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ABSTRACTS

RAPID COMMUNICATIONS

Magnetophoretic deposition of nanocomposites

J.L. Katz, Y. Xing, R.C. Cammarata
(The Johns Hopkins University)

This communication reports the novel idea of using a magnetic field gradient to hold magnetic nanoparticles at desired densities in a fixed location (e.g., on an electrode surface), while metal atoms are deposited electrochemically in the interstices between them. Using it, nanocomposites consisting of γ–Fe_2O_3 nanoparticles (with a mean size of about 40 nm) in a copper metal-matrix were reproducibly fabricated, with particle volume fractions ranging from 0.2% to 50%. These nanocomposites, ceramic magnetic particles in a conductive metal matrix, are expected to have unusual or enhanced mechanical, electrical, and magnetic properties.

Order No.: JA912-001

Subsolidus phase equilibria in the La_2O_3–Ga_2O_3–CeO_2 system

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(Jožef Stefan Institute)

Subsolidus equilibria in air in the La_2O_3–Ga_2O_3–CeO_2 system were studied with the aim of obtaining information on possible interactions between a $LaGaO_3$–based solid electrolyte and CeO_2 during preparation of the anode in solid oxide fuel cells. No ternary compound was found. The tie lines are between $La_4Ga_2O_9$ and the end of CeO_2 solid solution range with composition $La_{0.5}Ce_{0.5}O_{1.75}$ and between the $LaGaO_3$ and CeO_2 range of solid solutions.

Order No.: JA912-002

Liquid immersion technique coupled with infrared microscopy for direct observation of internal structure of ceramic powder compact, with alumina as an example

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Infrared microscopy was applied to observe the internal structure of an alumina powder compact, which was made transparent with an immersion liquid. It provided clear images of nonuniformity in the structure for a specimen as thick as 1 mm. Two types of nonuniformity found in this paper are the large pore made from the pore in powder granules and low-density region forming network structure, which was formed by the presence of a binder. The minimum size of nonuniformity detected in the structure is under 20 μm.

Order No.: JA912-003

On the evolution of tensile residual stress in thin metal films during energetic particle deposition

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Physical-vapor-deposited thin metal films often exhibit tensile residual stresses. We studied the stress evolution in thin Cr films and found that increasing bombardment with energetic particles (atoms or ions) at low energies leads to an increase of tensile stress to a maximum followed by a rapid decrease. Microstructural characterization by transmission electron microscopy revealed that two different microstructures are observed *for the same level of tensile stress:* films processed at low bombardment had columnar porosity, while no porosity was observed in films processed at higher bombardment. The observed stress evolution is interpreted by considering how the mean interatomic distance (and hence the force) in the inter-columnar regions is modified by energetic particle bombardment.

Order No.: JA912-004

Radiation stability of gadolinium zirconate: A waste form for plutonium disposition

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Zirconate and titanate pyrochlores were subjected to 1 MeV Kr^+ irradiation. Pyrochlores in the $Gd_2(Zr_xTi_{1-x})_2O_7$ system (x = 0, 0.25, 0.5, 0.75, 1) showed a systematic change in the susceptibility to radiation-induced amorphization with increasing Zr content. $Gd_2Ti_2O_7$ amorphized at relatively low dose (0.2 dpa at room temperature), and the critical temperature for amorphization was 1100 K. With increasing zirconium content, the pyrochlores became increasingly radiation resistant, as demonstrated by the increasing dose and decreasing critical temperature for amorphization. Pyrochlores highly enriched in Zr ($Gd_2Zr_2O_7$, $Gd_2Zr_{1.8}Mg_{0.2}O_{6.8}$, $Gd_{1.9}Sr_{0.1}Zr_{1.9}Mg_{0.1}O_{6.85}$, and $Gd_{1.9}Sr_{0.1}Zr_{1.8}Mg_{0.2}O_{6.75}$) could not be amorphized, even at temperature as low as 25 K.

