JMR Abstracts

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ABSTRACTS

COMMUNICATIONS

Preparation of a nanostructured organoceramic and its reversible interlayer expansion

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We described previously the liquid phase synthesis and characterization of a nanostructured composite from an aqueous solution containing organic polymer and inorganic ions [J. Mater. Res. **7**, 2599 (1992)]. The nanocomposite, termed an organoceramic, consisted of poly(vinyl alcohol) chains intercalated between the principal layers of a hydrated calcium aluminate ceramic. A key structural feature of the organoceramic is the polymer-induced expansion of the interlayer spacing by approximately 1 nm compared to the unmodified ceramic. In this paper, we describe the synthetic scheme that favors organoceramic formation and prove the existence of intercalated polymers by observation of reversible interlayer expansion and contraction in response to changes in ambient humidity. This property is unique to the organoceramic and is not observed in the unmodified calcium aluminate ceramic.

Order No.: JA902-001

Power spectra of roughness caused by grinding of metals

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The roughness of metallic surfaces generated by machining depends on the intended intervention by the tool and the inadvertent consequences determined by the response of metals. The roughness generated in four different metals by grinding is studied using the power spectrum method. It was found that the level of power is determined by the intended intervention such as the depth of cut and, to some extent, by hardness because of its possible influence on micropileup geometry. The power gradient is, however, influenced by inadvertent damage which may be related to material properties such as thermal conductivity and adhesion.

Order No.: JA902-002

Stability of fullerenes under hydrothermal conditions

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Stability of fullerenes C_{60} under hydrothermal conditions (200–800 °C, 100 MPa, 20 min–168 h) has been investigated. The reaction products have been characterized by Raman spectroscopy and x-ray diffraction. The fullerenes were stable up to 500 °C, but they decomposed immediately at 800 °C into amorphous carbon. In the transition region between 600 and 750 °C, longer times and higher temperatures of the hydrothermal treatment favored decomposition of C_{60} with the formation of amorphous carbon. Addition of nickel to the C_{60}–H_2O system neither suppressed hydrothermal decomposition of C_{60} nor induced formation of other phases, except of the amorphous carbon.

Order No.: JA902-003

Improving the synthesis of alkyl phosphates as sol-gel precursors
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Alkyl phosphates can be used as sol-gel precursors for phosphate-based glasses and glass-ceramics. An improvement in the synthesis of alkyl phospates is presented. Following the procedure here described, it is possible to limit the fraction of condensed phosphates to 1–2%. At the same time, a ratio between mono- and disubstituted phosphates near to that given by the reaction stoichiometry may be attained.
Order No.: JA902-004

Third-order nonlinear optical properties of the Na_2S–PbS–GeS_2 sulfide glasses and the Na_2S–PbO–GeS_2 oxysulfide glasses
Z.H. Zhou, H. Nasu, T. Hashimoto, K. Kamiya
(Mie University)

The third-order optical nonlinearity of glasses of the Na_2S–PbS–GeS_2 and Na_2S–PbO–GeS_2 systems was measured by the third-harmonic generation method. The third-order nonlinearities of glasses of both systems increased with the increasing lead content. The maximum value of the third-order optical nonlinearity was 3.00×10^{-12} esu. The addition of PbO had basically little influence on third-order optical nonlinearity, and the largest nonlinearity is 1.49×10^{-12} esu. The minimum appeared at 15 mol% PbO can be explained by the decrease of number density of lead and sulfur. Chemical durability of oxysulfide glasses is superior to that of a pure sulfide system, thus the addition of PbO is important in this sense.
Order No.: JA902-005

ARTICLES

Synthesis and crystal chemistry of the new compounds $GdBa_4Cu_3O_{8.5+\delta}$ and $DyBa_4Cu_3O_{8.5+\delta}$
Y.T. Zhu, E.J. Peterson, P.S. Baldonado, J.Y. Coulter, D.E. Peterson, F.M. Mueller
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Two new compounds, $GdBa_4Cu_3O_{8.5+\delta}$ (Gd143) and $DyBa_4Cu_3O_{8.5+\delta}$ (Dy143) were synthesized from precursors Gd_2O_3, Dy_2O_3, BaO_2, and CuO at 1000 °C in an oxygen atmosphere. The oxygen stoichiometric value δ was found to be 0.68 for Gd143 and 0.6 for Dy143 by iodometric titration. Rietveld refinement of x-ray powder diffraction data showed that Gd143 belongs to the space group Pm3 while Dy143 belongs to the space group P23. The two space groups, Pm3 and P23, are very similar. Their main difference is that P23 does not have the inversion symmetry of Pm3. Both compounds have a cubic unit cell with a lattice parameter of 8.16528 ± 0.00006 Å for Gd143 and 8.10807 ± 0.00010 Å for Dy143. Superconducting quantum interference device (SQUID) measurement indicated that neither compound was superconductive down to 5 K.
Order No.: JA902-006

The effect of lead content on the critical current density, irreversibility field, and microstructure of Ag-clad $Bi_{1.8}Pb_xSr_2Ca_2Cu_3O_y$ tapes
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We studied the effect of lead content ($x = 0.20$–0.40) on the critical current density J_c(0T, 77 K), irreversibility field H*(77 K), and microstructure of monocore, Ag-clad $Bi_{1.8}Pb_xSr_2Ca_2Cu_3O_y$ (2223) tapes, finding that tapes with lower lead contents ($x = 0.20$–0.25) required higher processing temperatures (840 and 832 °C, respectively) to complete 2223 formation, as compared to the optimum 820 °C reaction temperature of the $x = 0.30$–0.40 tapes. We found that both the zero-field and the in-field properties correlated strongly to the phase purity with J_c (0T, 77 K) reaching a maximum of ~20 kA/cm^2 for $x = 0.30$, and then decreasing with in-creasing lead content to ~12 kA/cm^2 for $x = 0.40$. H*(77 K) increased from ~165 mT at $x = 0.20$ to ~265 mT at $x = 0.30$, then declined to 195 mT at $x = 0.40$. Optimizing the lead content at $x = 0.30$ maximized both the connectivity and the flux pinning contributions to the critical current density.
Order No.: JA902-007

