. It is revealed that the t'→m transformation temperature depends largely on the heating atmosphere, but only weakly on the cooling one. Based on the findings of this work, surface oxygen deficiencies are attributed to be responsible for low-temperature tetragonal metastability. A crystallite growth model to explain the decline of t'-ZrO_2 phase is proposed. Kinetic and thermodynamic factors are also discussed in connection with the existing theories of tetragonal metastability.

Order No.: JA808-021

Characterization of aluminosilicate (mullite) precursors prepared by a mechanochemical process

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Aluminosilicate precursors were prepared by mechanochemical treatment of gibbsite-silica gel mixtures. The effect of grinding on their structure and thermal behavior has been examined by ^{27}Al and ^{29}Si MAS NMR, XRD, DTA-TG and FT-IR. After 8 hours grinding, the hydrated alumina was completely changed to an amorphous phase which showed a new exothermic DTA peak at about 980°C due to the formation of γ-Al_2O_3 or spinel-phase. This behavior was related to changes in the Al and Si environments, as deduced from the MAS NMR spectra. With increased grinding time, some 4 coordinated Al appears, together with an Al resonance at about 30 ppm. Simultaneously, a new ^{29}Si resonance appears at about -90 ppm, indicating a greater degree of homogeneity in the ground samples. Mullite crystallizes at 1200°C from samples ground for 8–20 hours, its XRD intensity increasing with increased milling times, in agreement with the NMR, DTA and FT-IR data. Changes in the Al and Si environments during heat treatment, as reflected by the NMR spectra, are also reported.

Order No.: JA808-022

Conductivity behavior of *n*-type semiconducting ferrites from hydrothermal powders

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The frequency and temperature dependencies of the dielectric permittivity and of the electrical conductivity of excess ferrous ions hydrothermal NiZn ferrites were analyzed before and after sintering. A decreasing tendency with frequency of the dielectric responses was observed, but the high permittivities attained ($\varepsilon' \approx 10^5$) masked any relaxation in these materials. This behavior is characteristic of *n*-type semiconducting ferrites, where electron hopping between Fe^{+2} and Fe^{+3} ions leads to very high conductivity values. The temperature dependence of the dielectric permittivities revealed the existence of broader peaks. The electron hopping mechanism leads to a frequency dispersion of the temperature where the permittivities attain their maxima. The electrical conductivity variations with temperature exhibited Arrhenius type behaviors, with activation energies ranging from 0.34 eV (hydrothermal powder) to 0.16 eV (for the highest sintering temperature). These results were correlated to the variations in Fe^{+2} concentration and microstructure.

Order No.: JA808-023

Epitaxial growth of 'infinite layer' thin films and multilayers by rf magnetron sputtering

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We report on the preparation and characterization of epitaxial $ACuO_2$ (A = Sr,Ca,Ba) thin films and multilayers with the so-called infinite layer (IL) structure, by RF magnetron sputtering. Films and multilayers without Ba have a remarkable crystal quality, whereas those containing this large ion are often multiphased and unstable. In spite of the excellent crystalline quality of these samples, the obtaining of thin films both having IL structure and displaying superconducting properties has not succeeded: our pure IL samples display semiconducting behavior, and the different procedures tried in order to dope them—annealings, introduction of disorder or

cation vacancies, artificial layering—have failed. These results support that the pure IL structure $ACuO_2$ (A = Alkaline earth) cannot superconduct.
Order No.: JA808-024

***In-situ* monitoring of the sintering behavior of microcomposite particles using a laser scanning micrometer**
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(Space Power Institute)

The densification behavior of silica-coated alumina particles was investigated during sintering using a laser scanning micrometer. Traditional dilatometric techniques require contact between a push-rod and the sample under study and thus place the sample under stress during the test. However, the utilization of a non-contact laser micrometer to measure dimensional changes during sintering enabled the densification behavior to be very accurately characterized under a stress-free condition. Thus higher temperature experiments, where densification rates are particularly temperature sensitive and the samples are especially soft, can be reliably investigated without the disturbing influence of an external force. The present paper describes an application of the technique to evaluate the densification behavior from 900–1300°C of silica-coated alumina microcomposite particles used for the fabrication of mullite.
Order No.: JA808-025