Order No.: JA912-005

Raman spectroscopic characterization of submicron vapor-grown carbon fibers and carbon nanofibers obtained by pyrolyzing hydrocarbons

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Variations of the properties of submicron vapor-grown carbon fibers (VGCFs) and nanofibers, with diameters around 0.1–0.2 μm and 80–100 nm, respectively, are observed by Raman spectroscopy as a function of heat-treatment temperature. The microstructural evolution strongly depends on the original properties of the material, such that the main transition temperatures associated with the onset for establishing two-dimensional graphene ordering are defined below 1500 °C for the nanofibers and 2000 °C for the submicron VGCFs, respectively. The relative intensities (I_D/I_G) of the as-grown phase for submicron VGCFs and nanofibers are 3.44 and 1.35, while those for the corresponding graphitized samples are 0.393 and 0.497, respectively.

Order No.: JA912-006

A new surface pretreatment approach for enhancing diamond nucleation

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In this paper we present a new approach of surface pretreatment for enhancing diamond nucleation. The copper substrates were fixed inside a plastic cylinder container with diamond powder diluted in water. This container was coupled to a vibration unit moving up and down at ~300 cycles/min with a stroke of 15 mm. Finally, samples pretreated for 30 min were deposited with diamond. A high nucleation density comparable to that on substrate abraded with diamond powder was achieved. This method proved to be more effective than our ultrasonic treatment, keeping the advantages of surface preservation. Being simple and straightforward, this "shaking" pretreatment most fits the cases when a thin interlayer has to be used (like diamond coating on steel) and where the samples have a complex shape.

Order No.: JA912-007

ARTICLES

Stability of Tl–Ba–Ca–Cu–O superconducting thin films

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We report the stability of $TlBa_2CaCu_2O_7$ and $Tl_2Ba_2CaCu_2O_8$ on $LaAlO_3$(100) epitaxial thin films under a variety of conditions. All films are stable in acetone and methanol and with repeated thermal cycling to cryogenic temperatures. Moisture, especially vapor, degrades film quality rapidly. These materials are stable to high temperatures in either N_2 or O_2 ambients. While total degradation, resulting from Tl depletion, occurs at the same temperatures for both phases, 600 °C in N_2 and 700 °C in O_2, the onset of degradation occurs at somewhat lower temperatures for $TlBa_2CaCu_2O_7$ than for $Tl_2Ba_2CaCu_2O_8$.

Order No.: JA912-008

A transmission electron microscopy investigation of sulfide nanocrystals formed by ion implantation

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Ion implantation was used to form compound semiconductor nanocrystal precipitates of ZnS, CdS, and PbS in both glass and crystalline matrices. The precipitate microstructures and size distributions were investigated by cross-sectional transmission electron microscopy techniques. Several unusual features were observed, including strongly depth-dependent size variations of the ZnS precipitates and central void features in the CdS nanocrystals. The morphology and crystal structure of the nanocrystal precipitates could be controlled by a selection of the host material. The size distribution and microstructural complexity were significantly reduced by implanting a low concentration of ions into a noncrystalline host and by using multi-energy implants to give a flat concentration profile of the implanted elements.

Order No.: JA912-009

Semiconductor nanowires from oxides

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Highly pure, ultralong, and uniform-sized semiconductor nanowires in bulk quantity were synthesized by thermal evaporation of laser ablation of semiconductor powders mixed with oxides. Transmission electron microscopy study shows that decomposition of semiconductor sub-oxides and defect structures play important roles in enhancing the formation and growth of high-quality nanowires. A new growth mechanism is proposed based on the microstructure and different morphologies of the nanowires observed.

Order No.: JA912-010

Intrinsic stress effects on the growth of planar SiO_2 films

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(Lehigh University)

We report here on the results of a numerical study on the effects of intrinsic stress on the growth of SiO_2 thin films. In accordance with a widely accepted model of stress effects upon silicon oxidation, we assume that the intrinsic stress affects only the oxidatant diffusion rate. We examine several different models of stress-assisted diffusion. In the first of these models, the diffusivity is taken to be an exponential function of the stress, while in the second, the stress gradient appears as an additional term in the standard diffusion equation. Intrinsic stress effects result in deviations of up to 18% in expected layer thickness, depending upon the mode of oxidation and the diffusion model adopted. The implications of these results for the measurement of diffusion coefficients in SiO_2 films are discussed.

