JMR Abstracts

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ABSTRACTS

COMMUNICATIONS

Growth of nanocrystalline PbS within a glass
M. Mukherjee, A. Datta, D. Chakravorty
(Indian Association for the Cultivation of Science)

Nanocrystalline PbS has been grown within a phase separated oxide glass of composition $10Na_2O$, 15PbO, 17CaO, $3Bi_2O_3$, $55SiO_2$ (in mole%) by passing H_2S gas over it at temperatures varying from 773 to 943 K. The particle size ranged from 2.5 to 12.9 nm. The dc resistivity of composites of nanocrystalline PbS and the phase separated glass has been measured over the temperature range 300 to 670 K. The resistivity variation in the temperature range 550 to 670 K is characterized by the sodium ion migration in the glass with an activation energy ~1.2 eV . The resistivity in the range 300 to 500 K was controlled by conduction in PbS particles with the estimated band gap showing an increase with a decrease in the particle size.

Order No.: JA710-001

Rapid thermal recrystallization of amorphous silicon films
G.D. Beshkov, D.B. Dimitrov, V. Lazarova, J. Koprinarova, K. Gesheva, E. Vlaev
(Bulgarian Academy of Sciences)

In this work the properties of polycrystalline silicon layers obtained by rapid thermal annealing have been discussed. Amorphous silicon layers with thickness of 3000 Å have been deposited on silicon wafers in RF sputtering system. The layers were annealed for 15 sec to 5 min at temperatures in the range 800–1200°C in vacuum 5.10^{-5} torr. A correlation was established between structure, morphology, sheet resistance and the parameters of the rapid thermal annealing.

Order No.: JA710-002

Melt-infiltration processing of TiC/Ni_3Al composites
K.P. Plucknett, P.F. Becher, R. Subramanian
(Oak Ridge National Laboratory)

A simple melt-infiltration processing route has been developed for the fabrication of TiC/Ni_3Al ceramic/intermetallic composites, which involves a combination of infiltration and subsequent liquid phase sintering. For Ni_3Al contents from 8 to 25 vol.%, densities in excess of 98% of theoretical are readily obtained when processing at 1450°C. TiC and Ni_3Al are the only phases detected in the densified materials. Ni_3Al ductility is retained after processing, leading to the possibility of ductile phase toughened TiC composites for elevated temperature applications (up to ~1100°C).

Order No.: JA710-003

Low temperature synthesis of ultrafine $Pb(Zr,Ti)O_3$ powder by sol-gel combustion
J. Schäfer, W. Sigmund, S. Roy, F. Aldinger
(Max-Planck-Institut für Metallforschung and Universität Stuttgart)

Lead zirconate titanate powders are derived from a novel aqueous-based citrate-nitrate/oxynitrate sol-gel combustion process. Aqueous solu-

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tions of metal nitrates or oxynitrates are transformed into gels with citric acid under heating. The received gels undergo a self-propagating combustion reaction on heating to 180°C and subsequently yield voluminous ashes. These ashes form single phase perovskite $Pb(Zr_{0.53}Ti_{0.47})O_3$ powder with a specific surface area of 8 m^2/g upon calcination at 550°C. The ashes show a homogeneous distribution of lead, zirconium and titanium ions which guarantees short diffusion paths in solid state formation of PZT-perovskite. The redox behavior of the gels was studied with the help of DTA experiments. Powders are characterized in terms of XRD, SEM and EDX analysis.

Order No.: JA710-004

ARTICLES

Growth of high-quality $Bi_2Sr_2CaCu_2O_z$ crystal and characterization

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We report growth of high-quality $Bi_2Sr_2CaCu_2O_z$ single crystals with dimensions 2 x 1 x 0.03 mm^3 with a melt and growth technique. The composition of this crystal is homogeneous and very close to the stoichiometric composition. Structure characterization of single crystal was realized by measuring the (001) x-ray diffraction.The lattice parameters of a typical crystal are a = 5.414(2) Å, b = 5.413(2) Å, and c = 30.893(10) Å. The superconducting temperature T_c = 95 K with a sharp transition width (10-90% level) between 6 and 10 K was determined from resistivity and DC susceptibility. We have measured the magnetization of $Bi_2Sr_2CaCu_2O_z$ single crystal under magnetic field applied along the c-axis. The anomalous second peak effect appeared between 20-30 K. We discuss the qualities to these crystals.

Order No.: JA710-005

Phase identification and superconducting transitions in Sr doped $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$

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Sr-doped $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples have been prepared with accurate control of the oxygen content. The stability of both T' and T* phases is strongly dependent of Sr and oxygen content. An electron diffraction study indicates that, in some cases, anionic vacancies are ordered leading to a pseudo-tetragonal superlattice with unit cell parameters $2\sqrt{2}a_t x c_t$. Structural transitions and superconducting phases created by hole doping in such a system are also reported.

