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Periodic fluctuation of Ba/Nd ratio in single crystals of high-Jc $NdBa_2Cu_3O_{7-\delta}$ superconductor

T. Hirayama*, Y. Ikuhara*, M. Nakamura+, Y. Yamada+, Y. Shiohara+
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A single crystal of $NdBa_2Cu_3O_{7-\delta}$ was synthesized by the top seeded solution growth (TSSG) method. Then, the crystal was heat-treated at 500°C for 400 hours and then 340°C for 200 hours in a pure oxygen gas flow. This sample showed critical current density (Jc) as high as 15,000 A/cm^2 under a magnetic field applied along the c-axis of the crystal. Electron microscopic studies with energy dispersive x-ray spectroscopy (EDS) have revealed that the Ba/Nd ratio fluctuates between 2.0 and 0.7 with a wavelength of a few tens of a nanometer. This implies that superconducting phase of $Nd_{1.0}Ba_{2.0}Cu_3O_{7-\delta}$ and nonsuperconducting phase of $Nd_{1.8}Ba_{1.2}Cu_3O_{7-\delta}$ mingle with each other, which is the ideal structure for high-Jc superconducting material.

Order No.: JA702-001

High temperature x-ray and calorimetric studies of phase transformations in quasicrystalline Ti-Zr-Ni alloys

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We present the first high temperature x-ray diffraction (HTXRD) studies of *in-situ* quasicrystal-crystal and crystal-crystal transformations in Ti-Zr-Ni alloys. Together with differential scanning calorimetry studies, these x-ray measurements indicate three separate paths for the Ti-Zr-Ni quasicrystal-crystal transformation: single exothermic, single endothermic, or multiple endothermic. The mode of transformation depends on the alloy composition and the level of environmental oxygen. The crystalline products include the Ti_2Ni, $MgZn_2$ Laves, α-(Ti,Zr) and β-(Ti,Zr) phases. In the absence of oxygen, the endothermic transformation of the quasicrystal demonstrates that it is the lowest free energy (stable) phase at the $Ti_{53}Zr_{27}Ni_{20}$ composition. Oxygen stabilizes the Ti_2Ni phase, eliminating both the quasicrystal and the $MgZn_2$ Laves phase, at partial pressures as low as a few hundred ppm.

Order No.: JA702-002

Internal friction and Mössbauer study of C-Cr associates in MANET steel

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Internal friction and Mössbauer techniques have been used to investigate the structure of C-Cr associates and the arrangement of Fe atoms near them in the Cr martensitic steel MANET subjected to different thermal treatments. After slow rate cooling from the austenitic field, the Mössbauer spectra exhibit, besides the complex magnetic pattern of martensite, a low intensity singlet attributed to the presence of a Cr-rich b.c.c. phase. In correspondence, the internal friction curves show, among others, a Snoek-type peak due to anelastic processes involving C-Cr associates with 6 Cr atoms. To explain the experimental results a simple structural model is suggested.

Order No.: JA702-003

Deformation-induced planar defects in Al-Cu-Fe quasicrystals

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Planar defects were observed in a hot isostatically pressed Al-Cu-Fe alloy. The defects were determined to be perpendicular to the fivefold direction. They were also found to be regions where the quasiperiodicity in the fivefold direction was disrupted, resulting in a periodicity along this direc-

tion of 1.06 nm. The defects were stable up to approximately 750°C. The defects were determined to be formed by the applied shear forces associated with the consolidation process. The displacement vector of the defects was determined to be in a twofold direction perpendicular to the periodic direction.
Order No.: JA702-004

Lowering the formation temperature of the C54-$TiSi_2$ phase using a metallic interfacial layer
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We demonstrate that the formation temperature of the C54 $TiSi_2$ phase from the bilayer reaction of Ti on Si is lowered by approximately 100°C by placing an interfacial layer of Mo or W between Ti and Si. Upon annealing above 500°C, the C49 $TiSi_2$ phase forms first, as in the reaction of Ti directly on Si. However, the temperature range over which the C49 phase is stable is decreased by approximately 100°C, allowing C54 $TiSi_2$ formation below 700°C. Patterned submicron lines (0.25–1.0 μm wide) fabricated without the Mo layer contain only the C49 $TiSi_2$ phase after annealing to 700°C for 30 s. With a Mo layer less than 3 nm thick between Ti and Si, however, a mixture of C49 and C54 $TiSi_2$ was formed, resulting in a lower resistivity. The enhanced formation of the C54 $TiSi_2$ is attributed to an increased density of nucleation sites for the C49-C54 phase transformation, arising from a finer grained precursor C49 phase.
Order No.: JA702-005

Trapping levels in hydrothermal and solution grown bismuth *titanium oxide*
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Deep trapping levels in $Bi_{12}TiO_{20}$ obtained by top seeded solution growth and by the hydrothermal technique have been compared. This was undertaken as such levels directly influence the photorefractive behavior of the material. It is found that the most predominant of the peaks revealed by thermally stimulated conductivity measurements represents two rather than a single defect level, and that the deeper of the two becomes more significant in hydrothermally grown material. One defect found in the solution-pulled material is notably absent from that produced hydrothermally. The consequence of adding phosphorus doping and the manner in which it affects the deep levels has also been examined.
Order No.: JA702-006