Order No.: JA912-011

Preparation of $Cu(In,Ga)Se_2$ thin films from In–Ga–Se precursors for high efficiency solar cells

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Growth of $Cu(In,Ga)Se_2$ (CIGS) films from In–Ga–Se precursors was characterized by scanning Auger electron spectroscopy (SAES), secondary ion mass spectroscopy (SIMS), x-ray diffraction, scanning electron microscopy, and transmission electron microscopy (TEM). In–Ga–Se precursor layers were deposited on Mo-coated soda-lime glass, and then the layers were exposed to Cu and Se fluxes to form CIGS films. The SIMS and SAES analyses showed a homogeneous distribution of Cu throughout the CIGS films during the deposition of Cu and Se. The phase changes observed in the CIGS films during the deposition of Cu and Se on the In–Ga–Se precursor films were as follows: $(In,Ga)_2Se_3 \rightarrow [Cu(In,Ga)_5Se_8] \rightarrow Cu(In,Ga)_3Se_5 \rightarrow Cu(In,Ga)Se_2$. The grain size increased from the submicron grains of the $(In,Ga)_2Se_3$ precursor film to several micrometers in the stoichiometric $Cu(In,Ga)Se_2$ film. A growth model of CIGS crystals is introduced based on the results of TEM observations. CIGS crystals are mainly grown under (In,Ga)-rich conditions in the preparation from In–Ga–Se precursor films.

Order No.: JA912-012

Residual stresses in spray-formed A2 tool steel

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The objective of this work was to investigate the fundamental factors that govern the formation and magnitude of residual stresses in A2 tool steel fabricated using spray forming techniques. To that effect, a finite-element method (FEM) was performed by using a commercial code, ABAQUS, to solve for the temperature and displacement fields. Moreover, the residual stresses in the spray-formed materials were measured using x-ray diffraction to compare the FEM results with experimentation. Two types of substrate material, copper and Rescor™ 780 cer-cast ceramic, were used to investigate the influence of heat conduction on residual stress in the preforms. Relatively good agreement was found between experimentation and theory. The results show that the residual stress varies greatly with the position in deposited preform and that heat-transfer coefficient at the interface of spray-formed material/substrate affects the distribution and magnitude of the residual stresses significantly.

Order No.: JA912-013

Oxidation behavior of platinum–aluminum alloys and the effect of Zr doping

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The isothermal and cyclic oxidation behavior of PtAl and PtAl + Zr was studied followed by postoxidation microstructural and microchemical analyses. Their isothermal oxidation performance at 1200 °C was similar to that of NiAl and NiAl + Zr. In short (1-h) cycles, the cyclic oxidation resistance of undoped PtAl was found to be substantially better than NiAl. However, with longer (100-h) cycles, little improvement in the metal consumption rate was observed relative to NiAl. The addition of Zr to PtAl significantly improved cyclic oxidation performance in both short- and long-cycle tests. Spatially resolved energy dispersive spectroscopy indicated Zr segregation to both the metal–oxide interface and Al_2O_3 grain boundaries.

Order No.: JA912-014

Static and cyclic creep behavior of *in situ* TiB_2 particulate reinforced aluminum composite

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Static and cyclic creep tests of Al–15 vol% TiB_2 *in situ* composite were carried out at 573–623 K. The values of apparent stress exponent and activation energy for cyclic creep of the composite were much higher than that for static creep. Furthermore, the cyclic creep rate tended to decrease with

increase of the percentage of unloading amount, but it was independent of the loading frequencies under the frequency ranges investigated. Finally, the true stress exponent of the composite was equal to 8, and the true activation energy was close to the value for the lattice self-diffusion of aluminum by incorporating a threshold stress into the analysis.
Order No.: JA912-015

Phase segregation in binary SiO_2/TiO_2 and SiO_2/Fe_2O_3 nanoparticle aerosols formed in a premixed flame

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Binary SiO_2/TiO_2 and SiO_2/Fe_2O_3 nanoparticle (diameter < 100 nm) aerosols of varying mole ratios of Ti or Fe to Si were generated in a premixed Bunsen-type aerosol flame reactor. The distribution of species within the particles was investigated using transmission electron microscopy, electron energy loss spectrometry, x-ray diffraction, and Fourier-transform infrared spectroscopy. Phase segregation was observed to varying degrees in qualitative agreement with segregation expected from binary phase diagrams for the bulk systems. Differences between the SiO_2/TiO_2 and SiO_2/Fe_2O_3 systems can be explained by considering the variation in the thermodynamically stable liquid-phase solubility and differences in the ability of iron and titanium ions to substitute for silicon ions in the network structure.
Order No.: JA912-016