Order No.: JA710-006

Structural studies of diamond thin films grown from DC arc plasma

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Diamond thin films grown from a DC-arc discharge in CH_4/H_2 mixtures on Si wafers were examined by transmission electron microscopy and Raman spectroscopy. This deposition method provides good diamond crystallinity at high CH_4 concentrations (3–9%). Seeding the substrate with 5 nm diamond particles at a density of 2 x 10^{12} cm^{-1} followed by argon laser irradiation to reduce their agglomeration gives just after starting deposition, a density of growth centers of 10^{10} cm^{-2}. At 3% CH_4 concentration, the film grows with almost perfect crystallites. Richer CH_4 mixtures (5% and 9%) produce crystallites with twins and stacking faults. An amorphous 20–70 nm SiC interlayer is present at these CH_4 concentrations, which was not observed at 3% CH_4. Amorphous sp^3- and sp^2-bonded carbon was detected by Raman spectroscopy at all CH_4 concentrations and correlated with TEM data.

Order No.: JA710-007

Scanning tunneling microscope study of polyacrylonitrile based carbon fibers

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Scanning tunneling microscope (STM) was used to characterize the surface topography of polyacrylonitrile (PAN) based carbon fibers before and after electrochemical treatment, stretch resistance test and high-temperature treatment. A new kind of spiral structures was found which was not only on the surface but also in the inner layer. The spiral structure of the fibers was caused by the spinning process. The fiber structure contained the shape of the precursor. There were some large cracks in the carbon fibers after a stretching resistance test. The large cracks can result in carbon fiber breaking under certain stress conditions. The difference in the structures of the carbon fibers before and after the high-temperature treatment was acquired.

Order No.: JA710-008

On the formation of solid state crystallized intrinsic polycrystalline germanium thin films

Z. Meng, Z. Jin, B.A. Gururaj, P. Chu, H.S. Kwok, M. Wong
(The Hong Kong University of Science and Technology)

A two-step heat treatment process has been employed to crystallize low pressure deposited thin films of amorphous germanium. Large grain p-type polycrystalline germanium with a Hall Effect hole mobility of greater than 300 cm^2/Vs has been obtained. Films with near intrinsic conductivity necessary for the construction of practical enhancement-mode insulated-gate thin film transistors, were obtained by introducing phosphorus as a compensating dopant. High Hall Effect electron mobility of 245 cm^2/Vs has been measured on the resulting n-type polycrystalline germanium thin films.

Order No.: JA710-009

Quantum size effect of ZnSe microcrystals-doped SiO_2 glass thin films prepared by RF-sputtering method

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Semiconductor ZnSe microcrystals-doped SiO_2 glass thin films were prepared by RF-magnetron sputtering method. The particle size of ZnSe microcrystals in the films depended on sputtering conditions such as input power, substrate temperature and relative surface area ratio ($ZnSe/SiO_2$) in the target. The blue shift of the optical absorption edge was observed in these glass films. This blue shift energy was explained in terms of the independent confinement of electrons and positive holes, Coulomb force and the influence of a collapsed exciton and the dielectric constant of the matrix glass being taken into consideration.

Order No.: JA710-010

Shear faults and dislocation core structures in B2 CoAl

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(Virginia Polytechnic Institute)

Interatomic potentials of the embedded atom and embedded defect type were derived for the Co-Al system by empirical fitting to the properties of the B2 CoAl phase. The embedded atom potentials reproduced most of the properties needed, except that, in using this method, the elastic constants cannot be fitted exactly because CoAl has a negative Cauchy pressure. In order to overcome this limitation and fit the elastic constants correctly, angular forces were added using the Embedded Defect technique. The effects of angular forces to the embedded atom potentials were seen in the elastic constants, particularly C_{44}. Planar fault energies changed up to 30% in the {110} and {112} γ surfaces and the vacancy formation energies were also very sensitive to the non-central forces.

Dislocation core structures and Peierls stress values were computed for the (100) and (111) dislocations without angular forces. As a general result, the dislocations with a planar core moved for critical stress values below 250 MPa in contrast with the nonplanar cores for which the critical stress values were above 1500 MPa. The easiest dislocations to move were the 1/2(111) edge superpartials and the overall preferred slip plane was {110}. These results were compared with experimental observations in CoAl and previously simulated dislocations in NiAl.
Order No.: JA710-011

Fatigue crack initiation at Nd-rich particles in an Nd-containing high-temperature titanium alloy
J.F. Lei, Q.J. Wang, Y.Y. Liu, S.X. Guan, Z.G. Wang, D. Li, Z.Q. Hu
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Scanning electron microscopy (SEM) and surface replica method have been employed to study the micromechanism of fatigue crack initiation at Nd-rich phase particles in a high-temperature titanium (Ti-55) alloy. It was found that the microcrack initiates near the equator of Nd-rich particle in the matrix. The microcrack grows first at an angle of around 45° with respect to the tensile axis, and then its growth direction becomes approximately normal to the tensile axis. The experimental results are analyzed in terms of the elastic stress distribution around soft particles imbedded in the matrix to account for the experimental findings of particle cracking and the associated surface microcrack initiation near the particle "equator." A model of fatigue crack initiation at a soft surface particle is proposed.
Order No.: JA710-012