Anharmonicity in metals from the universal energy equation
L.A. Girifalco, K. Kniaz
(University of Pennsylvania-Philadelphia)

A theoretical computation of vibrational anharmonicity is presented which is a generalization of the simple Gruneisen approach. The calculation was based on a model which defines a simple relationship between the binding energy of a solid and the variation of vibration frequencies with volume. The agreement between calculated and experimental Gruneisen constants is good.
Order No.: JA702-007

Metastable liquid phase separation in undercooled molten $Pd_{40.5}Ni_{40.5}P_{19}$
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(The Chinese University of Hong Kong)

It was demonstrated that molten $Pd_{40.5}Ni_{40.5}P_{19}$ undergoes liquid state phase separation in the undercooling regime $\Delta T = T_1 - T$ where T_1 is the liquidus of $Pd_{40.5}Ni_{40.5}P_{19}$ and T is the kinetic crystallization temperature. Liquid state phase separation by nucleation and growth takes place for $\Delta T \leq 60$ K while that by spinodal decomposition occurs for $\Delta T \geq 100$ K. Microstructural analysis of the undercooled specimen obtained in the undercooling regime of $60 \leq \Delta T \leq 100$ K indicates that it is the transition regime. Finally, it was found that when undercooled molten $Pd_{40.5}Ni_{40.5}P_{19}$ undergoes liquid state spinodal decomposition it first decomposes into two liquid networks, which is finally replaced by a system of three liquid networks.
Order No.: JA702-008

Rietveld analysis of the cubic crystal structure of Na-modified zirconia
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Using x-ray Rietveld analysis the fcc (fluorite-type) structure of a nanocrystalline zirconia powder (9.5 nm of crystallite size) containing sodium as impurity, and obtained by precipitation and subsequent calcination, has been confirmed. The result shows that using conventional x-ray diffraction techniques, the cubic crystallographic form of ZrO_2 can be distinguished from the tetragonal one, also in nanometrically sized powders. These conclusions are supported by the findings of independent Raman scattering experiments.
Order No.: JA702-009

Composition of SiCN crystals consisting of a predominantly carbon-nitride network
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We report here synthesis of large crystals of Si-containing carbon nitride, consisting of a predominantly C-N network, by microwave chemical vapor deposition (CVD). The Si content in this material varies from crystal to crystal and also with the deposition conditions, and has been observed to be as low as less than 5 at.% in some crystals, wherein the Si atoms are believed to substitute for some of the C sites only. This is the first time that such large and well faceted crystals consisting almost entirely of carbon-nitride network have been synthesized. Moreover, there is no obvious deposition of amorphous CN material.
Order No.: JA702-010

Chemical synthesis of a new tin dioxide based (SnO_2 : Co,Al,Nb) varistor
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A new varistor composition based on SnO_2 doped with Co, Al and Nb has been successfully synthesized by a chemical route. It exhibits excellent non-linear current-voltage (I-V) characteristics with $\alpha \approx 72$ and $E_{1mA} \approx$ 1820 volts/mm.
Order No.: JA702-011

Analysis of SCS-6 silicon carbide fibers by Fourier transform infrared spectroscopy
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(UES, Inc.)

Fourier transform infrared (FTIR) spectroscopy analysis of SCS-6 silicon carbide fibers was performed to detect the presence of oxygen in the form of SiO_2. The results showed infrared peaks corresponding to SiC fundamental lattice absorption as well as reflection. No absorption peak due to SiO_2 was observed. These results are in agreement with previously reported data indicating low levels of oxygen in this fiber.
Order No.: JA702-012

ARTICLES

Bi-Sr-Ca-Cu-O superconducting thin plates prepared by glass-ceramic processing: Dependence of Tc on the thickness
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The melt of Bi-Sr-Ca-Cu-O (BSCCO) was quenched by splatting using iron plates, resulting in formation of the glassy plates (0.3 ~ 0.7 mm thickness). The plates were converted into superconductors by reheating in air. The critical temperature, Tc, depends on the thickness. The change in Tc is

discussed in terms of the difference in the amount of the oxygen absorption and in crystallization behavior of the glassy plate during the reheating process between the glassy phase in the interior and that at around the surface. It was found that high-Tc glass-ceramic thin plates can be prepared by controlling the amount or the rate of oxygen supply.
Order No.: JA702-013