Structure and misorientation angle distributions of (001) twist grain boundaries in $Bi_2Sr_2Ca_1Cu_2O_y$/Ag composite tapes processed in different oxygen partial pressures
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We investigated the relationship between the structure and misorientation angle of (001) twist grain boundaries in $Bi_2Sr_2Ca_1Cu_2O_y$/Ag composite tapes processed in different oxygen partial pressures (P_{O2} = 0.01, 0.21, and 1 atm). Large-angle misoriented twist boundaries (>10°) essentially had no amorphous layers at the interface and the misorientation angles of these boundaries mostly corresponded to low-energy misorientations. This large-angle misoriented boundary structure was independent of P_{O2}. Small-angle misoriented twist boundaries (<10°), on the other hand, corresponded to high-energy misorientations, and sometimes had amorphous layers at the interface. The population of the small-angle boundary with an amorphous layer was very low in the tape processed in P_{O2} = 1 atm. This suggests that high P_{O2} during the heat treatment is effective in the improvement of grain coupling, and hence, to increase critical current density.
Order No.: JA902-008

High-temperature deformation of vertical gradient freeze melt-textured YBCO
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The deformation behavior of melt-textured YBCO prepared by the vertical gradient freeze (VGF) method was investigated by high-temperature deformation experiments at temperatures ranging from 850 to 950 °C. The experiments were performed in an atmosphere of pure oxygen under uniaxial pressure with constant strain rates in the range from 1×10^{-5} to 5×10^{-4} s^{-1}. An analysis of the dependence of the steady state flow stress on the strain rate and the deformation temperature reveals that the predominant deformation mechanism is dislocation glide and climb controlled by climb at Y-211 particles and that no significant grain boundary sliding occurs. Furthermore, transmission electron microscope (TEM) observations of deformed and undeformed samples support a deformation mechanism based on dislocation movement. The total fracture strain, however, does not depend on the temperature or strain rate. Scanning electron microscope (SEM) investigations of the fracture faces of samples deformed until fracture reveal that fracture does not occur within the Y-123 matrix but along platelet boundaries. An improvement of the fracture behavior is expected by introducing large Y-211 particles interconnecting neighboring platelets.
Order No.: JA902-009

Silicon and zinc telluride nanoparticles synthesized by low-energy density pulsed-laser ablation into ambient gases
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The size distributions of Si and ZnTe nanoparticles produced by low-energy density ArF (193 nm) pulsed-laser ablation into ambient gases were measured as a function of the gas pressure, P, and target-substrate separation, D_{ts}. For both Si and ZnTe, the largest nanoparticles were found closest to the ablation target, and the mean nanoparticle size decreased with increasing D_{ts}. For Si ablation into He, the mean nanoparticle diameter did not increase monotonically with gas pressure but reached a maximum near P = 6 torr. High resolution Z-contrast transmission electron microscopy and energy loss spectroscopy revealed that ZnTe nanoparticles consist of a

crystalline core surrounded by an amorphous ZnO shell; growth defects and surface steps are clearly visible in the crystalline core. A pronounced narrowing of the ZnTe nanocrystal size distribution with increasing D_{ts} also was found. The results demonstrate that the size of laser-ablated nanoparticles can be controlled by varying the molecular weight and pressure of an ambient gas and that nanometer-scale particles can be synthesized. Larger aggregates of both ZnTe and Si having a "flakelike" or "weblike" structure were formed at the higher ambient gas pressures; for ZnTe these appear to be open agglomerates of much smaller (~10 nm) particles.

Order No.: JA902-010

Formation process of interface states at grain boundaries in sputtered polycrystalline Si films

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A systematic investigation has been made on surface defect states of crystallites in the crystallization process of sputtered amorphous silicon films by isothermal annealing. Transmission electron microscopic observations indicate a pronounced vertical columnar structure in the upper part of the films, where the crystallization is delayed. Admittance spectroscopy reveals that two newly generated energy levels with the crystallization are attributed to the crystallites in the lower and upper parts of the films in view of the anisotropic crystallization. These thermally induced changes can be well explained by Si–Si shearing modes at the interfaces of crystallites through the process of crystallization.

Order No.: JA902-011

Phase selection in a mechanically alloyed Cu–In–Ga–Se powder mixture

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Formation of a homogeneous nanocrystalline $CuIn_{0.7}Ga_{0.3}Se_2$ alloy was achieved by mechanical alloying of blended elemental Cu, In, Ga, and Se powders in a planetary ball mill. X-ray diffraction and transmission electron microscopy and diffraction techniques were employed to follow the structural evolution during milling. It was observed that, depending upon the milling conditions, either a metastable cubic or a stable tetragonal phase was produced. The grain size of the mechanically alloyed powder was about 10 nm. The mechanically alloyed powder was consolidated to full density by hot isostatic pressing of the powder at 750 °C and 100 MPa for 2 h. Irrespective of the nature of the phase in the starting powder, the hot-isostatically-pressed compact contained the well-recrystallized tetragonal $CuIn_{0.7}Ga_{0.3}Se_2$ phase with a grain size of about 50 nm.