Crystallization of hafnia and zirconia during the pyrolysis of acetate gels
M. Yashima, T-A. Kato, M. Kakihana, M.A. Gulgun, Y. Matsuo, M. Yoshimura
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Hafnia and zirconia gels were prepared by drying hafnyl or zirconyl acetate solutions. Hafnia and zirconia gels contain both hydroxyl group and bidentate acetates which are directly bonded to the metal ions. Thermal decomposition and crystallization behavior of the gels were investigated through XRD, FTIR and TEM. Hafnium containing gels crystallized directly into stable monoclinic hafnia around 500–540°C, while zirconium containing gels first formed metastable tetragonal zirconia around 450°C. The dissimilar crystallization behavior of the gels into metastable, tetragonal zirconia or into stable, monoclinic hafnia can be explained through the difference in free-energy changes of the tetragonal-to-monoclinic phase transformation.
Order No.: JA710-013

Spinel solid solutions in the systems $MgAl_2O_4$-$ZnAl_2O_4$ and $MgAl_2O_4$-Mg_2TiO_4
M.A. Petrova, G.A. Mikirticheva, A.S. Novikova, V.F. Popova
(Russian Academy of Sciences)

Phase relations in two binary systems $MgAl_2O_4$-$ZnAl_2O_4$ and $MgAl_2O_4$-Mg_2TiO_4 have been studied and phase diagrams for them have been constructed. Based on the data of x-ray phase and crystal-optical analyses, the formation of a continuous series of solid solutions with spinel structure between the terminal members of the systems studied has been established. In the $MgAl_2O_4$-$ZnAl_2O_4$ system the solid solution is stable in the range from room temperature to melting temperature. In the $MgAl_2O_4$-Mg_2TiO_4 system the solid solution decomposes below 1380°C yielding the formation of limited regions of homogeneity on the basis of $MgAl_2O_4$ and $Mg_{2+2\delta}Ti_{1-\delta}O_4$. Decomposition of the solid solution is accompanied by crystallization of $MgTiO_3$.
Order No.: JA710-014

Phase instability in ZrO_2-NiAl functionally graded materials
Y-R. He, V. Subramanian, J.J. Lannutti
(Ohio State University)

Sedimentation in organic solvents was followed by hot-pressing to produce 2 mole% yttria stabilized zirconia-NiAl functionally graded materials (FGMs). These FGMs were better able to accommodate high levels of residual stress than alumina-NiAl FGMs; this is possibly due to enhanced tetragonal phase retention. However, we found that the zirconia layer in these FGMs subsequently experiences room temperature transformation of t-ZrO_2 to m-ZrO_2.
Order No.: JA710-015

Phase structure and thermal evolution in coating films and powders obtained by the sol-gel process: Part II. ZrO_2-2.5 mole% Y_2O_3
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Powders and coatings of zirconia doped with 2.5 mole% yttria have been produced via the sol-gel route. The phase structure and subsequent thermal evolution in heating and cooling cycles have been investigated using mainly perturbed angular correlations spectroscopy. Thermal analyses and XRD as a function of temperature have also been performed to obtain complementary information. Upon heating, the amorphous gels crystallized into the tetragonal structure and showed the same hyperfine pattern and thermal behavior as observed in tetragonal zirconia obtained by the ceramic route: the two vacancies' configurations around zirconium ions denoted as t_1- and t_2-forms and their mutual $t_1 \rightarrow t_2$ transformation. While the powder sample exhibited an incipient thermal instability above 1000°C and underwent completely the t_2-form to m-ZrO_2 transition during subsequent, gradual cooling below 500°C, the coating retained the tetragonal phase within the whole temperature range investigated. Hyperfine results suggest that the tetragonal phase stabilization is favored by the highly defective nature of the t_1-form and consequently hardened by the availability of oxygen. The PAC-derived activation energy for the oxygen vacancies' fast diffusion inherent to the t_2-form was determined as (0.54±0.14) eV.
Order No.: JA710-016

A structural study of amorphous alkoxide-derived lead titanium complexes
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We studied amorphous lead titanium alkoxide-derived heterometallic complexes, prepared from lead acetate and titanium n-propoxide or n-butoxide in parent alcohol medium. According to gas-liquid chromatography (GLC) and thermogravimetric analysis with mass spectrometry of evolved species (TGA/EGA) analyses, the type of alkoxide group influences oxo or acetate bridging, as well as the amounts of hydroxyl and organic groups bound to the metal network. From XANES and EXAFS analysis, local environments of lead and titanium atoms were determined within the analyzed range of 3.4 Å. Local environment depend weakly on the type of alkoxide used. Titanium atoms are pentacoordinated. A Pb-Ti correlation is established with lead atoms bound to titanium atoms by oxygen linkages.
Order No.: JA710-017