Chemical analysis in $YBa_2Cu_3O_{7-x}$ melt-textured samples
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Melt-textured process which involves the peritectic reaction Y_2BaCuO_5 + liquid → $YBa_2Cu_3O_{7-x}$ is the best method to develop bulk $YBa_2Cu_3O_{7-x}$ superconductors with improved transport and magnetic properties. Up to date, information regarding cationic stoichiometry in textured samples is rather lacking in the literature. In this work, wavelength dispersive analysis (WDS) at a microscopic level and energy dispersive x-ray analysis (EDX) at a nanoscopic level were used to characterize the chemical composition of $YBa_2Cu_3O_{7-x}$ textured samples. Melt-textured process generally modifies the sample stoichiometry. Thus, textured sample composition cannot be directly obtained even from an accurate knowledge of the starting composition. We have shown that WDS can be used to determine the overall composition and therefore the Y_2BaCuO_5 content in these samples. It is also a powerful method to control chemical homogeneity and to investigate chemical modifications occurring during processing, especially those resulting from interaction between melt and substrate. The exact nature of $YBa_2Cu_3O_{7-x}$ nucleation and crystallization still present many unsolved questions. Nanoanalysis allowed us to study Y_2BaCuO_5 dissolution in the peritectic liquid and we have confirmed that it takes place exclusively by yttrium removing from Y_2BaCuO_5 particles. We have also shown the existence of yttrium-rich liquid phase, i.e. with a higher yttrium concentration that can be deduced from the equilibrium phase diagram. Liquid phases having compositions close to that of $YBa_2Cu_3O_{7-x}$ can be inferred from this work. This suggests that $YBa_2Cu_3O_{7-x}$ nucleation and crystallization take place homogeneously from this liquid.
Order No.: JA702-014

Metallization schemes for dielectric thin film capacitors
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A detailed analysis of Pt/Ti, Pt/TiO_2, and Pt/ZrO_2 electrodes was carried out to develop a bottom electrode stack for sol-gel derived thin film capacitors. For the Pt/Ti stack, the choice of layer thickness and deposition temperature is found to affect adhesion to the SiO_2/Si substrate as well as the extent of hillock formation and Pt-Ti interaction. By using elevated temperature deposition, Pt films close to 1 μm in thickness can be produced with relatively good adhesion and morphological stability using Ti adhesion layers. In addition, Pt films grown on ZrO_2 and TiO_2 adhesion layers exhibit little morphological change and no degradation in sheet resistance after annealing at 650°C. However, neither ZrO_2 nor TiO_2 are as effective as Ti metal in promoting Pt adhesion. Experiments aimed at establishing a correlation between hillock formation and capacitor yield revealed two important results. First, the behavior of Pt/Ti stacks during annealing in air is markedly different from their behavior during PZT film crystallization. Second, pre-annealing of the Pt/Ti in air prior to PZT film growth actually improves capacitor yield, even though hillock formation occurs during the pre-annealing treatment. Implications of these results regarding the role of hillocks in controlling capacitor yield are discussed.
Order No.: JA702-015

Chemical stability of $CuInS_2$ in oxygen at 298 K
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A thermochemical analysis is performed in the quaternary system Cu-In-S-O at 298 K including the respective four ternaries. The Cu-In phase diagram is updated with respect to the new experimental as well as to the new thermochemical results in the literature. Free energies of In_6S_7, $In_{2.8}S_4$, $CuIn_2$, and $Cu_2In_2O_5$ have been estimated. Consistent sets of data are used for the calculations of the ternary systems with the program THERMO, and the results are used to calculate the quaternary tetrahedron Cu-In-S-O with the program THERMOQ, the algorithm is given. Twelve quaternary two-phase equilibria have been found. They are used to calculate predominance area diagrams of the quaternary system with the program STADIAQ for different oxygen partial pressures. The algorithm of this program is given. From these diagrams it becomes obvious that $CuInS_2$ is unstable in air and even in UHV systems, and should react to form $In_2(SO_4)_3$ and Cu_2S at oxygen pressures larger than log p(pascal) = -51.5. The results are of utility for research in fields such as oxidation and crystal growth of $CuInS_2$ and for development of processes for producing this compound.
Order No.: JA702-016

The stability of $Si_{1-x}Ge_x$ strained layers on small-area trench-isolated silicon
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The combined effects of isolation stress, active area size and SiGe misfit strain on dislocation generation in an advanced SiGe heterojunction bipolar transistor (HBT) process were studied. Eight-inch wafers were patterned with polysilicon-filled deep, and oxide-filled shallow, trench isolation similar to that used in IBM's analog SiGe heterojunction bipolar transistor (HBT) technology. Half of the wafers were subjected to an additional stress-producing oxidation prior to SiGe growth. $Si_{1-x}Ge_x$ films containing 0, 5.5, 9, and 13 at.% Ge were grown epitaxially by ultra-high vacuum chemical vapor deposition (UHV CVD). The films were of constant thickness with an intrinsic Si cap. Some samples received an additional relaxation anneal following deposition. After the growth and anneal cycles, the dislocation density was determined by transmission electron microscopy (TEM). On non-stressed samples, no dislocations were observed in the device areas, even at Ge concentrations which are not stable to misfit dislocation generation in blanket form. This small area effect has been observed on patterned substrates which do not have functional device isolation. On the stressed-isolation wafers, the compressive stress from the oxidation of the trench sidewalls was found to intensify stress in the SiGe films, and to lower the critical strain at which misfit dislocations appeared. In large active areas on these wafers, two distinct dislocation regions were observed. Defects at the edge resembled those caused by isolation stress, while the defects in the center were more typical of the misfit dislocations associated with lattice-mismatch epitaxial films. It is clear that isolation stress must be minimized when fabricating integrated circuits using SiGe epitaxial films. It is also evident that SiGe films grown on non-stressed isolation exhibit the same increase in critical thickness with decreasing lateral dimension that has been observed on much simpler patterned substrates.
Order No.: JA702-017