Microstructure of columnar-grained $SrTiO_3$ and $BaTiO_3$ thin films prepared by chemical solution deposition
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The microstructure and lattice defects of $SrTiO_3$ and $BaTiO_3$ thin films with columnar grains prepared by a chemical solution deposition technique has been investigated by means of transmission electron microscopy. The columnar grains in the $SrTiO_3$ films exhibit a preferential orientation with a crystallographic <111> direction parallel to the normal of film, which, in turn, follows the orientation texture of the substrate Pt layer. Cubic-to-cubic relationships have been found for the two materials. For the $BaTiO_3$ films the columnar grains are oriented in a random way without any preferential relationship to the substrate Pt layer. Pores, lattice defects and grain boundaries occur in either type of film, however in different configurations. This reflects the individual nature of the materials and the different formation and growth mechanisms of the films under the preparation conditions.
Order No.: JA808-026

Structural and morphological features of MgO powders. The key role of the preparative starting compound
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The present paper reports data concerning magnesia samples obtained by calcination of different precursor salts at different increasing temperatures (873 K–1253 K). The oxides are characterized by x-ray diffraction, scanning electron microscopy and N2 adsorption at subcritical temperatures. The samples appear to be composed, at any temperature, of pure periclase with a degree of crystallinity which increases with the temperature of calcination. Morphologically, the products have the shape either of lamellas or of cubes of variable dimensions, depending on the nature and route of preparation of the precursor salts. The variation of the specific surface area and the degree of porosity with the nature of the precursors and the temperature is discussed.
Order No.: JA808-027

Bi-axial stretching of superplastic yttria stabilized zirconia polycrystals, yttria stabilized zirconia polycrystals/Al_2O_3 and yttria stabilized zirconia polycrystals/LAS-glass composites in air atmosphere
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The bi-axial stretching behavior of superplastic Y-TZP (yttria stabilized zirconia polycrystals) ceramics and Y-TZP/Al_2O_3 composites in air atmosphere was investigated. Stretching deformation can be made within a limited range. Larger grain size of Y-TZP led to higher applied load needed to obtain the same amount of deformation. However, if some monoclinic phase was present in the materials, which was caused by the over-large grain sizes, defects would occur and thus deformation was easier. Microstructure study of the deformed specimen showed the occurrence of crack-like defects on the outside surface of the stretched disc specimen. Limited grain growth of single phase Y-TZP was obtained while Y-TZP grains in Y-TZP/Al_2O_3 composites grew extensively after stretching.
Order No.: JA808-028

Effect of microstructure on damage tolerance in grinding micaceous glass-ceramics
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This study investigated the modes of grinding-induced subsurface damage in dental glass-ceramics and the influence of microstructure on strength degradation. A series of micaceous glass ceramics crystallized from the same glass composition was tested. The diameter of the mica platelets in these glass-ceramics was varied via heat-treatment. Grinding was performed using three diamond wheels (with diamond particle size of 40, 100, and 180 μm, respectively) at depth of cut ranging from 5 μm to 100 μm. A bonded-interface technique was employed to examine the machining-induced subsurface damage. Relatively large median and lateral cracks were found in the glass-ceramic with the smallest mica platelets. In contrast, no cracks were found in the material containing large mica platelets. The ground specimens were fractured in four point flexure to measure strength as a function of grinding conditions and mica platelet sizes. The strength of the ground specimens was reduced to approximately 30% of the strength of the polished specimens for the glass-ceramic containing the smallest mica platelets; that of the glass-ceramic with the intermediate mica platelet size was reduced to 60%. In contrast, virtually no strength loss occurred with the glass-ceramic containing large mica platelets. Microstructure was shown to determine the mode and degree of strength-controlling damage in the machining of these dental glass ceramics. Polishing after grinding removes subsurface damage and recovers strength for the glass-ceramics containing fine mica crystals.
Order No.: JA808-029

Microstructural factors influencing the properties of high surface area molybdenum nitride films converted from molybdenum trioxide films deposited via solution spray pyrolysis
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Molybdenum trioxide (MoO_3) films, 15 μm thick, have been deposited on 50 μm thick polycrystalline titanium substrates from 250 to 500°C via liquid spray pyrolysis. Molybdenum pentachloride ($MoCl_5$) dissolved in methanol was used as the molybdenum source; ambient conditions provided the oxygen source. X-ray diffraction (XRD) data indicated that amorphous MoO_3 films were produced at deposition temperatures below 400°C. Randomly orientated polycrystalline MoO_3 films were produced at 400°C and higher deposition temperatures. The deposition temperature also influenced the surface area of the films and their average grain size. Subsequent conversion of the MoO_3 films to high surface area (HSA) conductive films containing both Mo_2N and MoN was accomplished via programmed reactions with anhydrous NH_3 and involved the formation of MoO_2 and MoO_xN_{1-x} as intermediate phases. The degree of crystallinity, surface area and average grain size of the MoO_3 films strongly influenced the average grain size and surface area of the resultant Mo_xN films.
Order No.: JA808-030