Domain structures in $Pb(Zr,Ti)O_3$ and $PbTiO_3$ thin films
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The microstructure of $Pb(Zr,Ti)O_3$ (PZT) and $PbTiO_3$ thin films deposited by the sol-gel method and chemical vapor deposition, respec-

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tively, were examined by transmission electron microscopy (TEM). Domains with ~7 and ~20 nm widths were found for the PZT and PT thin films, respectively. The traditional parallel twin or wedge-type structures found in bulk ceramics have been observed in thin films. Finally, a classification scheme for domains in PZT and $PbTiO_3$ thin films based on these and other published results of several researchers is presented. Domain sizes varied according to three categories: mono-domains (2–50 nm in diameter); domains in spherulite lamellae (28–130 nm wide) and twins in conventional large grains (5–150 nm wide). The mono-domains are related to small grain sizes, while the lamellae are a function of the nucleation and growth associated with sol-gel processing.

Order No.: JA710-018

Processing and characterization of lead magnesium tantalate ceramics

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(University of Pennsylvania)

Using a processing route that employed closed platinum crucibles, single phase ceramics of $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT) relaxor ferroelectrics were prepared with densities greater than 95% of their theoretical value. The improvements in the sintering characteristics of this system that result from this route were reflected by the dielectric properties, $\varepsilon'_{max} = 6300$ at 182 K, which are similar to those reported for single crystal PMT. Contrast originating from nano-sized polar clusters was evident in dark-field TEM images collected from the PMT ceramics at room temperature and showed little change upon cooling through the permittivity maximum. The electron diffraction patterns contained weak superlattice reflections at (h±1/2, k±1/2, 1±1/2) that originate from a 1:1 ordering of the B-site cations. High resolution imaging indicated that the length-scale of the chemical ordering in PMT is essentially identical to niobate relaxors such as PMN, with the 1–2 nm ordered domains being surrounded by a disordered matrix.

Order No.: JA710-019

Elastic properties of tetragonal $PbTiO_3$ single crystals by Brillouin scattering

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(University of Illinois at Urbana-Champaign)

Brillouin light scattering was used to obtain the elastic and piezoelectric constants for tetragonal $PbTiO_3$ single crystals at room temperature. Approximately 170 measurements of longitudinal and transverse acoustic wave velocities were inverted using literature dielectric constant values to obtain the full set of elastic and piezoelectric constants. Our data indicate a greater electromechanical anisotropy in the polar *c* direction than previously reported, but are otherwise in general agreement with previous studies. We discuss briefly the degree to which individual elastic and piezoelectric constants are resolved.

Order No.: JA710-020

Impedance spectroscopy of $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ ceramics correlation with fatigue behavior

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In this research, a fatigue model for ferroelectric materials is proposed. The reasons for the electrical fatigue resistance of $SrBi_2Ta_2O_9$ (SBT), $SrBi_2Nb_2O_9$ (SBN) and $PbZr_{1-x}Ti_xO_3$ (PZT) are discussed in terms of the bulk ionic conductivities of the compounds. To obtain the bulk ionic conductivity of SBT and SBN, we have used impedance spectroscopy which provides an effective method that allows us to separate the individual contributions of bulk, grain boundaries and electrode-ferroelectric interfaces from the total capacitor impedance. The bulk ionic conductivities of SBT and SBN (~10^{-7} S/cm) are much higher than those of the perovskite ferroelectrics, e.g., PZT (~10^{-11}–10^{-10} S/cm). The high ionic conductivities led us to conclude that the good fatigue resistance of $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ is due to easy recovery of defects. Specifically, oxygen vacancies entrapped within the capacitors are easily released, resulting in limited space charge build up and domain wall pinning during the polarization reversal process. However, the oxygen vacancies in PZT are trapped at trap sites to become space charges, resulting in capacitor fatigue.

Order No.: JA710-021

Estimation of Weibull parameter with a modified weight function

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The Weibull modulus is widely used for estimating the reliability of ceramic components in engineering applications. An improvement in the evaluation of the Weibull modulus is achieved by using an appropriate weight function to the data points while fitting a straight line to the Weibull plot by least square method. The conventional weight function is a function of the probability of failure.

This paper describes an alternate method of obtaining the weight function based on first principles. This modified weight function is a function of the stress at failure rather than probability of failure. Evaluation of the two-parameter Weibull modulus was estimated on a simulated strength distribution data with both the weight functions. A comparative analysis indicates that the modified weight function gives a different result than the conventional weight function. The paper also highlights the effect and importance of uncertainties in the measurement of strength on the calculated Weibull modulus.