Microstructure of nitrate polycrystals solidified under ultrasonic vibration
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Molten nitrates in the system (1-x)$NaNO_3$-x$Ba(NO_3)_2$ were solidified in the presence of a power ultrasound of 20 kHz. Their microstructures were compared with those of controlled samples which were solidified normally. Grain size in the controlled sample of monolithic $NaNO_3$ (x = 0) was reduced by sonication. In the hypo- (x = 8 wt.%) and the hypereutectic (x = 28 wt.%) binary samples, the sonication completely eliminated the dendritic structure of the primary crystals and induced equiaxed particles of the primary phase. At eutectic (x = 18 wt.%), the sonication removed oriented structures of the eutectic lamellae. Several mechanisms of the microstructural modification were mentioned.
Order No.: JA702-018

Crystal structure and defects of $Zr_4Co_4Si_7$ (V-phase) investigated by high- resolution transmission electron microscope

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The results of high resolution transmission electron microscope (HRTEM) observation and image simulation show that $Zr_4Co_4Si_7$ possesses the same structure type as $Zr_4Co_4Ge_7$. With the addition of Fe or Ni into the $Zr_4Co_4Si_7$ compound, except for the dimensions changing slightly, the lattice type and coordination do not change in the crystal structure, remaining with the structure of V-phase. Besides, twins with coherent boundaries and partially coherent at the interfaces are observed. The image conditions of $Zr_4Co_4Si_7$ and the structure differences between $Zr_4Co_4Si_7$ and tetrahedral close-packed phases are also discussed.

Order No.: JA702-019

Uniformity and interfaces in ion-beam deposited Al/Ni multilayers

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The uniformity and reaction kinetics of ion-beam deposited Al/Ni multilayer samples with the same composition, $Al_{8.18}Ni_{18.2}$, and modulation wavelength, Λ = 20 nm, but with different total film thicknesses, were investigated by x-ray diffraction and differential scanning calorimetry measurements. The total film thicknesses varied between approximately 0.5 and 2.0 μm. It was found that the interface widths were approximately 1 nm and the Ni layers are much more disordered than the Al layers. The thicker samples show an increase in disorder on a length scale comparable to Λ. In other experiments, a change was observed with increasing modulation wavelength from semicoherent interfaces with a low density of misfit dislocations to semicoherent interfaces with a high density of misfit dislocations. The reaction kinetics for forming the Al_9Ni_2 phase is independent of the sample thickness.

Order No.: JA702-020

Effect of calcium modification on the microstructure and oxidation property of submicron spherical palladium powders

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Ca modified spherical palladium particles were prepared from the mixed solution of $Pd(NO_3)_2$ and $Ca(NO_3)_2$ by ultrasonic spray pyrolysis. Pure palladium powder and that modified with less than 55 ppm Ca were composed of single crystal particles. However, Ca addition of more than 500 ppm resulted in polycrystalline particles. Crystallite size of the particles decreased with the increase of Ca addition and changed dramatically at the addition of some hundred ppm. Ca additive did not form solid solution with palladium but formed $CaPd_3O_4$. 50 ppm ~ 1% of Ca addition significantly reduced the oxidation of palladium powder. More addition of Ca resulted in excess oxidation due to the reaction between palladium and calcium oxide.

Order No.: JA702-021

Nanoparticles of Ag, Au, Pd and Cu produced by alcohol reduction of the salts

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Nanoparticles of Ag, Au, Pd and Cu have been prepared by the reduction of their salts by ethyl alcohol under refluxing conditions in the presence of polyvinylpyrrolidone (PVP). In the case of Au and Cu, it was necessary to use magnesium metal as a catalyst during the reduction. The nanoparticles are in the 5–35 nm range in the case of Ag, Au and Pd, but there is considerable agglomeration in the case of Cu, even in the presence of PVP.

Order No.: JA702-022

Synthesis of pure amorphous Fe_2O_3

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A method for the preparation of pure amorphous Fe_2O_3 powder with particle size of 25 nm is reported in this letter. Pure amorphous Fe_2O_3 can be simply synthesized by the sonication of neat $Fe(CO)_5$ or its solution in decalin under an air atmosphere. The Fe_2O_3 nanoparticles are converted to crystalline Fe_3O_4 nanoparticles when heated to 420°C under vacuum or when heated to the same temperature under a nitrogen atmosphere. The crystalline Fe_3O_4 nanoparticles were characterized by x-ray diffraction and Mössbauer spectroscopy. The Fe_2O_3 amorphous nanoparticles were examined by transmission electron micrography (TEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and quantum design SQUID magnetization measurements. The magnetization of pure amorphous Fe_2O_3 at room temperature is very low (<1.5 emu/g) and it crystallizes at 268°C.

Order No.: JA702-023

Auger valence electron spectra in Ca-silicides

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$CaSi_2$ and CaSi have been investigated by Auger valence electron spectroscopy (AVES). Some drastic differences of the Auger peak due to 3s states in the Si atoms were observed in the Si[2s,2p,V] Auger spectra. The peak that arose from valence electron states in the Ca atoms were observed in the Ca[2p,3p,V] Auger spectra for both Ca-silicides. This result suggests that the Ca-Si bonds are partially ionic. However, the number of the valence electrons in Ca atoms for CaSi was larger than that for $CaSi_2$. This result implies that the part of homopolar bonds between the Si and Ca atoms in CaSi is stronger than that in $CaSi_2$. Based on these results, it has been concluded that the change of the Si [2s,2p,V] Auger spectra is associated with the difference of the part of homopolar bonds between the Si and Ca atoms.