Order No.: JA902-012

Precipitation behavior in the early stage of aging in an Al–Li–Cu–Mg–Zr–Ag (Weldalite 049) alloy

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The precipitation behavior of various phases during the aging process of an Al–Li–Cu–Mg–Zr–Ag (Weldalite 049) alloy was investigated by high-resolution electron microscopy and *in situ* hot-stage microscopy. Two kinds of domains with $L1_2$-type ordered structures, which are considered to be δ′ and β′ phases, are observed with different domain sizes in the alloy quenched from 530 °C. In the early stage of aging at 190 °C, the δ′ phase is precipitated as surrounding the β′ phase, and the δ′ domains appear with inphase and antiphase relationships to the β′ lattices. *In situ* observations at 190 °C clearly show that the T1 phase precipitates predominantly on dislocations at subgrain boundaries and then is homogeneously formed in the matrix with increasing aging time. The nucleation of the S′ phase is associated with clustering of Cu and Mg in the matrix, and the S′ domains are grown with {210} habit planes.

Order No.: JA902-013

Grain boundary filmlike Fe–Mo–Cr phase in nitrogen-added type 316L stainless steels

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The precipitates in nitrogen-added type 316L stainless steels (SS) were investigated by transmission electron microscopy (TEM) after thermal aging. Besides carbides ($M_{23}C_6$ and M_6C) and intermetallic phases, an unknown phase of an Fe–Mo–Cr(–Si) system in a filmlike morphology precipitated at grain boundaries. In spite of the similarity in its chemical composition to that of the Laves phase, the phase of the Fe–Mo–Cr(–Si) system exhibited five-, three-, and twofold symmetries, which are generally observed in quasicrystals having icosahedral symmetry. This phase was formed from the intergrowth of small crystalline clusters of the Laves phase. Decreasing the nitrogen content to that of commercial type 316L grade suppressed the formation of the filmlike fivefold phase. This was attributed to the dissipation of small Laves clusters by $M_{23}C_6$ carbides, which increased as a result of the decreased nitrogen content.

Order No.: JA902-014

The preparation and characterization of ultrafine Fe–Ni particles

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Ultrafine Fe, Fe–Ni, and Ni particles were prepared by using hydrogen plasma-metal reaction method in a mixture of H_2 and Ar of 0.1 MPa. The particles were characterized by x-ray diffraction, transmission electron spectroscopy, energy disperse spectroscopy, chemical analysis, and Mössbauer spectroscopy. In contrast with bulk Fe–Ni alloys, the distinguished features in corresponding ultrafine particles are that two phases with fcc and bcc structures coexist in a wide composition range. Ultrafine Fe–Ni particles have higher resistance to oxidation than Fe and Ni particles. The mechanism of forming particles was analyzed by means of structural and magnetic measurements. It was found that quenching is a dominant mechanism for forming paramagnetic particles. Hyperfine interactions were studied by Mössbauer spectroscopy in comparison with those in bulk Fe–Ni alloys.

Order No.: JA902-015

Haasen plot analysis of the Hall-Petch effect in Cu/Nb nanolayer composites

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We investigate the effects of layer thickness (t) on hardness (H) and rate sensitivity of the hardness ($\partial H/\partial \ln \dot{\varepsilon}$) in 1 μm-thick Cu/Nb nanolayer composites. For t > 10 nm, we find that H correlates with t according to $H = H_0 + H_1 t^{-1/2}$, suggestive of a Hall-Petch mechanism with layer interfaces replacing grain boundaries as barriers against dislocation motion. The measured levels of $\partial H/\partial \ln \dot{\varepsilon}$ clearly indicate the operation of bulklike dislocation mechanisms consistent with a Hall-Petch mechanism. However, based on a Haasen-plot activation analysis, it appears that the Hall-Petch coefficient, H_1, is strongly rate-dependent, inconsistent with a conventional Hall-Petch mechanism. For specimens with t < 10 nm there is a saturation in hardness, but the rate sensitivity data indicate no clear evidence of a corresponding change in mechanism. Simple models are proposed.

Order No.: JA902-016

Preparation of poly lactic acid composites containing β-$Ca(PO_3)_2$ fibers

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Novel biomaterials for application to artificial bone with modulus of elasticity close to that of natural bone were prepared using bioresorbable poly-L-lactic acid (PLLA) and high-strength β-$Ca(PO_3)_2$ fibers treated with dilute NaOH solution. PLLA dissolved by using methylene chloride was mixed with the fibers. After drying the mixture, it was hot-pressed uniaxially

under a pressure of 40 MPa at 180 °C, resulting in fabrication of a PLLA-composite containing β–$Ca(PO_3)_2$ fibers. Almost no degradation in the bending strength was observed even when a large amount of the fibers (≈50 wt%) was introduced, and the modulus of elasticity was increased effectively with increasing the fiber content. The PLLA-composite with modulus of elasticity of >5 GPa, similar to that of natural bone, was found to be prepared when the fiber content was over 35 wt%. The bending test of the composites showed that very high energy is consumed for their fracture and that the fracture proceeds step by step, even beyond the maximum stress.