Stabilization of aqueous $BaTiO_3$ suspensions with ammonium salt of poly(acrylic acid) at various pH values
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Ammonium salt of poly(acrylic acid) (PAA-NH_4) has been used to stabilize aqueous $BaTiO_3$ suspensions at various pH values. Adsorption of PAA-NH_4 causes the zeta potential to become more negative, although this effect becomes less dramatic as the pH increases. The concentration of

PAA-NH_4 required to stabilize aqueous $BaTiO_3$ suspensions decreases with increasing pH. The critical amount of PAA-NH_4 as a function of pH is plotted in a stability map, as determined by adsorption, rheology and sedimentation studies.
Order No.: JA808-031

Mass transfer and kinetics of the chemical vapor deposition of SiC onto fibers
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An internally consistent set of data was generated for the chemical vapor deposition (CVD) of SiC from methyltrichlorosilane (MTS) and H2 at atmospheric pressure. A moving fiber tow was used as the substrate. Coating rates between 0.3 and 3.7 μm/min and deposition efficiencies between 24 to 48% were obtained for MTS and H_2 flow rates in the range 30 to 200 cm^3/min and 300 to 2000 cm^3/min, respectively. The data were analyzed and found to be best fit under a mass transfer regime. Based on this fit, a value of the constant in the Chilton-Colburn j factor expression for a moving fiber tow was estimated to be 2.74×10^{-6} with a standard deviation of 3.2×10^{-7}. The efficiency of the reaction was found to decrease with increases in the total flow rate, indicating that the effect of the decreased residence time of reagents in the reactor was larger than the increase in the mass transfer coefficient. Finally, a comparison between the efficiencies for a stationary and a moving tow revealed that the moving tow had a higher efficiency, possibly due to a disruption of the boundary layer by the tow motion or due to the decrease in the canning of the moving tow.
Order No.: JA808-032

A micromechanistic model of the combustion synthesis process: Influence of intrinsic kinetics
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A micromechanistic model of the combustion synthesis of NbC has been developed by combining the results of an experimental study of the intrinsic, pore-level kinetic mechanism and a theoretical model developed previously, in order to account for the various physical and chemical processes that take place during the combustion synthesis process. Results of the present investigation are interpreted from both a macroscopic and a microscopic point of view. Moreover, the relationship between the microscopic processes and macroscopic features of the combustion synthesis process is discussed. The results show that the formation of a combustion wave in the Nb-C system corresponded to establishment of a proper balance between the rates of enthalpy redistribution within the sample. Furthermore, the pore size had a significant influence on the combustion synthesis process: smaller pores gave rise to a higher area of contact between the reactants, which in turn gave rise to a higher rate of enthalpy increase due to the enhanced rate of product formation. The influence of the pore size distribution on the process is also discussed.
Order No.: JA808-033

Growth, microstructure and resistivity of RuO_2 thin films grown by metal-organic chemical vapor deposition
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Polycrystalline RuO_2 thin films were grown by metal-organic chemical vapor deposition (MOCVD) on both SiO_2/Si(001) and Pt/Ti/SiO_2/Si(001) substrates. Films having a controllable and reproducible structural texture and phase purity were synthesized by carefully controlling deposition parameters. Moderate growth temperatures (~350°C) and low growth rates (<30 Å/min) produced highly (110)-textured RuO_2 films. Highly (101)-textured RuO_2 films were favored at slightly lower temperatures (~300°C) and much higher growth rates (>30 Å/min). The most conductive RuO_2 films had resistivities of 34 to 40 μΩ-cm at 25°C, an average grain size of 65 ± 15 nm, and a surface roughness (rms) of 3 to 10 nm. Both single phase Ru and mixed Ru/RuO_2 phase material were also fabricated at low temperatures (<350°C) by using lower oxygen flow concentrations (<10%).
Order No.: JA808-034