Improved densification by nano-sized sintering aids for Si_3N_4

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The densification of Si_3N_4 with nano-sized sintering aids that were *in situ* incorporated by a combustion process was studied in comparison with that of sintering aids mixed by ball milling. The combustion process directly produces amorphous and nano-sized Y–Al oxides within the Si_3N_4 powder. X-ray diffraction results indicate that amorphous Y–Al oxides begin to crystallize into $Y_3Al_5O_{12}$ (YAG) at about 600 °C. Additionally the nano-sized sintering aids are more homogeneously distributed and thereby promote the formation of eutectic melts at lower temperatures during liquid-phase sintering. Therefore, the densification process of Si_3N_4 during liquid-phase sintering is strongly accelerated. The microstructure of as-sintered parts from combusted powder seems more dense and homogeneous.
Order No.: JA912-017

On a combined effect of grain size and tensile stresses on the ferroelectric properties of sol-gel $(Pb,La)TiO_3$ thin films

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Transmission electron microscopy has shown that the grain size of sol-gel-prepared lanthanum-modified lead titanate films increases from ~100 nm to ~1 μm when the excess of PbO in the precursor solution is reduced from 20 to 10 mol%. Switchable polarization is higher in the films with a smaller grain size. Profilometry and the temperature dependence of the dielectric permittivity indicate that films are tensile stressed by the substrate. The grain-size effect on polarization switching is explained by taking into account this tensile stress, which is thought to induce some *a*-domain orientation and 90° domain wall clamping in the grains attached to the substrate.
Order No.: JA912-018

Study of the structure and dielectric relaxation behavior of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ ferroelectric ceramics

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$(1-x)$PMN–xPT [PMN: $Pb(Mg_{1/3}Nb_{2/3})O_3$; PT: $PbTiO_3$] system ferroelectric ceramics with $x = 0.30$, 0.33. 0.35, and 0.38 were synthesized by the columbite precursor method. Their structure and dielectric behavior were investigated. X-ray diffraction results demonstrate that no two-phase region is presented, but a quasi-cubic to tetragonal phase boundary lies between $x = 0.30$ and 0.33. Examination of the dielectric behavior reveals that the transformation from relaxor to normal ferroelectric behavior across the morphotropic phase boundary (MPB) is successive and continuous. It is suggested that $x = 0.30$ to 0.33 is the composition of MPB for PMN-PT system. The MPB is also a boundary for the PMN-PT system to transform from relaxor to normal ferroelectrics.
Order No.: JA912-019

Carbon–silica alloy material as silicon carbide precursor prepared from phenol resin and ethyl silicate

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Three kinds of inorganic–organic hybrid gel sheets were prepared from the liquid mixtures of ethyl-silicate and water-soluble phenol resin. The prepared transparent gel sheets were fired at various temperatures. The density of the fired sheets jumped up at 773–1023 K with disappearance of organic groups. The sheets kept the prepared shape after the 1273 K firing, and their density increased with the silica content. After the firing at 1873 K, the sheets with high carbon content (C/SiO_2: 5.60, 3.52) were converted into the sheets composed of silicon carbide aggregate with excess carbon, while the sheet with low carbon content (C/SiO_2: 1.43) was converted into the fragile powders.
Order No.: JA912-020

Synthesis of nanocrystalline manganese oxide powders: Influence of hydrogen peroxide on particle characteristics