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Hydrothermal synthesis of ferroelectric perovskites from chemically modified titanium isopropoxide and acetate salts

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The feasibility of the acetylacetonate-Ti isopropoxide complex as a new precursor for synthesis of Ti-based perovskite particles under hydrothermal conditions has been demonstrated. Ferroelectric powders including $BaTiO_3$, $PbTiO_3$, PZT, PLZT, and $SrTiO_3$ were prepared by reacting the acetylacetonate-modified Ti precursor in metal acetate aqueous salt solution under hydrothermal conditions. Synthesis parameters including reaction time and temperature, feedstock concentration, and reaction medium significantly influence particle characteristics of the hydrothermally derived perovskite powders. It is proposed that use of the acetylacetonate-modified Ti precursor promotes intimate mixing among multicomponent reacting species at the molecular level and promotes particle formation through a dissolution/recrystallization mechanism.

Order No.: JA902-018 **© 1998 MRS**

New approach in the monitoring and characterization of titanium nitride thin films

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In situ and *ex situ* spectroscopic ellipsometry (SE), Raman spectroscopy (RS), x-ray photoelectron spectroscopy (XPS), and auger electron spectroscopy (AES) have been used to study the stoichiometry and to characterize TiN_x thin films deposited by magnetron sputtering at various stoichiometries. *In situ* SE can provide parameters, such as the plasma energy, that can be utilized for monitoring of the film stoichiometry. Besides plasma energy, optical phonon position in RS was also found to be a sensitive probe of TiN_x stoichiometry as detected by RS, XPS, and *ex situ* SE. Under these conditions, AES faces difficulties for reliable film characterization, and the complementary use of other techniques is required for determining the exact film stoichiometry.

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Structural characterization of TiO_2 ultrafine particles

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Four samples of TiO_2 ultrafine particles (UFP) were obtained through different processes. The structure of TiO_2 ultrafine particles and the factors influencing the structure were investigated with Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and x-ray diffraction (XRD). Both Raman spectra and x-ray diffractogram show the similar regularity of the phase transformation among the four samples. The observed bimodal lineshape-structure in the Raman spectra is attributed to the intragrain and grain-boundary components of TiO_2 UFP. The crystal structure of TiO_2 UFP is found to be distorted by the surface structure such as OH and OCH_2CH_3 groups coordinated on the surface of TiO_2 UFP.

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Phase equilibria and crystal chemistry in the Y_2O_3–Al_2O_3–SiO_2 system

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In order to clarify inconsistencies in the literature and to verify assumed ternary solubilities, the phase equilibria in the Y_2O_3–Al_2O_3–SiO_2 system at 1600, 1400, and 1300 °C were experimentally determined using x-ray diffraction (XRD), scanning electron microscope with attached energy-dispersive detector system (SEM-EDX), and electron probe microanalyzer (EPMA). Six quasibinary phases were observed: $Y_4Al_2O_9$ (YAM), $YAlO_3$ (YAP), $Y_3Al_5O_{12}$ (YAG), Y_2SiO_5, $Y_2Si_2O_7$ (C and D modifications), and ~$3Al_2O_3 \cdot 2SiO_2$ (mullite). $Y_4Al_2O_9$ forms an extended ternary solid solution with the formula $Y_4Al_{2(1-x)}Si_{2x}O_{9+x}$ ($x = 0$ - ~0.3.I). The lowest ternary eutectic temperature was determined at 1371 ± 5 °C by high-temperature differential scanning calorimetry (DSC). The results were compared with previous data available for the Y_2O_3–Al_2O_3–SiO_2 system and with data for other RE_2O_3–Al_2O_3–SiO_2 (RE = rare-earth element) systems.

Order No.: JA902-021 **© 1998 MRS**

High-temperature powder x-ray diffraction of yttria to melting point

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Powder x-ray diffraction data of yttria (Y_2O_3) were obtained from room temperature to melting point with the thin wire resistance heating technique. A solid-state phase transition was observed at 2512 ± 25 K, and melting of the high-temperature phase at 2705 ± 25 K. Thermal expansion data for α–Y_2O_3 (*C*-type) are given for the range 298–2540 K. The unit cell parameter increases non-linearly, especially just before the solid-state transition. The x-ray diffraction spectrum of the high-temperature phase is consistent with the fluorite-type structure (space group Fm3) with a refined unit cell parameter $a = 5.3903(6)$ Å at 2530 K. The sample recrystallized rapidly above 2540 K, and above 2730 K, all the diffraction lines and spots disappeared from the x-ray diffraction spectrum that suggests complete melting.

Order No.: JA902-022 **© 1998 MRS**

Phenomenological analysis of α'_L-to-β martensitic transformation in phosphorus-bearing dicalcium silicate

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Crystals of $(Ca_{1.95}\square_{0.05})(Si_{0.9}P_{0.1})O_4$, where □ denotes a vacancy, composed of both the α'_L and β-phases, were prepared and examined by the precession method. The β-phase was exclusively twinned on $(100)_\beta$ and the relative volume of the twin-related variants were almost identical with each other. On the basis of the lattice correspondence between the two phases and their cell parameters, the phenomenological crystallographic theory was applied to determine the habit planes and the shape deformations upon α'_L-to-β martensitic transformation. The habit planes, which define the coherent interphase boundaries between α'_L and β, were nearly parallel to either $(100)_{\alpha'_L}$ or $(010)_{\alpha'_L}$. The alternate shape deformations that produce the former habit planes resulted in the actual (100) twin structure of the β-phase. The total displacement was along $[\bar{1}00]_{\alpha'_L}$ with the magnitude of 0.008. Because the transformation involved a very small volumetric shrinkage of 0.6%, the strain accommodation would be almost completed. The coherency at the interface boundaries between the two phases and the effective strain accommodation probably caused the thermoelasticity of the Ca_2SiO_4 solid solutions.