Order No.: JA702-024

Selective chemical etching of hexagonal BN compared to cubic BN

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A BN film containing comparable amounts of sp^2 and sp^3 phases was subjected to a gas-phase chemical etch in a hot-filament environment containing 1% CH_4 in H_2. After a partial etch, examination by FTIR shows that the sp^2 was preferentially etched, leaving a larger sp^3 fraction than in the unetched film. The possibility that preferential etching could be used to increase the purity of cBN films is discussed.

Order No.: JA702-025

The oxygen deficiency effect of VO_2 thin films prepared by laser ablation

M. Nagashima, H. Wada
(Japan Defense Agency)

Vanadium dioxide thin films (VO_2) have been deposited by laser ablation. The temperature dependence of resistivity and temperature coefficient of resistance (TCR) for each deposition condition were investigated. It was clarified that the TCR at room temperature (RT) can be optimized by controlling the oxygen pressure introduced during deposition as the deposition parameter. In the result, larger TCRs at RT were observed for the oxygen deficient condition of VO_2 than for oxygen richer samples. Obtained TCR values were 0.072/K and 0.045/K at 25°C for VO_2 thin films deposited onto R-cut sapphire and SiO_2/Si, respectively.

Order No.: JA702-026

An analysis for geometrical effects on the cooling performance of $(Bi,Sb)_2Te_3/Bi_2(Te,Se)_3$-based thin film thermoelectric modules

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Geometrical effects on the cooling performance of the thin film thermoelectric (TFTE) modules were investigated by varying the film thickness and the number of p/n couples of a $(Bi,Sb)_2Te_3/Bi_2(Te,Se)_3$-based system which were fabricated by the flash evaporation technique. Maximum temperature difference (ΔT_{max}; maximum cooling) and optimum input current (I_{opt}) increased with film thickness for a fixed number of couples. For the case of given thickness, however, I_{opt} decreased with the number of couples maintaining almost constant ΔT_{max}. The measured values for the cooling characteristics were compared with the results obtained through computer simulation work by the finite difference method (FDM). The thinner the film and the larger the number of p/n couples of the modules, the larger was the deviation between the experimental and the simulated values.

Order No.: JA702-027

Particle aggregation in alumina aerogels

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Alumina aerogels were synthesized by low temperature CO_2 supercritical drying (SCD) of gels via the Yoldas process. The aerogels have a surface area of ~425 m^2/gr, similar to that obtained under high pressure/temperature SCD. The surface area and the cluster size of the aerogels are strongly influenced by the amount of acid during gelation. Gels and aerogels were studied by small angle x-ray scattering (SAXS) and the data was analyzed using the Fisher-Burford equation. The SAXS results along with TEM observations support the existence of a hierarchical aggregation at the gelation stage, having a mass fractal dimension of D_m = 2.6–2.8. During the SCD the morphology collapses to form a structure with surface fractal dimension D_s = 2.6–2.9.

Order No.: JA702-028

Modification of the phase transition temperatures in titania doped with various cations

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Titania matrices prepared by a sol-gel technique were doped with several cations (La, Zn, Al, K, Na, Ca, Ba and Co). The effect of the dopants on the thermal and structural properties of the materials is analyzed. The dopant concentration was 2% mol with respect to titanium, and in all cases the same anion (nitrate) was used. The transition temperatures from amorphous to anatase and from anatase to rutile were measured using x-ray diffraction. The amorphous-anatase transition is independent, for almost all samples, of the type of dopant used; however, the anatase to rutile phase transition depends strongly on the kind of cation. This means that the temperature range where the anatase phase exists can be controlled by choosing the appropriate dopant. We have found a correlation between the anatase-rutile phase transition temperature and the radius of the cations and their electric charge.

Order No.: JA702-029

Comments on the effects of solution precursor characteristics and thermal processing conditions on the crystallization behavior of sol-gel derived PZT thin films

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Lead zirconate titanate (PZT 40/60) thin films were fabricated on electroded silicon wafers using chemical solution deposition. Two different chelating agents, acetic acid and acetylacetone, were used in the synthesis of the precursor solutions. The microstructure of the acetylacetone-derived film was characterized by nucleation at the platinum electrode and a columnar growth morphology (~100–200 nm lateral grain size). In contrast, the acetic acid-derived film was characterized by both columnar grains nucleated at the electrode, and larger (~1 μm) grains nucleated at the surface of the film. Using FTIR diffuse reflectance spectroscopy, we also noted that the pyrolysis behavior of the films was dependent on the chelating agent employed. The acetylacetone-derived films, which displayed only one nucleation event, were also characterized by a higher pyrolysis temperature than the acetic acid-derived films.