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Nanocrystalline manganese oxide powders have been prepared at 25 °C by precipitation from $Mn(NO_3)_2$ aqueous solution. The presence and addition sequence of H_2O_2 significantly influence particle characteristics of the resulting manganese oxides, including crystal structure, particle size and morphology, and surface area, depending upon molar ratio of H_2O_2 with respect to Mn. The precipitation from pre-oxidized manganese solution by H_2O_2 results in flakelike-shaped amorphous hydrous manganese oxide ($MnO_2 \cdot xH_2O$). In the absence of H_2O_2, on the other hand, amorphous $Mn(OH)_2$ is obtained, and a part of $Mn(OH)_2$ subsequently transforms into crystalline Mn_3O_4 by oxidation in air. Relative population of amorphous $Mn(OH)_2$ decreases by dissolution when post-treated with H_2O_2. At $Mn:H_2O_2 = 1:4$, the well-defined 16-nm-sized nanocrystalline Mn_3O_4 with homogenous particle morphology is prepared. The treatment with excess H_2O_2, however, destroys crystalline Mn_3O_4 and leads to further oxidation on the aqueous manganese species. Under these conditions, a mixture of needlelike Mn_2O_3 and cubelike Mn_3O_4, including amorphous $MnO_2 \cdot xH_2O$ is obtained.
Order No.: JA912-021

The role of zirconia addition in pore development and grain growth in alumina compacts

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The role of 12.4 vol% ZrO_2 addition in the microstructure evolution of alumina compacts during the intermediate and final stages of sintering was investigated by means of small-angle neutron scattering measurements and stereological analysis. Both the pore-size evolution results and the grain-growth data indicate a narrowly defined onset density for the transition to the final sintering stage. The presence of ZrO_2 as a second phase apparently maintains the stability of the intermediate sintering stage out to significantly higher density than in single-phase alumina and plays an important role in inhibiting grain growth and in preventing pore–grain boundary separation. The influence of the ZrO_2 second phase on pore evolution, grain growth, and sinterability of the alumina–zirconia composite is discussed and compared to the behavior of single-phase alumina. The samples were prepared from commercially available powders, with naturally occurring porosity distributions, rather than from artifact (model) pore compacts prepared from nominally pure research-grade materials. The goal was to gain an improved understanding of microstructure development in real materials.
Order No.: JA912-022

Effect of oxygen partial pressure on texture development in lead zirconate titanate thin films processed from metalorganic precursors

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Metalorganic liquid precursors were used to examine the effects of processing atmosphere on texture development in oriented $Pb(Zr_{0.60}Ti_{0.40})O_3$ thin films. After removal of organic ligands via pyrolysis, the films were heated at 25 °C/min in a 5% H_2/Ar atmosphere until a switching temperature, after which the atmosphere was switched to pure oxygen. The films were heated to a maximum temperature of 650 °C with switching temperatures ranging from 450 to 600 °C. The degree of (111) orientation in the lead zirconate titanate (PZT) films increased with increasing switching temperature,

resulting in highly textured (111) PZT films. These results suggest that atmosphere control plays a significant role in texture development during rapid thermal processing.
Order No.: JA912-023

Microstructure of a bearing-grade silicon nitride

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The microstructure of a bearing-grade silicon nitride, prepared by pressureless sintering with Y_2O_3, AlN, and TiO_2 additives and then hot-isostatically pressed, is examined with high-resolution transmission electron microscopy, scanning electron microscopy, and x-ray diffraction. The material consists of large acicular β–Si_3N_4 grains and small equiaxial α–Si_3N_4 grains. An amorphous phase containing the sintering aids is observed at the two-grain boundaries and at the grain pockets. No crystalline boundary phase is identified. The α-to-β and β-to-β grain boundaries appear straight and well defined. The dominant crystalline planes observed at the β-grain boundaries are $(10\bar{1}0)$ and $(11\bar{2}0)$. The intergranular spacing of the two-grain boundaries (α-to-β and β-to-β) is 1.0 nm when a high-contrast boundary phase is present, and it is 0.8 nm when a low-contrast boundary phase is present, confirming that the film thickness is strongly dependent on the boundary-phase composition. The α-to-α boundaries are often curved, and the thickness of the amorphous film at these boundaries varies from 0.7 to 1.1 nm. Evidence of near-intimate contact between β-grains is also observed.
Order No.: JA912-024