Crystallization kinetics of sputter-deposited $LaNiO_3$ thin films on Si substrate
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The kinetics of *in-situ* crystallization of $LaNiO_3$ thin films in sputtering deposition at temperatures ranging from 250 to 450°C and isothermal crystallization of room-temperature (RT) sputtered $LaNiO_3$ thin films in annealing at 350–500°C were investigated by the x-ray diffraction method. The crystallization in both cases basically followed the Johnson-Mehl-Avrami (JMA) relation. However, different crystallization kinetics were observed. The transformation index and activation energy of crystallization in high temperature sputtering were about 1.5 and 33 kJ/mole, respectively, while in the annealing of RT sputtered films, 1.0 and 63 kJ/mole were found. From the determined transformation index, it is suggested that the crystallization rate in high temperature sputtering was determined by a diffusion-controlled process of lateral growth with a decreasing nucleation rate of crystallites in the adsorption layer. However, the annealed films crystallized by an interface controlled and one-dimensional growth of existing nuclei.
Order No.: JA808-035

Effect of intercalation in graphite epoxy composites on the shielding of high energy radiation
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The half-thickness and mass absorption coefficient of 13.0 keV x-rays, 46.5 keV γ-rays, and 1.16 MeV $\beta^{\ominus}$ particles have been measured for pristine, bromine intercalated, and iodine monobromide intercalated pitch-based graphite fiber composites. Since these materials have been proposed to replace aluminum structures in spacecraft, the results were compared to aluminum. Pristine graphite epoxy composites were found to have about 4.0 times the half-thickness, and 40 percent of the mass absorption of aluminum for ionizing radiation. Bromine intercalation improved performance to 90 percent of the half-thickness, and 1.7 times the mass absorption coefficient of aluminum. Iodine monobromide extended the performance to 70 percent of the half-thickness and 3.0 times the mass absorption of aluminum. Thus, intercalation not only makes up the deficiency conventional composites have in shielding components from ionizing radiation but actually confers advantages in mass and thickness over aluminum. The $\beta^{\ominus}$ particle shielding of all the materials tested was found to be very effective. The shielding of all of the materials was found to have nearly the same mass absorption coefficient of 17.8 ± 0.9 cm^2/g. Inelastic scattering processes were found to be important in $\beta^{\ominus}$ particle shielding, however, the extent of inelastic scattering and thus the distribution of energies of the transmitted electrons did not vary with material.
Order No.: JA808-036

Microstructural characteristics of conductive $SrRuO_3$ thin films formed by pulsed-laser deposition
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Transmission electron microscopy and high-resolution electron microscopy have been used to study microstructural properties of conductive $SrRuO_3$ films grown by pulsed laser deposition on (001) $LaAlO_3$ and (001) $SrTiO_3$ substrates. It was found that the $SrRuO_3$ films deposited on both substrates consist of mixed domains of [001] and [110] orientations, with orientation relationships that can be described as (a) $(001)_f$//$(001)_s$ and $[110]_f$//$[100]_s$ and (b) $(110)_f$//$(001)_s$ and $[001]_f$//$[100]_s$, respectively. The $SrRuO_3$ films deposited on $SrTiO_3$, in particular, were found to have a layered domain structure, with the [110] domain grown initially on the substrate, followed by growth of the [001] oriented domain with increasing thickness. The films on $SrTiO_3$ are strained and have a coherent interface with the substrate. The $SrRuO_3$ films deposited on $LaAlO_3$, on the other hand, contain a high density of structural defects such as stacking faults and microtwins on the (022) planes. Microtwins as large as 50 nm in thickness are observed in the films deposited on $LaAlO_3$. Possible causes for the observed structural defects in the films are discussed.
Order No.: JA808-037

Growth kinetics of chemically vapor deposited SiO_2 films from silane oxidation

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The growth kinetics of SiO_2 thin films obtained by low-pressure CVD from $SiH_4/O_2/N_2$ gas mixtures has been determined at different temperatures and flow rates. The results show that the film growth is originated by some intermediate species (e.g., SiO_xH_y) produced in the gas-phase. At low temperatures the deposition rate is limited by some homogeneous reaction with an apparent activation energy of 1.42 eV. Furthermore, the observation of critical limits when total pressure, oxygen/silane flow ratio and temperature are decreased gives support to a branching-chain mechanism of deposition. Finally, we have observed that the deposition rate shows a hysteresis behavior when varying the temperature within the 300°–400°C range, which has been attributed to the inhibition of silane oxidation by the Si-OH surface groups of the films grown on the reactor walls.