Previously, microstructural differences of this nature were attributed to variations in "precursor structure." In this paper, we discuss an alternative mechanism for the observed microstructural variations in films prepared from different solution precursors. In the model proposed, we discuss how changes in film pyrolysis temperature result in a change in film crystallization temperature, and hence, a change in the effective driving force for crystallization. We show how the change in crystallization driving force is expected to impact the thin film microstructure due to the accompanying variations that occur in the barrier heights for interface (lower electrode) and surface nucleation. A standard approach to nucleation in glasses is used as the basis of the proposed model. Finally, we also discuss how the model can be used to understand the observed effects of heating rate and thickness on the microstructure of solution-derived thin films.

Order No.: JA702-030

Determination of displacement vector on 180° domain boundary and polarization arrangements in lead titanate crystals

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180° domain boundaries in flux-grown lead titanate single crystals show intriguing domain boundary extreme fringe contrast using transmission electron microscopy. Symmetrically distributed domain boundaries with alternate contrast have been observed, indicating that opposite displacement vectors exist one by one at boundaries. If appropriate reflection vectors were employed, an inclined domain boundary shows reversed fringe contrast. An analysis based upon the two beam dynamical theory and a rule similar to stacking-fault contrast analysis was employed to predict the geometric configuration of a 180° domain boundary using the extreme fringe contrast (EFC) behavior. Appropriately choosing reflection vectors and utilizing the EFC reversal, a displacement vector as well as the polarization vector arrangement across a 180° domain boundary can be unambiguously identified. Employing the information derived from diffraction patterns and a tilting experiment across a nearby 90° boundary, the whole polarization configuration can be uniquely determined.

Order No.: JA702-031

Measurement of solid state diffusion coefficients by a temperature-programmed method

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This paper presents a method for determining diffusivities in solids where the diffusing species desorbs or reacts at the external surfaces, and where the diffusivity does not vary appreciably with concentration. The method involves measuring the flux of the diffusive species out of the solid under the influence of a temperature program. A general model is developed, based on non-isothermal Fickian diffusion, which is applicable to solid particles with slab or spherical geometry. The solution is presented both as an analytical expression and as correlation charts of experimentally observable quantities. These charts are contour diagrams of the temperatures of peak diffusion rate with $\ln(E/R)$ and $\ln(D_0/h^2)$ as the axes, where E and D_0 are the activation energy and pre-exponential terms of the diffusivity expression $D = D_0 \exp(-E/RT)$, R is the gas constant, and h is the size of the particles.

This paper deals exclusively with the case of oxygen diffusion in the vanadium oxide system. In this case, vanadium oxide was reduced in a reactive ammonia stream at conditions in which the surface reaction was

fast compared to the diffusive transport process. Using this method the diffusion parameters were found to be $D_0 = 1.9 \times 10^{-5}$ cm^2s^{-1} and E = 101 kJ/mol. The method was checked by varying the crystallite size of the vanadium oxide sample in the range $2h = 0.14$–0.29 μm.
Order No.: JA702-032

Linear free energy relationships in solid state diffusion processes
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This paper presents a new form of linear free energy (LFE) relationship for diffusive mass transport in oxides and other binary compounds. The relationship applies to a family of related compounds. For a given sub stance, *i*, solid-state diffusivity is related to the equilibrium constant K_i or the free energy of transformation, ΔG^o_i, via a transfer coefficient γ, through the expression $\ln D_i = \gamma \ln K_i$ + constant ($= -\gamma \Delta G^o_i / R T_p$ + constant). The system investigated here is the series of suboxide intermediates of vana-dium pentoxide formed during temperature programmed synthesis of vanadium nitride. The value of γ for this series is 0.27. The diffusivity values are determined by fitting a mathematical model to the experimental data. Diffusivity data are represented graphically in contour diagrams which correlate pre-exponential values, activation energies, particle sizes, and heating rates used in the temperature programmed syntheses. An Evans-Polanyi linear relation, $\Delta E_i = \alpha \Delta(\Delta H^o_i)$, relating activation energy, E_i, to enthalpy change of transformation, ΔH^o_i via a transfer coefficient $\alpha = 0.53$, is also shown to exist for the above system. The discrepancy between α and γ is resolved by using the Horiuti concept of the stoichiometric number of the rate determining step.
Order No.: JA702-033

Superplastic forming of an α-phase rich silicon nitride
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The deformation behavior of fine-grained α-phase rich silicon nitride materials has been studied between 1823 and 1923 K, both in compression and in tension. It is first shown that the higher the α-phase content, the better the superplastic forming ability. A large tension-compression flow asymmetry was evidenced. For instance, shear-thickening flow shows up in compression whereas shear-thinning is observed in tension. Furthermore, much higher flow stresses and hardening rates are reported in compression than in tension. Elongations of more than 80% were achieved for strain-rates between 2.5 and $5 \times 10^{-5} s^{-1}$. In light of our results and of the abundant literature dealing with the high temperature deformation in silicon nitride, a sketch of the different deformation stages is proposed, which emphasizes the tension-compression asymmetry. Starting from the promising results obtained at the laboratory scale, the feasibility for net-shaping of a real part was demonstrated by hot-forging of a parabolic shell.
Order No.: JA702-034