Order No.: JA902-023 **© 1998 MRS**

Commonalties of the influence of lower valent A-site and B-site modifications on lead zirconate titanate ferroelectrics and antiferroelectrics

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Studies of the structure-property relations of lead zirconate titanate (PZT) modified with lower valent substitutions on the A- and B-sites have been performed as a function of substituent concentration. These investigations have yielded common changes induced by these substitutions on ferroelectric phases. The commonalties are the presence of fine domains and polarization pinning effects. Differences in domain morphologies were observed between the rhombohedral and tetragonal ferroelectric phases. Rhombohedral ferroelectrics were found to exhibit "wavy" domain patterns with increasing dopant concentrations, whereas a lenticular domain shape was preserved as the domain size was decreased for tetragonal ferroelectrics. These differences were explained in terms of different pinning mechanisms based on the differences in local elastic strain accommodations. Investigations of high Zr-content PZT have revealed that the ferroelectric rhombohedral phase becomes stabilized over the antiferroelectric orthorhombic with increasing concentrations of lower valent modifications. This change was explained in terms of the enhanced coupling between oxygen octahedra due to the bonding of oxygen-vacancies dipoles.

Order No.: JA902-024

Dielectric, piezoelectric, and pyroelectric anisotropy in KCl-modified grain-oriented bismuth vanadate ceramics

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The effect of the additive KCl on the structural, microstructural, and polar properties of bismuth vanadate (BiV) ceramics are investigated. The scanning electron microscopic (SEM) studies reveal a remarkable modification in the microstructure and the occurrence of high grain-orientation (75%) on KCl addition. The energy-dispersive x-ray (EDX) analyses indicate the presence of chemically inhomogeneous distribution of KCl with core-shell-like grain structure. The KCl modified BiV samples exhibit a broad and depressed phase transition, with no frequency dispersion, as a result of the increased internal stress and the formation of core-shell-like grain structure. Significant anisotropies are observed in the dielectric, pyroelectric, and piezoelectric responses of these grain-oriented ceramic samples. These samples are characterized by near rectangular ferroelectric hysteresis loops with a significant anisotropy in the $P_r(P_{r\perp}/P_{r\parallel} \approx 2.43$, at 300 K) and E_c ($E_{c\parallel}/E_{c\perp} = 2.22$, at 300 K) values, between the directions parallel and perpendicular to the cold-pressing axis.

Order No.: JA902-025

Fabrication and characterization of ferroelectric $Pb(Zr_xTi_{1-x})O_3$ thin films by metalorganic chemical vapor deposition

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Ferroelectric $Pb(Zr,Ti)O_3$ (PZT) thin films were grown on $Pt/Ti/SiO_2/Si$, $RuO_2/Pt/Ti/SiO_2/Si$, and Pt/MgO substrates at the substrate temperature of 600 °C by the metalorganic chemical vapor deposition (MOCVD) method. $Pb(C_{11}H_{19}O_2)_2(Pb(DPM)_2)$, $Ti(O^iC_3H_7)_4$, $Zr(O^tC_4H_9)_4$ as source material and Ar and O_2 as a carrier gas and oxidizing agent were selected, respectively. In order to investigate the effect of Zr and Ti component changes on the growth aspect of PZT thin films, Zr and Ti source materials were varied by controlling Zr and Ti flow rate. From the Rutherford backscattering spectroscopy (RBS) measurement, it was confirmed that the composition of the films, particularly Pb content, changed with the increasing Zr flow rate. In addition, the x-ray diffraction (XRD) spectra analysis showed the existence of a Pb-deficient pyrochlore phase as well as ZrO_2 as a secondary phase. From these results, it is believed that the higher Zr partial pressure in the gas phase reduces the sticking of the Pb precursor to the substrate. The film with Pb : Zr : Ti = 1 : 0.42 : 0.58 showed a dielectric constant of 816 at 1 MHz. The spontaneous polarization, remanent polarization, and coercive field measured from the RT66A by applying 3.5V were 44.1 μC/cm², 24.4 μC/cm², and 59.6 kV/cm, respectively. The fatigue analysis of PZT thin films with Pb : Zr : Ti = 1 : 0.42 : 0.58 at an applied voltage of $V_{p-p} = 5.4$ V showed 40% degradation on the basis of initial polarization value after 109 cycles.

Order No.: JA902-026

Rapid thermal processing of lead zirconate titanate thin films on Pt–GaAs substrates based on a novel 1,1,1-tris(hydroxymethyl)ethane sol-gel route

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Thin films of lead zirconate titanate (PZT) having a nominal composition of $Pb(Zr_{0.53}Ti_{0.47})O_3$ have been prepared on platinized GaAs (Pt–GaAs) substrates using a new 1,1,1-tris(hydroxymethyl)ethane (THOME) based sol-gel technique. Rapid thermal processing (RTP) techniques were used to decompose the sol-gel layer to PZT in an effort to avoid problems of Ga/As outdiffusion into the PZT. A crystalline PZT film was produced by firing the sol-gel coatings at 600 or 650 °C for a dwell time of 1 s using RTP. A single deposition of the precursor sol resulted in a 0.4 μm thick PZT film. X-ray diffraction measurements revealed that the films possessed a high degree of (111) preferred orientation. Measured average values of remanent polarization (P_r) and coercive field (E_c) for the film annealed at 650 °C for 1 s were 24 μC/cm² and 32 kV/cm respectively, together with a low-requency dielectric constant and loss tangent at 1 kHz of 950 and 0.02. These values are comparable to those obtainable on platinized silicon (Pt–Si) substrates using conventional sol-gel methods and are an improvement on PZT thin films prepared on platinized GaAs using an earlier sol-gel route based on 1,3-propanediol.

