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ABSTRACTS

COMMUNICATIONS

Synchrotron x-ray study of interstitial oxygen ordering in the superconducting phase of La2CuO4+δ
X. Xiong*, Q. Zhu+, Z.G. Li*, S.C. Moss*, H.H. Feng*, P.H. Hor*, D.E. Cox+, S. Bhavaraju*, A.J. Jacobson*
*(*University of Houston, +Brookhaven National Laboratory)*

A synchrotron x-ray powder-diffraction study has been carried out on two samples with well-defined excess oxygen concentrations, δ = 0.045 and 0.055. Evidence for one dimensional interstitial oxygen ordering along the c-axis was observed from the appearance of a pair of superlattice satellite peaks at $(0, 1, 2 \pm \Delta)$ in both samples. In $La_2CuO_{4.045}$, a ~5% oxygen-poor Bmab phase coexists with a stage-6 phase and with a small amount of the high-temperature-tetragonal (HTT) phase below the phase separation temperature (~280 K). $La_2CuO_{4.055}$ shows a single stage-5 phase below 170 K, but with two unindexed peaks between $(0, 1, 2 \pm 0.2)$ satellites which may well result from a further domain modulation. The critical temperature T_c is increased by 1.5 K by reducing the stage number from 6 to 5.
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Preparation of large single grains of the quasicrystalline icosahedral Al-Cu-Fe ψ-phase
T.A. Lograsso, D.W. Delaney
(Ames Laboratory/Iowa State University)

A cyclic heat treatment process was used to prepare single grains of the quasicrystalline icosahedral phase, ψ-$Al_{65}Cu_{23}Fe_{12}$. Alloys of appropriate composition are melted and chill cast into copper molds. Multiple cyclic heat treatments at successively higher temperatures below 860°C (the peritectic decomposition temperature of the quasicrystal phase) are used to enhance the growth of the ψ phase. Single grains up to 10 mm x 5 mm x 5 mm have been prepared.
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Fabrication of submicrometer-grained Zn-22% Al by torsion straining
M. Furukawa*, Z. Horita+, M. Nemoto+, R.Z. Valiev#, T.G. Langdon§
*(*Fukuoka University of Education, +Kyushu University, #Ufa State Aviation Technical University, §University of Southern California-Los Angeles)*

The Zn-22% Al eutectoid alloy is capable of exhibiting very high superplastic elongations, in excess of 2000% in tension, when the grain size is in the range of ~1–10 μm. This paper describes the fabrication of a submicrometer grain size in the Zn-22% Al alloy by subjecting the samples to intense plastic straining in torsion under high pressure (~5 GPa) at room temperature. Observations after straining revealed a heterogeneous microstructure with grain sizes in the range of ~0.1–0.5 μm. As a result of the low melting temperature of the alloy, the high internal stresses introduced by torsion straining are relaxed and the grain boundaries are close to an equilibrium configuration.
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Synthesis of nanocrystalline Ni-Fe alloy powders by spray pyrolysis
S. Eroglu*, S.C. Zhang+, G.L. Messing+
*(*TUBITAK-Marmara Research Center, +Pennsylvania State University)*

Nanocrystalline 70 wt% Ni-30 wt% Fe alloy powders were synthesized by spray pyrolysis from a solution of nickelcene $(C_2H_5)_2Ni$ and ferrocene $(C_2H_5)_2Fe$ dissolved in 2-methoxyethanol. The alloy powder consisted of <10 nm and 70 to 80 nm particles. Thermodynamic analysis is shown to be a useful tool for gaining insight into the thermochemistry of the spray pyrolysis process.
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ARTICLES

Al_2O_3 additions for isothermal melt processing of $Bi_2Sr_2CaCu_2O_y$
T.G. Holesinger
(Los Alamos National Laboratory)

It is shown that additions of Al_2O_3 (1.0 wt.%) can significantly aid in the isothermal melt processing of $Bi_2Sr_2CaCu_2O_y$ (Bi-2212). Al_2O_3 additions provide a means for grain refinement of phases present in the partial melt. By limiting grain growth in the partial melt, solidification to form Bi-2212 proceeds more efficiently resulting in fewer secondary phases and improved transport properties. Aluminum does not substitute into the superconducting phase to any appreciable extent and is present in fully processed material as small, secondary grains of approximate composition $Sr_{2-x}Ca_xAlO_y$ or $Bi_2Sr_{4-x}Ca_xAl_3O_y$. Al_2O_3 additions were applied to the isothermal melt processing of Bi-2212 thick films and current leads.
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An investigation of the invariant reactions in BiPbSrCaCuO system
L. Liu, Z. Jin
(Central South University of Technology)