Phase structure and thermal evolution in coatings and powders obtained by sol-gel process: Part I. ZrO_2 - 11.3 mol% Y_2O_3
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Yttria stabilized cubic zirconia powders and coatings produced by the sol-gel method have been investigated by perturbed angular correlation spectroscopy. Results indicate that the metastable cubic phase is retained during heating and cooling cycles. The hyperfine interaction which describes this cubic phase, once crystallized, exhibits two components in a constant ratio of 4:1. The components represent different vacancies configurations. For the fast movement of oxygen vacancies starting at 750°C, which is reflected by the damping of the hyperfine pattern, an activation energy of 0.96 eV was determined.
Order No.: JA702-035

Interactions between lead oxide and ceramic substrates for thick film technology
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The paper deals with the mechanisms and kinetics of interactions between screen printed and fired PbO layers and ceramic substrates: alumina and beryllia.

The interaction with alumina occurs via two main processes: 1) a reaction between PbO and Al_2O_3 grains, which induces the formation of a crystalline phase, $Pb_2Al_2O_5$, and 2) an interdiffusion process involving Pb and the intergranular amorphous phase in the ceramic substrate. This latter process results in a compositional change of the intergranular phase at considerable depths inside the ceramic substrate, as well as in the formation of a high lead glass layer on the substrate surface. Until PbO is not completely reacted, the Pb penetration in the ceramic is diffusion limited (penetration depth $w \approx t_d^{1/2}$, where t_d is the reaction time) with an activation energy of 1.20 ± 0.05 eV. The ceramic microstructure significantly affects the interaction processes.
Order No.: JA702-036

***Processing and characterization of compositionally modified $PbTiO_3$* thin films prepared by pulsed laser deposition**
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Modified lead titanate of $0.9PbTiO_3$ - $0.1Pb(Mg_{0.5}W0_{0.5})O_3$ thin films have been deposited onto Pt-coated Si substrates by pulsed laser deposition. Films were crystallized *in situ* during deposition or by post depositional heat treatment (post annealing). Compositional and structural characterization showed that the phase formation and microstructure of the films were highly sensitive to deposition conditions. Perovskite single phase films were formed *in situ* at 650°C, $P_{02} = 40$ Pa as well as by post annealing amorphous films at 650°C. In the post annealing process, the amorphous as-deposited phase was crystallized to perovskite and/or pyrochlore and the ratio of perovskite to pyrochlore was found to be influenced by the depositional P_{02}. Depending on the deposition temperature, the grain structures of the crystallized films were columnar or equiaxed. A relatively homogeneous surface morphology was obtained by deposition at a lower pressure ($P_{02} = 13$ Pa). The *in situ* crystallized films showed variable crystallographic orientation. The more (111) oriented films had the lowest remanent polarizations and the highest coercive fields. A method for preparing randomly oriented films, via a two-step deposition process with intermediate annealing, is believed to give the most consistent results and the best ferroelectric properties at the present level of development.
Order No.: JA702-037

Ordering and microwave dielectric properties of $Ba(Ni_{1/3}Nb_{2/3})O_3$ ceramics
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Ordering and microwave dielectric properties of $Ba(Ni_{1/3}Nb_{2/3})O_3$ have been investigated using x-ray diffraction, transmission electron microscopy, energy-dispersive spectroscopy, and network analyzer. Samples sintered at 1400°C for 2 h were disordered and showed the presence of Nb-rich liquid phase at grain boundary junctions. Degree of ordering increased following annealing at 1300°C. Growth of ordered region during the annealing process was discussed in terms of nucleation and growth. Long-range order parameter was calculated using structure factor. Measurements of microwave dielectric properties showed that permittivity and temperature coefficient of resonant frequency decreased with ordering, and quality factor increased with ordering. The correlation between microwave dielectric properties and ordering was discussed in terms of covalency of bonding, inhomogeneous charge distribution, and defects concentration.
Order No.: JA702-038

Dielectric properties of barium titanium niobates

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The results of measurements of the dielectric constants, in the vicinity of ambient temperature, are presented for eight barium titanium niobium oxides ($BaTi_{1+2n}Nb_4O_{13+4n}$ for n = 0, 1, 2, 3, 4; $Ba_3Ti_4Nb_4O_{21}$, $Ba_3Ti_5Nb_6O_{28}$, and $Ba_6Ti_2Nb_8O_{30}$) in polycrystalline ceramic form. The dielectric constants are in the range of 30 to 70. The results of dielectric measurements on solid solutions obtained by partial substitution of Ta for Nb are also reported. These substitutions do not dramatically increase the dielectric constants. One material, Ta substituted $Ba_3Ti_5Nb_6O_{28}$, has a very low temperature coefficient of dielectric constant at a $K \approx 45$.