Order No.: JA710-022

On the fluctuation field in multidomain barium hexaferrite particles

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A complete study of the thermally activated demagnetization phenomenology taking place in multidomain barium hexaferrite sample is presented. From the irreversible magnetization dependence of the fluctuation field, it is concluded that a demagnetization mechanism independent of the magnetization value rules the reversal in samples having large enough particles. Differently from this, in a sample having a broad particle diameter distribution (and including a minority percentage of small, single domain particles) our results clearly indicate the occurrence of two different demagnetization processes. Also, it was observed that the activation volume was, in all the samples, of the same order of magnitude and clearly smaller than the particle volume.

Order No.: JA710-023

Giant magnetoresistance in bulk $La_{0.6}Mg_{0.4}MnO_3$

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A bulk sample $La_{0.6}Mg_{0.4}MnO_3$ has been prepared in this study from coprecipitated carbonate precursor for the first time. Structure analysis conducted by powder x-ray diffraction indicates that the sample is in cubic perovskite phase. It shows a metal-insulator transition at 115 K (Tp). When applied on an external field, GMR effects are observed in the whole measured temperature range. The maximum negative MR value reaches as large as 480% at 105 K and 5 T. There may be two different mechanisms governing the GMR effects in the sample for the temperature below and above Tp.

Order No.: JA710-024

Decomposition behavior of $Ln_2Mn_{4/3}W_{2/3}O_7$ (Ln = Eu and Er) in reducing atmosphere and their thermodynamic properties

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Decomposition behavior of $Ln_2Mn_{4/3}W_{2/3}O_7$ (Ln = Eu and Er) in reducing atmosphere at 1273 K was determined. These compounds decomposed to $LnMnO_3$ and Ln_2MnWO_7 at $PO_2 = 10^{-8.46}$ atm for Ln = Eu and $10^{-7.46}$ atm for Ln = Er, respectively. Decomposition product Eu_2MnWO_7 decomposed to Eu_2MnWO_6 at $PO_2 = 10^{-15.67}$ atm, while Er_2MnWO_7 decomposed to Er_2O_3, MnO and W less than 10^{-17} atm. The

standard Gibbs free energy changes of decomposition for $Eu_2Mn_{4/3}W_{2/3}O_7$, Eu_2MnWO_7 and $Er_2Mn_{4/3}W_{2/3}O_7$ at 1273 K were determined to be 34.4 kJ·mol^{-1}, 191.9 kJ·mol^{-1} and 44.8 kJ·mol^{-1}, respectively. The standard Gibbs free energy changes of formation of $Er_2Mn_{4/3}W_{2/3}O_7$ and Er_2MnWO_7 were also determined to be -2429.5 and -2463.2 kJ·mol^{-1} at 1273 K, respectively.

Order No.: JA710-025

Reaction path in the magnesium thermite reaction to synthesize titanium diboride

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TiB_2, along with MgO and $Mg_3B_2O_6$ was formed by a thermite reaction between Mg, amorphous B_2O_3, and TiO_2 powders in argon. The mixture 5Mg-TiO_2-B_2O_3 along with binary mixtures and single components were analyzed using DTA and XRD. Large (25 g) specimens were also ignited in bulk using a resistance-heated nichrome wire. The reaction path in forming TiB_2 in the three-component mixture was deduced: Mg reduces TiO_2 and B_2O_3 to form Ti and MgB_2, respectively, which in turn react to form TiB_2. In an oxidizing atmosphere, the significant speed of the reaction permitted solid state reaction to form TiB_2 before atmospheric oxygen could diffuse into the powder mass and react to form oxide phases. Thermite reactions in air have the advantage (over furnace heating in air) of not providing time at elevated temperatures for Mg and intermediate products to become consumed in the formation of oxides, nor time for oxidation degradation of TiB_2.

Order No.: JA710-026

Strontium and calcium zirconyl citrates as precursors for the low-temperature synthesis of $SrZrO_3$ and $CaZr_3$ fine powders

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(Indian Institute of Science)

Synthesis and the thermal decomposition behavior of new molecular precursors, strontium and calcium zirconyl citrates are presented. The pathway to the metazirconate formation has been found to proceed through a multistep process. The precursors yield $SrZrO_3$ and $CaZrO_3$ fine powders at temperatures as low as 650°C. Physico-chemical, spectroscopic, thermoanalytical and microscopic techniques have enabled the identification of the sequence of events leading to the perovskite formation and proposition of a thermolysis scheme. Retention of the molecular level mixing of the metal ions during the course of the precursor decomposition is supported by these techniques. Prior to the formation of $MZrO_3$ (M = Sr and Ca) an ionic oxycarbonate $M_2Zr_2O_5CO_3$ (M = Sr and Ca) intermediate is produced by the thermal decomposition of the citrate precursors.