The phases present around the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223) phase between 830–880°C have been studied by x-ray diffraction (XRD) and electron probe microanalysis (EPMA) methods. The decomposition and melting temperatures of the 2223 phase in these samples have been measured by differential thermal analysis (DTA) method. Partial substitution of Bi with Pb (Pb : Bi = 3 : 22) does not change the 850°C phase relations around 2223 phase. 2223 decomposes to liquid, $Sr_7Ca_7Cu_{24}O_{41}$ (7724) and Ca_2CuO_3, at 875°C. The invariant

reactions (degree of freedom is zero) among 2223, 7724, Ca_2CuO_3, CuO, $Bi_2Sr_2CaCu_2O_8$(2212), and liquid were proposed to be: $L+7724+Ca_2CuO_3 \rightarrow 2223+2212$, $L+7724+Ca_2CuO_3 \rightarrow 2223+CuO$, $L+7724 \rightarrow 2223+2212+CuO$. The reaction temperatures were estimated to be 860°C, 860°C, and 854°C, respectively. An invariant reaction scheme and a tentatively liquidus projection were sketched out.

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Low-energy electron-beam induced regrowth of isolated amorphous zones in Si and Ge

I. Jenčič*, I.M. Robertson+
(*J. Stefan Institute, +University of Illinois)

Spatially isolated amorphous regions in Si and Ge have been regrown at room temperature by using an electron beam with an energy less than that required to cause displacement damage in crystalline material. The rate at which the zones regrow is a function of the energy of the electron beam. As the electron energy is increased from 25 keV (lowest energy employed) the regrowth rate decreases and reaches a minimum below the threshold displacement voltage. With further increases in the electron energy the rate again increases. It is suggested that at the lower electron energies this room temperature regrowth process is stimulated by electronic excitation rather than by displacive type processes.

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On the substrate temperature dependence of the properties of $In_{0.52}Al_{0.48}As/InP$ structures grown by molecular beam epitaxy

S.F. Yoon, Y.B. Miao, K. Radhakrishnan, S. Swaminathan
(Nanyang Technological University)

Growth of $In_{0.52}Al_{0.48}As$ epilayers on InP(100) substrates by molecular beam epitaxy at a wide range of substrate temperatures (470–550°C) is carried out. Low temperature photoluminescence (PL) and double-axis x-ray diffraction (XRD) measurements showed a strong dependence of the PL and XRD linewidths and lattice-mismatch on the substrate temperature. Minimum PL and XRD linewidths and lattice-mismatch were found to occur at substrate temperatures of between $\approx$500–520°C under the beam fluxes used in this study. The XRD intensity ratios (I_{epi}/I_{sub}) were generally higher within the same substrate temperature range at which the lattice-mismatch was the lowest. XRD rocking-curves of samples grown at low temperatures showed the main epilayer peak to be composed of smaller discrete peaks, suggesting the presence of regions with different lattice constants in the material. PL spectra taken at increasing temperatures showed the quenching of the main emission peak followed by the evolution of a distinct lower energy peak which is possibly associated with deep lying centers.

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Mechanics of shaped crystal growth from the melt

J.C. Lambropoulos, C-H. Wu·
(University of Rochester)

We present the numerical formulation of the thermal stress driven steady-state dislocation generation during the growth of shaped crystals from the melt, with Czochralski (CZ) growth of solid cylinder III-V compound semiconductors as an example. We use and compare the Haasen-Alexander model, coupling dislocation multiplication and creep strain rates, and the Jordan model, based on thermoelastic stresses. Growth parameters may be chosen so as to produce an overall approximately flat interface, leading to reduced dislocation density in the majority of the crystal's cross section. Calculation of final dislocation density requires the initial dislocation density and all stress components along the solid-liquid interface, microstructural features which depend on the physical processes leading to solidification. The final dislocation density is not sensitive to the initial dislocation density along the solid-liquid interface, but strongly depends on the interface stress: Significant stress relaxation at the interface is required to pro-

duce experimentally observed "W" shaped dislocation patterns. Crystal growth direction and crystalline anisotropy couple elastic (lattice) and plastic (slip systems) crystalline anisotropy.