Order No.: JA702-039

Influence of texture on the switching behavior of $Pb(Zr_{0.70}Ti_{0.30})O_3$ sol-gel derived thin films

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Rhombohedral $Pb(Zr_{0.70}Ti_{0.30})O_3$ thin films of four different well-defined textures, namely, (100), (111), and bimodal (110)/(111), and (100)/(111), were prepared by a sol-gel method. The films were characterized in terms of grain size, presence of second phases, surface roughness, columnarity of grains and other microstructural features. The dielectric, ferroelectric, and fatigue properties were investigated, with emphasis on the hysteresis switching characteristics. Results are discussed from the reference point of the allowable spontaneous polarization directions available for the different textures. The values of coercive field, remanent and saturation polarizations, and slope of the loop at the coercive field, at saturating fields can be qualitatively explained based on the texture, independent of microstructural differences. The occurrence of surface pyrochlore, however, is observed to effect the functionality of the saturation curves, particularly for the samples of bimodal texture. Shearing of the hysteresis curves of the bimodal films is also attributed to surface microstructural features. The occurrence of non-switching 71 or 109° domains in the (111) and (110)/(111) textured films is hypothesized based on a comparison with the data from the (100) textured film. Corrected saturation polarization values agree with the spontaneous polarization values of rhombohedral PZT single crystals and published calculated values for rhombohedral PZT ceramics. The fatigue characteristics show increases in the switching component of polarization in the range 10^3–10^7 bipolar cycles, particularly for the (111) textured sample. Onset of fatigue is observed for all samples between 10^7 and 10^8 switching cycles.

Order No.: JA702-040

Preparation of epitaxial $La_{1-x}Sr_xMnO_3$ films on $SrTiO_3$ (001) by dipping-pyrolysis process

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$La_{1-x}Sr_xMnO_3$ (LSMO) (x = 0-0.3) films were prepared on $SrTiO_3$ (001) substrates by dipping-pyrolysis process using metal naphthenates as starting materials. Epitaxially grown LSMO films were obtained by heat treatment at 800–1200°C; the fluctuation of alignment of these films, evaluated by reciprocal-space mapping of a symmetric x-ray diffraction, was markedly small, as comparable to that of the substrates. The LSMO films with x = 0.1–0.3 showed metallic conduction behavior at 25–300 K, and the resistivity was as low as that of LSMO single crystals, e.g., 4.5×10^{-4} Ω·cm at 150 K for the film with x = 0.3.

Order No.: JA702-041

Waveguide refractometry as a probe of thin film optical uniformity

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Optical inhomogeneities through the thickness of a sol-gel-derived, spin-coated $Pb(Zr,Ti)O_3$ (PZT) thin film have been evaluated using prism-coupled waveguide refractometry. Unusual waveguide coupling angle behavior has been treated using a multilayer model to describe the optical characteristics of the film. Waveguide refractometry measurements, performed after incremental reductions in film thickness, were used to develop a consistent model for optical inhomogeneity through the film thickness. Specifically, a thin film layer model, consisting of alternating layers of high and low refractive index material, was found to accurately predict irregularities in TE mode coupling angles exhibited by the film. This layer structure has a spatial periodicity that is consistent with the positions of the upper film surface at intermediate firings during film synthesis. The correlation emphasizes the impact of the multistep thin-film deposition approach on the optical characteristics of the resulting thin film.

Order No.: JA702-042

Gas-phase coating of TiO_2 with SiO_2 in a continuous flow hot-wall aerosol reactor

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The feasibility of *in situ* coating of titania particles with silica using a high-temperature, gas-phase process was demonstrated. Titania was produced from the reaction of $TiCl_4$ and O_2 in a hot-wall, tubular, aerosol reactor and directly coated in the gas-phase via the reaction of O_2 with $SiCl_4$ vapor. Rough SiO_2 coatings were obtained at 1300°C while uniform, dense coatings were obtained at all conditions examined for 1500°C. The presence of water in the reactor significantly influenced the morphology of the coatings and resulted in smooth, dense and uniform coatings at 1300°C. Coating thicknesses could be controlled from 5 nm to roughly 100 nm corresponding to growth rates on the order of 10–100 nm/sec. The characteristics of the coatings depended upon the concentration of $SiCl_4$ and the coating temperature. These process variables influenced the coating mechanism, growth rate and densification which directly influenced the coating uniformity and thickness.

Order No.: JA702-043

Synthesis, structure and gas sensitivity properties of SnO_2-CuO mixture phase obtained by pyrolysis of an aerosol

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SnO_2-CuO mixture phase has been prepared by pyrolysis of an aerosol produced by ultrahigh frequency of different precursor solutions. As-received samples were annealed in different conditions to study the influence of the temperature on the microstructure. Scanning electron microscopy shows that samples are constituted by hollow spherical particles and rings, the morphology being a consequence of the precursor solution utilized. The evolution of conductance under both pure and polluted air is discussed.

Order No.: JA702-044

New microstructural model of polymer-ceramic nanocomposite materials

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Organoceramics are a new class of polymer/ceramic nanocomposite materials where polymer chains are molecularly mixed with the ceramics. A structural model for poly(vinyl alcohol) organoceramic nanocomposite materials proposed by Messersmith et al. claims that polymer chains disperse in the interlayers of the ceramic precursor causing a broadening of the basal plane spacing. The present research revealed this basal plane broadening does not exist. A new model was constructed where the polymer acts as a template for the ceramic microcrystals to nucleate, and grow to reach a size of 20 Å. The ceramic microcrystals (hydrogen bonded to the polymer), further agglomerate and grow to the resulting rosette morphology whereby the polymer is molecularly dispersed on the nanoscale throughout the ceramic.

Order No.: JA702-045