Order No.: JA710-027

Investigation of a new fracture mechanics specimen for thin film adhesion measurement

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(University of Minnesota)

We have investigated a precracked fine line structure as a new type of thin film fracture mechanics specimen. An idealized mechanics analysis is first presented. Experimentally two types of precracks are formed. A thin carbon layer to which other layers weakly adhere creates a "processed precrack" by integrated circuit processing techniques. An "indented processed precrack" is formed by precision alignment of a sharp microwedge. The processed precrack is found to reduce the critical tangential load by 50% from a non-precracked line, while the indented processed precrack lowers the load by 200%. From this, a reasonable value of adhesion may be directly calculated. Crack path behavior is observed to depend on strength of the interface. In the case of a weak interface, the crack remains in the interface as it extends. For a strong interface, it kinks into the substrate if the crack is initially short, but remains in the interface if it is initially long. Given the experimental evidence, the mechanics are slightly modified to quantitatively model the experimental data.

Order No.: JA710-028

A sequential Raman analysis of the growth of diamond films on silicon substrates in a microwave plasma assisted chemical vapor deposition reactor

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A sequential analysis of the growth of diamond films on silicon substrates in a microwave plasma assisted chemical vapor deposition (CVD) reactor has been performed by Raman spectroscopy. The plasma has been switched off during measurements, but the substrate heating was maintained to minimize thermoelastic stresses. The detectivity of the present experimental set-up has been estimated to be about a few tens of μg/cm^2.

From such a technique, one expects to analyze different aspects of diamond growth on a non-diamond substrate. The evolution of the signals arising from the substrate shows that the scratching treatment used to increase the nucleation density induces an amorphization of the silicon surface. This surface is annealed during the first step of deposition. The evolution of the line shape of the spectra indicates that the non-diamond phases are mainly located in the grain boundaries. The variation of the integrated intensity of the Raman signals has been interpreted using a simple absorption model. A special emphasis was given to the evolution of internal stresses during deposition. It was verified that compressive stresses were generated when coalescence of crystals took place.

Order No.: JA710-029

Pulsed laser deposition of $KNbO_3$ thin films

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The laser ablation of stationary $KNbO_3$ single crystal targets induces a Nb enrichment of the target surface. In rotated targets this effect is only observed in those areas irradiated with low laser fluence. The composition of the plasma formed close to the target surface is congruent with the target composition, however at further distances, K-deficient films are formed due to the preferential backscattering of K in the plasma. This loss may be compensated for by using K-rich ceramic targets. Best results so far have been obtained with [K]/[Nb]=2.85 target composition, and crystalline $KNbO_3$ films are formed when heating the substrates to 650°C. Films formed on (100)MgO single crystals are usually single phase and oriented with the (110) film plane perpendicular to the (100) substrate surface. (100) NbO may coexist with $KNbO_3$ on (100)MgO. At substrate temperatures higher than 650°C, niobium diffuses into MgO forming $Mg_4Nb_2O_9$ and NbO, leading to K evaporation from the film. Films formed on (001) α-Al_2O_3 (sapphire) show the coexistence of (111), (110) and (001) orientations of $KNbO_3$ and the presence of NbO_s is also observed. $KNbO_3$ films deposited on (001) $LiNbO_3$ crystallize with the (111) plane of the film parallel to the substrate surface. For the latter two substrates the Nb diffusion into the substrate is lower than in MgO and consequently the K concentration retained in the film is comparatively larger.

Order No.: JA710-030

Nanoindentation measurements of amorphous carbon coatings

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In this study, amorphous carbon coatings were deposited with thicknesses ranging from 20 nm to 100 nm on single-crystal silicon substrates by sputtering, ion beam and cathodic arc deposition techniques. An indentation system with a three plate transducer with electrostatic actuation and capacitive sensor has been used to make load displacement measurements and subsequently carry out *in-situ* imaging of the indents. Indentation experiments were carried out using a three-sided pyramidal (Berkovich) diamond tip. Measurements include load-displacement curves and calculation of hardness and Young's modulus of elasticity at various indentation depths, studies of hysteresis behavior, creep behavior and strain rate effect of various carbon coatings. The cathodic arc coating exhibited the highest

hardness and elastic modulus followed by the sputtered and ion beam coatings.
Order No.: JA710-031

Effect of Nd content on the magnetic properties and crystallographic alignment of Fe-Nd-B-Al sintered magnets
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The magnetic properties and crystallographic alignment for Fe-Nd-B-Al magnets having different Nd contents were studied. It was found that higher Nd concentration (above 18 at.%) resulted in deterioration of the alignment. Also, extended ball milling of the powder particles resulted in poorer alignment of the grains in the final sintered magnet. This behavior was attributed to the cold welding of the small particles of $Fe_{14}Nd_2B$ phase by mechanically soft Nd-rich phase in the course of ball milling.
Order No.: JA710-032

Preparation of nanocrystalline copper by electrodeposition
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Copper particles of sizes in the range 3.1 to 11.4 nm have been grown within gel compositions of the system $CuO\text{-}SiO_2$ by electrodeposition process applying voltages varying from 5 to 15 volts. Composite films of these metal particles dispersed in polystyrene matrix have been prepared on Corning No. 7059 glass slides by a dip coating technique and their optical absorption characteristics have been delineated. The spectra show maxima at wavelengths in the range 380 to 470 nm depending on the particle size. The results have been analyzed using Mie theory. The electrical conductivity as extracted from this analysis is found to have reasonable correspondence with data reported earlier for copper nanoparticles in glass-ceramic systems.
Order No.: JA710-033