Thermochemistry of $Si_{6-z}Al_zO_zN_{8-z}$ (z = 0 to 3.6) materials

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Enthalpies of formation were determined for β-sialon phases ($Si_{6-z}Al_zO_zN_{8-z}$, z = 0.46 to 3.6) by high-temperature oxidative drop solution calorimetry using an alkali borate (52 wt% $LiBO_2$ • 48 wt% $NaBO_2$) solvent. Oxygen gas was bubbled through the melt to accelerate oxidation of the oxynitride samples during dissolution. Sialons near z = 2 appear less stable energetically than ones with higher or lower nitrogen content. A large configurational entropy contribution for sialons with $z > 2$ may further stabilize these materials. This larger free energy driving form may be the reason for success in pulse-activated processing of these materials. The enthalpies of formation further suggest that a greater driving form for oxynitride formation exists in batch synthesis using SiO_2 rather than Al_2O_3.
Order No.: JA912-025

Hydrolysis of tetracalcium phosphate in the presence of a poly(alkenoic acid)

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$Ca_4(PO_4)_2O$ (TetCP) reacts with an acidic polyelectrolyte in the absence of a solvent to form a composite composed of $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite, or HAp) and the Ca salt of the polyelectrolyte. Mixtures of an acrylic copolymer and $Ca_4(PO_4)_2O$ powders were hot pressed, and the effects of temperature, pressure, and time on HAp formation were studied. Reaction starts when the copolymer is heated to above T_g. Initial carboxyl site neutralization liberates water, continued TetCP hydrolysis liberates Ca^{2+} ions, which react with the copolymer forming its Ca salt. When 90% conversion to HAp was achieved, the composite had an average tensile strength of 51 MPa, a Vickers hardness of 145 kg/mm^2 and a $T_g \sim 250$ °C.
Order No.: JA912-026

Effect of heat treatment on elastic properties of separated thermal barrier coatings

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Elastic response behavior of four different plasma-sprayed deposits has been investigated using depth-sensing micro-indentation technique. Due to the high degree of porosity and inhomogeneity of the coatings, the characteristic elastic moduli were found to be in the range of 20–75% of that of the dense bulk material (200 GPa). Considering the wide variation of properties, 150 data points were generated with five different indentation loads for each coating, and statistical tools were employed to represent the scatter of the data. The characteristic elastic moduli of all the coatings were observed to be almost doubled when the magnitude of indentation load was reduced form the highest (1000 mN) to the lowest (30 mN). The coatings were subsequently heat treated at 1100 °C, the operational temperature of a gas-turbine, for 2, 25, and 100 h, and in all the coating grades the corresponding elastic moduli increased significantly. However, the stiffening effect was not uniform in two grades and was more pronounced for the smaller indentation loads. The increase in elastic modulus is attributed to elimination of fine porosity and sintering neck formation, an assumption also supported by the results of mercury porosimetry.
Order No.: JA912-027

Diffused phase transition in fine-grained bismuth vanadate ceramics

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Nanocrystalline powders of ferroelectric bismuth vanadate, $Bi_4V_2O_{11}$ (n-BiV) with crystallite size less than 50 nm, were obtained by mechanical milling of a stoichiometric mixture of bismuth oxide and vanadium pentoxide. The n-BiV powders on sintering yielded high-density, fine-grained ceramics with improved dielectric and polar characteristics. Dielectric studies on samples obtained from milled powders indicated that the ferroelectric-to-paraelectric phase transition temperature is strongly frequency dependent. The Curie–Weiss law is found to be valid only at a temperature away from the transition temperature, confirming the diffused nature of the transition, which is attributed to the presence of compositional inhomogeneity, because of partial reduction of vanadium.
Order No.: JA912-028

Effect of film composition on the orientation of $(Ba,Sr)TiO_3$ grains in $(Ba,Sr)_yTiO_{2+y}$ thin films

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Thin films of composition $(Ba,Sr)_yTiO_{2+y}$, with $0.43 \leq y \leq 1.64$, were deposited by metalorganic chemical vapor deposition on (100)MgO substrates at various growth conditions. X-ray diffraction and transmission electron microscopy studies showed that the films were composed of epitaxial $Ba_{1-x}Sr_xTiO_3$ ($x \approx 0.06$) grains and an amorphous phase. The orientation of the tetragonal $Ba_{1-x}Sr_xTiO_3$ grains (pure *a* axis, pure *c* axis, or a mix of the two) was found to be strongly dependent upon film composition. This composition dependence is explained for the majority of the Ti-rich films by an analysis of average strains in the two-phase films, assuming a compressive strain of ≈1% in the amorphous phase.
Order No.: JA912-029