Order No.: JA902-027

Polaron conduction loss in microwave dielectric ceramics

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It has been generally accepted that the product of the unloaded quality factor and resonant frequency is the universal parameter for comparison of dielectric resonators with different size {[Mater. Lett. **28**, 107 (1996)], [Jpn. J. Appl. Phys. **32**, 4327 (1993)]}. However, it is suggested in this study that this universal parameter should be modified due to the presence of the polarons. From the frequency dependence of the unloaded quality factor, it is possible to extract the factor determined only by the phonon scattering effects, and we denoted this parameter by Q_s. It was found that Q_s parameter for ZST and BZT ceramics showed constancy in the frequency range of 2–12 GHz, which supports the idea of polaron conduction loss contribution to the dielectric loss.

Order No.: JA902-028

Synthesis of cobalt oxide nanocrystal self-assembled materials

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Self-assembling of size-, shape-, and phase-selected nanocrystals into superlattices is a new approach for synthesizing a new generation of advanced materials with functionality. In this paper, high purity and monodispersive tetrahedral nanocrystals of CoO, with edge-lengths of 4.4 ± 0.2 nm, have been synthesized and separated from Co nanocrystals using colloidal chemistry and magnetic separation. The tetrahedral CoO nanocrystals behave like a molecular matter, and their assembling forms superlattices with translational symmetry. The phase transformation of the CoO nanocrystals is examined by *ex situ* annealing in oxygen, and the results showed the formation of Co_3O_4 with spinel structure.

Order No.: JA902-029

Two kinds of roles of MgO in the densification and grain growth of alumina under various atmospheres: Sensitive and insensitive roles to the experimental procedures

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Two kinds of high-purity Al_2O_3 powder were studied with respect to the effects of not only MgO doping, but also atmosphere, on both densification and grain growth. Controversial results for MgO doping were explained in terms of two roles that MgO can play during these processes: (1) governs the sintering kinetics and (2) does the sintering mode. Atmospheres, whether dry or wet, had little influence on densification or grain growth in the early stage. After closed pores appreciably formed, however, both N_2 and Ar atmospheres quickly reduced the densification rate.

Order No.: JA902-030

Low-temperature sintering and elongated grain growth of 6H–SiC powder with AlB_2 and C additives

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6H(α)–SiC fine powder was sintered at normal pressure with additives of 0.67 to 2.7 wt% of AlB_2 and 2 wt% of C. The powder could be densified at 1850 °C. This sintering temperature was lower than that for SiC with B and C additives by 150–300 °C. During sintering, 6H–SiC partially transformed into 4H–SiC, and the transtormation caused grain to grow and develop non-spherical shape. The fracture toughness of sintered SiC increased with increases in the amount of AlB_2 additive, the mean grain size, and the mean aspect ratio of grain shape. AlB_2 and C additives are believed to have formed an $Al_8B_4C_7$ compound which melted below 1800 °C and enhanced sintering and grain growth.

Order No.: JA902-031

High-temperature creep of polycrystalline $BaTiO_3$

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Compressive creep of dense $BaTiO_3$ having linear-intercept grain sizes of 19.3–52.4 μm was investigated at 1200–1300 °C by varying the oxygen partial pressure from 10^2 to 10^5 Pa in both constant-stress and constant-crosshead-velocity modes. Microstructures of the deformed materials were examined by scanning and transmission electron microscopy. The stress exponent was ≈1, the grain-size dependence was $\approx 1/d^2$, and the activation energy was ≈720 kJ/mole. These parameters, combined with the microstructural observations (particularly grain displacement and absence of deformation-induced dislocations) indicated that the dominant deformation mechanism was grain-boundary sliding accommodated by lattice cation diffusion. Because of the absence of an oxygen partial pressure dependence, diffusion was probably controlled extrinsically.

Order No.: JA902-032

Preparation and sintering of $CaSiO_3$ from coprecipitated powder using NaOH as precipitant and its apatite formation in simulated body fluid solution

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$CaSiO_3$ powders were prepared from an ethanol solution dissolving $Ca(NO_3)_2 \cdot 4H_2O$ and $Si(OC_2H_5)_4$ by coprecipitation method using various concentrations of NaOH as precipitants. Some amount of Na component remained in the precipitates without washing treatment and strongly affected the characteristics of the resultant powders, but the Na residue was removed by washing treatment. The precipitate prepared by using 0.33 mol/l of NaOH and twice washing contained the lowest amount of Na residue. It was calcined at 500 and 900 °C, respectively, to crystallize $CaSiO_3$ phase and ground by planetary potmill. The ground $CaSiO_3$ powder was sintered to about 89% theoretical density by firing at 1400 °C. By soaking the $CaSiO_3$ sintered bodies in simulated body fluid (SBF) solution for various times, an hydroxylapatite (HAp) layer formed as aggregates of ball-like particles on the surface of the $CaSiO_3$ sintered bodies after soaking for a short period, thereby the $CaSiO_3$ ceramic is suggested to have very good biocompatibility.