Order No.: JA808-038

Growth of diamond and diamond-like films using a low energy ion beam

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Ion beam deposition provides an additional control of ion beam energy over the chemical vapor deposition methods. We have used a low energy ion beam of hydrogen and carbon to deposit carbon films on Si (100) wafers. We found that graphitic films, amorphous carbon films and oriented diamond microcrystallites could be obtained at different ion beam energies. The mechanism of the formation of the oriented diamond microcrystallites was suggested to include three components: strain release after ion bombardment, hydrogen passivation of sp^3 carbon, and hydrogen etching. Such a process can be extended to the heteroepitaxial growth of diamond films.

Order No.: JA808-039

Synthesis, characterization, and reactivity of tungsten oxynitride

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High surface area tungsten oxynitride has been prepared by the temperature programmed reaction (TPR) of WO_3 with NH_3. All samples were characterized by x-ray diffraction (XRD), nitrogen physisorption, CO chemisorption, and elemental analysis. Samples were prepared at different heating rates (β), and a Redhead analysis yielded an activation energy for nitridation of 109 kJ mol^{-1}. A heating rate of 0.016 K s^{-1} gave optimal synthesis conditions. Solid state intermediates were studied by interrupting the temperature program at various stages. No distinct suboxide phases were found using XRD. The nitridation step was determined to be a continuous transformation from oxide to oxynitride. Surface area, CO uptake, and nitrogen weight % were all found to increase as the reaction progressed. Reactivity experiments showed reasonable hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN) activity, but little hydrogenation (HYD) or hydrodesulfurization (HDS) activity.

Order No.: JA808-040

Non-linear physical properties of some non-conventional semiconducting Bi-Pb-Ba-O glasses

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Semiconducting $Bi_{1-x}Pb_xBaO_{3-\delta}$ (or BPB) glasses with x = 0 to 0.8 have been prepared by fast quenching from the melt. Interesting anomalies in the temperature dependent polaronic conductivity and dielectric constant have been observed in all these glass compositions around temperature T_p (say) varying from 310 to 330 K (depending on Pb concentration). This non-linear behavior is considered to be associated with the local ordering or displacements of the BiO_3 type pyramidal structural units present in the glass matrix (observed from the infra-red spectra of these glasses). This type of ordering/displacement gives rise to a local instability in the glass network structure which is also supported by the observed heat capacity anomaly around the same temperature T_p.

Order No.: JA808-041

Constrained-film sintering of cordierite glass-ceramic on silicon substrate

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The densification behavior of cordierite glass-ceramic films constrained on rigid silicon substrate was studied in the temperature range from 900°C to 1000°C. An optical setup was used to obtain the thickness versus time profiles and in-plane stresses of the constrained glass-ceramic during isothermal sintering. The thickness profiles showed a rapid shrinkage due to sintering followed by an expansion corresponding to crystallization of the glass-ceramic. Measurements of in-plane stresses in constrained-sintering films showed a rapidly-rising tensile stress during densification followed by a slight drop during crystallization. In films sintered above 950°C, the tensile stress rose rapidly again near the end of crystallization, suggesting a further densification in a mostly crystallized film. SEM micrographs of the film cross-sections revealed the formation and growth of large pores along the interface between the glass-ceramic and silicon substrate that may have contributed to the observed film expansion. These pores are substantially larger than the initial pore size in the films, indicating that they were formed during sintering. We believe that poor wetting of the glass-ceramic on silicon may have contributed to the formation of the porous structure at the interface.

Order No.: JA808-042

Preparation, morphology and microstructure of diameter-controllable *vapor-grown carbon nanofibers*

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Pure vapor-grown carbon nanofibers (VGCNFs) with controllable diameter of 10–200 nm were prepared by an improved floating catalyst method. Through transmission electron microscopy observation, it was found that VGCNFs have a duplex structure, a hollow and high-crystallinity graphite filament called primary carbon fiber surrounded by a pyrocarbon layer with low graphitic crystallinity. It was observed using high-resolution TEM that VGCNFs have excellent graphitic crystallinity with graphite layers stacked neatly parallel to fiber axis. Moreover, x-ray diffraction results showed that the graphitic crystallinity of carbon fibers became higher with decreasing diameter of carbon fibers.

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