Synthesis of α–Al_2O_3 platelets using sodium sulfate flux

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When powder mixtures of {$Al_2(SO_4)_3$ + Na_2SO_4} or {γ–Al_2O_3 [obtained by heating $Al_2(SO_4)_3$ at 900 °C for 3 h] + Na_2SO_4} were heated in an alumina crucible at 1100 °C for 1 h, α–Al_2O_3 platelets were formed. The powder mixture of {$Al_2(SO_4)_3$ + $2Na_2SO_4$} yielded aggregations of platelets that were less than 5 μm in size. The size of the aggregations increased in proportion to the amount of Na_2SO_4, and aggregations of 120 μm were obtained using a mixture of {$Al_2(SO_4)_3$ + $6Na_2SO_4$}. The powder mixture of {γ–Al_2O_3+ $2Na_2SO_4$} yielded hexagonal platelets having an average diameter of 3.7 μm and an average thickness of 0.3 μm. In addition to aggregation size, the size of the hexagonal platelets also increased in proportion to the amount of Na_2SO_4, and platelets having an average diameter of 5 μm were obtained using a mixture of {γ–Al_2O_3 + $6Na_2SO_4$}.
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In situ transmission electron microscopy investigation of threading dislocation motion in passivated thin aluminum films

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In situ transmission electron microscopy (TEM) was performed to study dislocation motion during temperature cycles in aluminum films passivated with a SiO_2 layer. The films were cycled from room temperature to 450 °C. Wedge-shaped cross-sectional TEM samples were used to retain the constraint

of the Si substrate. Besides interactions between dislocations and interfaces, the movement of threading dislocations within the constrained aluminum film was observed. This observation provides an experimental corroboration of the occurrence of threading dislocation motion, which is the basis for rationalizing the high yield strength of thin films in available models of thin-film plasticity.
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Relationship between domain structure and film thickness in epitaxial $PbTiO_3$ films deposited on MgO(001) by reactive sputtering

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The epitaxial $PbTiO_3$ thin films of different thickness were prepared on MgO(001) substrates by the reactive direct-current magnetron sputtering. The volume fraction of *c* domains, α, which was measured by x-ray diffractometry, increased rapidly from zero with the film thickness, being saturated at about 90% above 100 nm. The films were annealed in a PbO atmosphere at 700 °C for 8 h, and they were used to study the composition change in the Pb/(Pb + Ti) ratio and the relaxation of the residual intrinsic stress. The relationship between change of α and composition was weak. The stress state was calculated through the finite-element method. As for the small thickness, the tensile epitaxial stress overwhelmed compressive intrinsic and thermal stresses, and the domain structure was *a*-domain oriented. As for the large thickness, the compressive intrinsic stress together with the thermal stress overcame the tensile epitaxial stress, and the population turned into *c* domain.
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Interface structure of AlN/TiN/MgO(001) prepared by molecular beam epitaxy

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Thin AlN films were grown by molecular beam epitaxy on MgO(001) substrate with a thin TiN buffer layer. The as-prepared AlN/TiN/MgO(001) interfaces have been characterized by cross-sectional high-resolution electron microscopy (HREM). It was found that the thin TiN buffer layer is *epitaxially* grown on the MgO(001) substrate and hexagonal AlN *epitaxially* on the as-received TiN(001). Based on the growth orientation relationship and HREM images, atomistic structure models for the AlN/TiN interface are proposed, image-simulated, and compared with experimental images.
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Mechanisms for enhanced C54–$TiSi_2$ formation in Ti–Ta alloy films on single-crystal Si