Order No.: JA902-033

A sol-gel derived $0.9Pb(Mg_{1/2}Nb_{2/3})O_3$–$0.1PbTiO_3$ ceramic

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Using inorganic chemicals, such as niobium pentachloride, titanium tetrachloride, lead nitrate, and magnesium nitrate, as the starting materials, 0.9PMN–0.1PT has been fabricated via a simple and low-cost sol-gel processing route. A colloidal solution was first prepared by adding an aqueous lead nitrate solution into an ethanol solution of niobium and titanium chlorides. Magnesium nitrate was then mixed into the solution when chloride ions were removed by forming precipitates of $PbCl_2$ with the excess lead nitrate. The gelation of the colloidal solution was facilitated in the presence of a small amount of polyethylene glycol (PEG 300) at 70 °C. A fine perovskite 0.9PMN–0.1PT powder was obtained when the resulting gel was dried at 300 °C for 4 h and subsequently calcined. It was observed that the sol-gel derived precursor underwent a pyrochlore phase at 500–600 °C, prior to the formation of a perovskite single phase at a calcination temperature of 850 °C. A sintered density of ~98% theoretical density was obtained when the fine 0.9PMN–0.1PT powder was sintered at 1250 °C for 2 h, and the sintered ceramic shows a maximum dielectric constant of 26682, together with a room temperature dielectric constant of 19206 at 1 kHz. The superb dielectric properties are correlated to the microstructural features of the sol-gel derived 0.9PMN–0.1PT, which has been characterized using techniques such as x-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Order No.: JA902-034

Effect of La_2O_3 substitutions on structure and dielectric properties of Bi_2O_3–ZnO–Nb_2O_5-based pyrochlore ceramics

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The effect of La_2O_3 substitutions on structure and dielectric properties of Bi_2O_3–ZnO–Nb_2O_5-based ceramics was investigated. $Bi_{1.5-x}La_x$-$Zn_{0.5}(Zn_{0.5}Nb_{1.5})O_7$ samples were prepared by conventional ceramic processing technology. The crystal structure of the $Bi_{1.5}Zn_{0.5}(Zn_{0.5}Nb_{1.5})O_7$ sample was characterized as a pure cubic pyrochlore. With a lower amount of La_2O_3 substitution, the crystal structures were still cubic pyrochlore. Superlattice x-ray diffraction line was identified for some compositions. With the increasing amount of La_2O_3 substitution, the crystal structure gradually transformed from pure cubic pyrochlore to $LaNbO_4$ phase. The dielectric properties regularly changed with the structure change. The structure-properties relations of the ceramics were discussed.

Order No.: JA902-035

On the applicability of the x-ray diffraction line profile analysis in extracting grain size and microstrain in nanocrystalline materials

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Measurements of x-ray diffraction (XRD) profiles have been performed on commercially pure Fe and Al powders, cryomilled Fe-3 wt% Al powders, cold-pressed (CP) pure Fe and Al, hot-pressed (HP), and hot-isostatically-pressed (HIP) Fe-3 wt% Al. Scherrer equation (SE), integral breadth analysis (IBA), and single-line approximation (SLA) methods have been employed to extract grain size and microstrain. The results demonstrate that in the case of the cryomilled nanocrystalline Fe-3 wt% Al powders, all these XRD techniques yielded reasonable, consistent grain size results. However, discrepancies were found in the cold-pressed (CP-Fe),

hot-pressed (HP-Fe-3 wt% Al), and hot-isostatically-pressed (HIP-Fe-3 wt% Al) samples. Transmission electron microscope (TEM) imaging revealed the presence of a certain density of dislocations inside the grains in the HP-Fe-3 wt% Al and HIP-Fe-3 wt% Al, which is thought to be partly or fully responsible for the observed discrepancies.

Order No.: JA902-036

Generation of carbon tripods on copper by chemical vapor deposition

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We report the first observation of large graphitic capped clusters with threefold symmetry (tripods). They were generated under the diamond growth conditions by the chemical vapor deposition process activated by hot filaments on a Cu(111) surface while conditions of very poor diamond nucleation (10^4–10^5 cm^{-2}) are fulfilled. They were characterized by direct high resolution imaging and selected-area diffraction. Further-more, a lot of them are connected. The behavior of hydrogen radicals to curl and to close limited-size graphitic planes is emphasized to explain their formation. These tripods appear to be readily stable carbon as they form only after other limited size graphitic clusters, such as graphite lumps or bucky onions. It is thus expected that the chemical vapor deposition proc-ess is a quite relevant preparation method to grow, in a controlled way, new forms of carbon with a narrow size distribution

Order No.: JA902-037

Processing and characterization of alumina thin films on chemically vapor-deposited diamond substrates for producing adherent metallizations

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In order to make the surface of chemically vapor-deposited diamond (CVDD) substrates amenable to metallization by both thin and thick film approaches currently utilized in electronic packaging, a thin, adherent, insulating aluminum oxide film was grown on diamond at low temperatures (<675 K). The film was produced by reactive thermal evaporation of Al and O in an oxygen atmosphere, followed by low-temperature annealing in oxygen. A Cr intermediate layer was deposited on diamond prior to the deposition of aluminum oxide in order to enhance adhesion between the oxide and diamond. The chemistry, crystal structure, and microstructure of the film were characterized in detail via scanning and transmission electron microscopy, as well as auger electron spectroscopy. Particular attention was given to the mechanisms of bonding across the CVDD-Cr and Cr-alumina interfaces, as well as the stability of the surface treatment following metallization by fritted pastes requiring firing at elevated temperatures. The Cr was found to be bonded with CVDD by C_3C_6 formation, while the bonding between the Cr and alumina layers was provided by the formation of a compositionally-modulated solid solution With Al_2O_3- and Cr_2O_3-rich regions.