Does the shear-lag model apply to random fiber networks?
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The shear-lag type model due to Cox [Br. J. Appl. Phys. **3** (1952), 72] is widely used to calculate the deformation properties of fibrous materials such as short fiber composites and random fiber networks. We compare the shear-lag stress transfer mechanism with numerical simulations at small, linearly elastic strains and conclude that the model does not apply to random fiber networks. Most of the axial stress is transferred directly from fiber to fiber rather than through intermediate shear-loaded segments as assumed in the Cox model. The implications for the elastic modulus and strength of random fiber networks are discussed.
Order No.: JA710-034

***In-situ* mass spectrometry during diamond chemical vapor deposition using a low pressure flat flame**
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A combination of experiments and detailed kinetic modeling was used to investigate diamond deposition chemistry in low pressure combustion synthesis. Microprobe sampling was employed to provide *in-situ,* quantitative measurements of the stable gas-phase species impinging the growth surface. The reactant gas ratio was found to be the most critical experimental variable. A detailed kinetic model was developed for the stagnation flow system. Comparison of experimental measurements showed very good agreement with model predictions. The model was then used to predict the concentration of radical species and analyze the sensitivity of predictions to γ_H, the probability of atomic hydrogen recombination on the surface. It was shown that γ_H dramatically effects the distribution of radical species near the diamond surface. The analysis also indicates that atomic carbon may be an important gas-phase precursor in this system. Comparison of mole fraction measurements and observations of film morphology were used to draw conclusions on the growth mechanism.
Order No.: JA710-035

Camber development during cofiring Ag-based low-dielectric-constant ceramic package
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Camber (curvature) development during the cofiring of a two-layered structure of Ag film/low-dielectric-constant, low-temperature cofired ceramic (LTCC) green tape has been investigated. At a given thickness of Ag film, both the camber and camber rate decrease linearly with increasing the square thickness of LTCC. Densification mismatch between Ag and LTCC is attributed to being the root cause for the camber generation during cofiring. Mathematical analysis is made to theoretically describe the camber development, and the results show a fairly good agreement with experimental observations.
Order No.: JA710-036

Schwertmannite: A unique mineral, contains a replaceable ligand, transforms to jarosites, hematites and/or basic iron sulfate
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An infrared study of the chemical changes of synthetic Schwertmannite, which normally is a coal oxidation by-product formed by Thiobacillus Ferrooxidan bacteria. Schwertmannite, a class of minerals, is a metastable compound that transforms to jarosite, hematite and/or basic iron sulfate at relatively low temperatures; and is analogous in structure to basic iron sulfate, but with a -Fe-O- cage. A proposed formula for Schwertmannite is $Fe_4O_4(OH)_2{\cdot}AN_{(2/e)}{*}nH_2O$, where AN is the anion and *e* is its charge, where sulfate can be replaced with other anions, a possible catalyst. The facile conversion of Schwertmannite to a black or yellow material might make a useful raw material for the pigment industry.
Order No.: JA710-037

Photooxidatively self-cleaning transparent titanium dioxide films on soda lime glass: The deleterious effect of sodium contamination and its prevention
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In the context of photocatalytically self-cleaning windows and windshields, clear, abrasion-resistant, thin (60±10 nm) photocatalytic films of TiO_2 were formed by a sol-gel process on (a) soda lime glass, (b) the proton-exchanged surface of soda lime glass, and (c) fused silica. The hypothesis that diffusion of sodium oxide from the soda lime glass into the titanium dioxide layer during the calcination step causes the lower photoefficiency in films on glass was tested and proven. At high concentration, sodium prevented formation of the photoactive anatase phase and, at low concentration, introduced surface and bulk recombination centers. Sodium transport was efficiently blocked by a thin layer at the interface of proton-exchanged ("hydrogen") glass and nascent TiO_2, formed at 400°C of a poly(titanyl acetylacetonate) TiO_2 precursor. The sodium transport blocking layer did not form and the highly photocatalytic film was not obtained when the TiO_2-precursor film was applied to glass that was not proton exchanged. Furthermore, only a much less effective sodium transport blocking layer was formed on glass that was proton-exchanged, but was calcined at 400°C prior to application of the TiO_2 precursor layer, showing that the sodium depleted glass surface, by itself, was a less effective barrier against sodium transport than the interfacial product of hydrogen glass and the TiO_2 precursor.
Order No.: JA710-038

Iron-silica and nickel-silica nanocomposites prepared by high energy ball milling

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Metal-silica nanocomposites with different metal volume fractions have been prepared via solid state exchange reactions induced by ball milling followed by a reduction treatment in H_2 flux.