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The mechanisms are studied for enhanced formation of C54–$TiSi_2$ at about 700 °C when rapid thermal annealing at 3 °C/s in N_2 is performed on 32-nm-thick codeposited Ti–5.9 at.% Ta on Si(100) single-crystal substrates. The enhancement is related to an increased C54–$TiSi_2$ nucleation rate due to the development of a multilayered microstructure. The multilayer microstructure forms at temperatures below 600 °C with the formation of an amorphous disilicide adjacent to the Si substrate and a M_5Si_3 (M = Ti, Ta) capping layer. This amorphous disilicide crystallizes at higher temperatures to C49–$TiSi_2$. The multilayer microstructure introduces an additional interface that increases the area available for the heterogeneous nucleation of C54. The capping layer is identified as hexagonal Ti_5Si_3 or its isomorphous compound $(Ti_{1-x}Ta_x)_5Si_3$. Crystal simulations demonstrate that C54(040) has a lattice mismatch of 6–7% relative to Ti_5Si_3(300) suggesting that a pseudomorphic epitaxial relationship may lower the interfacial energy between these two phases and reduce the energy barrier for C54 nucleation. A C40 disilicide phase was also observed at temperatures above that required to form C54–$TiSi_2$ suggesting that, in the present experiments, the C40 phase does not play a major role in catalyzing C54 formation.
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Phase transition and the soft lattice mode of a perovskite crystal studied by Raman scattering and thermal measurements

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The paraelectric–ferroelectric structural transition of potassium lithium tantalite niobate has been studied by both Raman scattering and thermal measurements. A condensed soft lattice vibrational mode at the phase transition has been analyzed. It originates from the symmetric O2/3–Nb/Ta–O3/2 in-plane bending of the Nb/TaO_6 group. The soft optical phonon mode concerns the extraordinary transverse optical phonons propagating along the $[1\bar{1}0]$ direction. The thermal expansion experiments show a displacive phase transition and a big thermal contraction in the *c* direction of the crystal, with an average linear expansion coefficient $\alpha_c = -4.52 \times 10^{-5}$ K^{-1}. The phase transition temperature and enthalpy are 358 K and 0.50 J/g, respectively. Curie temperature measured by four methods is within 353 and 360 K.
Order No.: JA912-035

An extended x-ray adsorption fine structure study of rare-earth phosphate glasses near the metaphosphate composition

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A variable temperature (79, 145, and 293 K) extended x-ray absorption fine structure study, using rare-earth L_{III} absorption edges, is reported for phosphate glasses doped with rare-earth elements (R, where R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er) with compositions close to metaphosphate, $R(PO_3)_3$. The results yield nearest neighbor R–O distances that demonstrate the lanthanide contraction in a glassy matrix and an R–O coordination intermediate between 6 and 7 for rare-earth ions with smaller atomic number (Z), and 6 for rare-earth ions with larger Z. Thermal parameters show no significant changes in R–O distances or coordination numbers between 293 and 79 K. There is evidence of an R–P correlation between 3.3 and 3.6 Å and the beginning of a second R–O correlation at approximately 4 Å. No R–R correlations up to a distance of approximately 4 Å were observed.
Order No.: JA912-036

Hydroxyapatite coatings grown by pulsed laser deposition with a beam of 355-nm wavelength

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Calcium phosphate coatings, obtained at different deposition rates by pulsed laser deposition with a Nd:YAG laser beam of 355-nm wavelength, were studied. The deposition rate was changed from 0.043 to 1.16 Å/shot by modification of only the ablated area, maintaining the local fluence constant to perform the ablation process in similar local conditions. Characterization of the coatings was performed by scanning electron microscopy, x-ray diffractometry, and infrared, micro-Raman, and x-ray photoelectron spectroscopy. The coatings showed a compact surface morphology formed by glassy gains with some droplets on them. Only hydroxyapatite (HA) and alpha-tricalcium phosphate (α–TCP) peaks were found in the x-ray diffractograms. The relative content of α–TCP diminished with decreasing deposition rates, and only HA peaks were found for the lowest rate. The origin of α–TCP is discussed.
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Silicide formation in implanted channels and interfacial reactions of metal contacts under high current density

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Silicide formation in implanted channels and interfacial reactions of Ni, Co, Ti, and Cu contacts under high current density have been investigated. Silicide lines, forming in the implanted channels, were observed in Ni and Cu/p^+–Si samples, but not in Ti and Co samples. The silicide line formation is correlated to the high diffusivity of metals in Si. For the Ni/p^+–Si samples, silicide line was found to initiate from the cathode contact. Network structures at the cathode were found in both Co and Ni samples. The depth of silicide formation was found to extend to the junction depth. The relationships between the silicide length and contact size, the applied current, and the method of the applied current are discussed.
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