Order No.: JA902-038

Preparation of microcrystalline diamond in a low-pressure inductively-coupled plasma

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A 13.56 MHz low-pressure inductively-coupled plasma (ICP) has been applied to prepare diamond films. The Faraday shield drastically suppressed the electrostatic coupling, which frequently causes contamination due to the etching of the quartz tube. The characterizations of the obtained deposits by scanning electron microscopy (SEM), transmission electron diffraction (TED), and reflection high-energy electron diffraction (RHEED) revealed that the deposits are composed of microcrystalline diamond and disordered microcrystalline graphite. The CO additive to a CH_4/H_2 plasma brought about the morphological change from a scalelike deposit to a particle one. Besides, the number of encountered particles was increased with an increase of CO additive. The TED and RHEED observations showed that non-diamond carbon was effectively removed with an increase of CO additive. These results indicate that oxygen-contained radicals produced by the addition of CO play an effective role in the removal of non-diamond carbon in the diamond growth conditions and that the CO additive makes the supersaturation degree of carbon large.

Order No.: JA902-039

Void nucleation in metal interconnects: Combined effects of interface flaws and crystallographic slip

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A micromechanical model of void nucleation in passivated metal interconnection lines is proposed. The model is based on the evolution of stress and strain fields in a two-dimensional model system obtained from numerical modeling. Interface flaws in the form of debond between the metal and the surrounding dielectric are assumed to exist. A unique pattern of shear stress resolved on the slip systems in the metal line, due to the presence of pre-existing debond, is found. A dislocation slip model is constructed in accordance with the shear mode. The mechanism of crystallographic slip is such that lateral thinning of the metal line at the debond region, together with the slip step produced at the edges of debond lead to a net transport of atoms away from the debond area, and a physical void is thus formed. The significance and implications of this proposed micromechanism are discussed.

Order No.: JA902-040

Dense and smooth epitaxial $BaTiO_3$ thin films by dipping-pyrolysis process

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Dense and smooth $BaTiO_3$ thin films were prepared on $SrTiO_3$ (100) substrates by dipping-pyrolysis process using a mixed precursor solution of barium and titanium naphthenates. Combination effects of prefiring (at 150–450 °C in air or low oxygen partial pressure, $p(O_2)$) and final heat treatment (at 850 °C in air or low-$p(O_2)$) on preparation of $BaTiO_3$ thin films were examined. An epitaxial $BaTiO_3$ thin film with a dense and smooth surface consisting of nanosized grains about 70 nm was prepared by prefiring under low-$p(O_2)$ at 250 °C and final heat treatment under low-$p(O_2)$ at 850 °C.

Order No.: JA902-041

Fracture of fused silica with 351-nm-laser-generated surface cracks

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Laser-induced surface-flaw experiments on fused silica at 351 nm and 500 ps pulse duration are reported here. Specimens with surface flaws produced at a measured exit-surface damage threshold fluence of $F_{exit/th}$ = 10 J/cm^2 were irradiated at a constant fluence of F_L= 1.8 x $F_{exit/th}$ by different numbers of laser pulses, N = 110 to 520. Micrograph observations show that (1) the produced cracks have a semielliptical shape, and (2) the material strength predictions based on the radial crack depth (normal to the surface) instead of the crack surface length (parallel to the surface) are in good agreement with measured strengths obtained using a four-point bending fixture. The underlying basis of conventional crack analysis is first examined critically and is argued to be deficient in the way the failure strength for the cracks is related to the characteristic parameters of crack geometry. In general, it is necessary to incorporate a residual term into the failure strength formulation. The crack depth and the failure strength are found to increase and decrease with the number of laser pulses, respectively.

Order No.: JA902-042

Coherent vibrations in percolative oil-resin systems: A Böse condensation effect observed by the technique of thermostimulated currents

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The analysis of thermostimulated currents by the fractional polarization procedure is used to understand percolative behaviors in conductor-insulator-like oil-resin mixtures. On the fundamental side, oil-poor systems are particularly attractive. They offer for the first time the opportunity to apply a pure Debye-like dielectric treatment of the quasi-elastic dipolar relaxation since the involved dipoles are independent, associated with spatially separated bounded clusters. An unusual compensation phenomenon is observed in the sense that, first, it does not describe hierarchically correlated motions, and, secondly, it is related to the conducting phase but exhibits characteristics of the insulating phase. This compensation phenomenon is interpreted within the framework of Fröhlich's approach of relaxation processes in biological materials as significative of a coherent vibration resulting from Böse condensation effects. On the practical side, the surveillance of this compensation phenomenon appears as a new way to follow the coalescence of conducting bounded clusters with aging.

Order No.: JA902-043

High corrosion resistant ZrC films synthesized by ion-beam-assisted deposition

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ZrC films with high hardness were deposited on A3 steel by ion-beam-assisted deposition and had a corrosion rate more than two orders less and a corrosion potential 0.19 V greater than those of the bare A3 steel. The corrosion current of ZrC films was 10 times less and the polarization resistance at least 7.82 times higher than those of both Teflon and ZrN films, respectively. The experimental results confirmed that ZrC films notably enhanced the corrosion resistance of steels.

Order No.: JA902-044

Room-temperature reduction of scheelite ($CaWO_4$)

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A mixture of scheelite and magnesium has been mechanically milled together for 100 h, either with graphite or in a nitrogen atmosphere with the intention of forming tungsten carbide or nitride. The resultant powders were examined by thermal analysis, isothermal annealing, and x-ray diffraction to determine the effect of milling on the reduction of scheelite. With graphite, nanocrystalline W_2C was the exclusive tungsten product; WC was not detected even after annealing at 1000 °C. No nitride formed in the system milled with nitrogen; however, 10 nm crystallites of elemental tungsten were formed. The unwanted phases, MgO and CaO, were readily removed by leaching in acid, leaving a fine powder composed of impact welded aggregates of either carbide or 99% pure tungsten metal.

Order No.: JA902-045