In nickel-containing mixtures, oxygen transfers directly from NiO to Si while NiO is reduced to Ni. When NiO is present in a large ratio its excess can be reduced by a thermal treatment in H_2 flux. Nickel crystallites are obtained with nanometer size in the milling process and there is no significant growth during thermal treatment. Similar process conditions applied to Fe containing mixtures give rise to a more complex reaction path which prevents the complete conversion of Fe(III) to Fe.

Nickel-silica and iron-silica nanocomposites are also produced by ball milling mixtures of either nickel or iron with amorphous silica.

Order No.: JA710-039

Studies on age-hardening characteristics of ceramic particle/matrix interfaces in Al-Cu-SiC_p composites using ultra low-load dynamic microhardness measurements

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Ultra low-load dynamic microhardness testing facilitates the hardness measurements in a very low volume of the material and thus is suited for characterization of the interfaces in MMCs. This paper details the studies on age-hardening behavior of the interfaces in Al-Cu-5 SiC_p composites characterized using this technique. Results of hardness studies have been further substantiated by TEM observations. In the solution treated condition, hardness is maximum at the particle/matrix interface and decreases with increasing distance from the interface. This could be attributed to the presence of maximum dislocation density at the interface which decreases with increasing distance from the interface. In case of composites subjected to high temperature aging, hardening at the interface is found to be faster than the bulk matrix and the aging kinetics becomes progressively slower with increasing distance from the interface. This is attributed to the dislocation density gradient at the interface leading to enhanced nucleation and growth of precipitates at the interface compared to the bulk matrix. TEM observations reveal that size of the precipitates decrease with increasing distance from the interface and thus confirms the retardation in aging kinetics with increasing distance from the interface.

Order No.: JA710-040

Preparation and characterization of Nd^{3+} and Er^{3+} doped silica sol-gel coatings by Rutherford backscattering spectroscopy and spectroscopic ellipsometry

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Neodymium or erbium doped silica films are deposited on single crystal silicon substrates using a sol-gel process and a spin-coating technique. These glasses are doped with neodymium or erbium in a various Nd/Si or Er/Si atomic ratio up to 8% using neodymium nitrate or erbium nitrate as precursor. A preparation method of such films is described. Film rare earth concentration measured by Rutherford backscattering spectroscopy (RBS) is the same as in the initial liquid solution. Film thickness and refractive index are obtained by variable angle spectroscopic ellipsometry. We have shown that both RBS analysis and spectroscopic ellipsometry are powerful tools to control rare earth doping level and optical properties of the silica films.

Order No.: JA710-041

Compensation phenomena in oil-resin mixtures: A new dielectric approach to percolative processes

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The methods of thermally stimulated currents (TSC) together with low frequency dielectric spectroscopy (LFDS) are combined for the first time to study percolation phenomena. These take place within oil-resin mixtures which constitute conductor-insulator like composite systems.

Each of these techniques is shown to describe selectively one of two different kinds of relaxation processes in the oil component: first, anelastic dipolar movements and secondly, the circulation of free charges.

The separate qualitative interpretations of the combined TSC/LFDS experiments lead to convergent estimations of the percolation thresholds of the two basic materials in oil-resin mixtures. The latter appear as critical concentrations for which the dielectric relaxation processes either comply suddenly with compensation laws, or pre-existing compensation phenomena change in nature.

Order No.: JA710-042

An alternative analysis of water vapor and gas transport in polyimide films

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The water vapor and gas transport in polyimide films were analyzed using Harmon's model which accounts for case I transport and case II transport. The Harmon's model was in good agreement with the experimental data. The diffusion coefficient obtained by Harmon's model was smaller than that obtained by using the short-time slope of mass uptake versus time with the exception of that of CO_2 in polyimide. A comparison of the present model and dual-mode sorption model, in which populations follow the Henry's law and Langmuir type, was made.

Order No.: JA710-043

The nature of residues following the ashing of arsenic implanted photoresist

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Extensive analytical characterization indicates that the most significant contaminant following dry processing of As -mplanted photoresist is not a carbon-based residue, but is in fact arsenic itself. The arsenic residue is an amorphous form of elemental arsenic, relatively free of oxygen or carbon, that is stable for long periods of time. Since arsenic is not particularly soluble in sulfuric acid, hydrogen peroxide or their mixtures, it makes sense to pose questions regarding the optimum choice for post-dry processing wet chemical cleans.

Order No.: JA710-044

Impression recovery of PMMA

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Impression recovery in which the deformation temperature is the same as recovery temperature is studied for the first time. PMMA is deformed by impression above the glass transition temperature to a depth of less than 0.3 mm and recovered at the same temperature. Almost complete recovery of dimension is observed every time. The dimensional changes obey second order kinetics and the temperature dependence of the rate constant shows two consecutive processes with activation energies, 440 kJ/mole (between 104 and 113°C) and 95 kJ/mole (between 113 and 140°C). Two pairs of defects of opposite signs are believed to be involved in the dimensional recovery processes.

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