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Solidification of Al-Cu-Fe alloys forming icosahedral phase

B. Grushko*, R. Wittenberg*, D. Holland-Moritz*+
(*Forschungszentrum Jülich GmbH, +Deutsche Forschungsanstalt für Luft-und Raumfahrt)

The solidification of a series of Al-Cu-Fe alloys containing an icosahedral phase has been studied by scanning electron microscopy, energy-dispersive x-ray spectroscopy, powder x-ray diffraction and differential thermal analysis. The constitution and morphology of alloys solidified at different rates are presented. The overall compositional range of the icosahedral phase was determined in as-cast, slowly solidified alloys and those annealed at 800 and 600°C. The solidification of this phase follows closely the Al_3Fe-AlCu compositional direction. The first icosahedral phase solidifies close to $Al_{65.5}Cu_{21.5}Fe_{13}$, its compositional region at 800°C lies between about $Al_{64.5}Cu_{23}Fe_{12.5}$ and $Al_{62}Cu_{26.5}Fe_{11.5}$ while at 600°C it lies between $Al_{62}Cu_{26.5}Fe_{11.5}$ and $Al_{60.5}Cu_{29.5}Fe_{10}$. The formation of the icosahedral and related structures observed in Al-Cu-Fe alloys is discussed.

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Effects of hydrogen on the microstructure and microchemistry of Ti_3Al-Nb intermetallics at high temperatures and high pressures

H.Z. Xiao, I.M. Robertson, H.K. Birnbaum
(University of Illinois at Urbana-Champaign)

The microstructural and microchemical changes produced in a Ti-25Al-10Nb-3V-1Mo alloy (at.%) by charging at high temperatures in high pressures of hydrogen gas have been studied using TEM and x-ray methods. Hydrides incorporating all of the substitutional solutes which formed during charging have a FCC structure and exhibit either a plate or fine grained morphology. With increasing hydrogen content, the size of the hydrides decreases and their microchemistry changes as they approach the stable binary hydride, TiH_2. Rejection of substitutional solute elements from the hydride produces changes in the microchemistry, and consequently in the crystal structure, of the surrounding matrix. In alloys containing 50 at.% H, this solute redistribution results in the formation of an orthorhombic substitutional solid solution phase containing increased levels of Nb. The driving force for this redistribution of solutes is the reduction in the chemical potential of the system as the amount of the most stable hydride, TiH_2, forms. The hydrides reverted to a solid solution on annealing in vacuum at 1073 K, and the original microchemistry of the alloy was restored. Reversion from the hydride structure to the original $\alpha2$ ordered DO_{19} structure proceeds via a disordered HCP phase.

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Creep behavior and microstructural correlation of a particle-strengthened Nb-1Zr-0.1C alloy

D.M. Farkas, A.K. Mukherjee
(University of California-Davis)

The steady-state creep behavior of a particle-strengthened alloy of niobium (Nb-1Zr-0.1C) was compared with pure niobium and a Nb-1Zr alloy. The approach to a threshold stress was indicated at stress levels below 16 MPa and was supported by a statistical analysis of mean particle size. Analysis of the crept microstructure showed a classic dislocation substructure whose cell size was inversely proportional to the applied stress except at very low stresses. The smaller than predicted cell size observed at low applied stresses was attributed to the particles preventing the dislocation cells from reaching their equilibrium dimension. Some amount of particle growth was observed which lead to a reduction in creep resistance with time.

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Electronic bonding characteristics of hydrogen in bcc iron: Part I. Interstitials

Y. Itsumi*, D.E. Ellis+

*(*Kobe Steel, Ltd., +Northwestern University)*

Electronic structure calculations were carried out for bcc iron (Fe) clusters with or without hydrogen (H), and also involving a vacancy, using the self-consistent Discrete Variational method (DV-Xα) within the local density functional formalism. Bonding characteristics investigated show the following: (i) interstitial H notably decreases interatomic Fe-Fe bond strengths, but acts over a small distance (within 0.3 nm); (ii) in the perfect Fe lattice field, interstitial H feels a repulsive force at any site. As a result of lattice relaxation, volume expansion may be expected; and (iii) H in combination with a vacancy prefers a position shifted from the octahedral site towards the vacancy. This is fairly consistent with an experimental result.

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Electronic bonding characteristics of hydrogen in bcc iron: Part II. Grain Boundaries

Y. Itsumi*, D.E. Ellis+

*(*Kobe Steel, Ltd., +Northwestern University)*

Electronic structure calculations were carried out for bcc iron grain boundaries (GB) with or without hydrogen, using the self-consistent Discrete Variational embedded cluster method within the first-principles local density formalism. Bonding characteristics were mainly investigated. Simple rigid body translations perpendicular to the GB plane were used for estimation of relaxed GB geometry. Analysis of bond order summation over the GB shows considerable volume expansion normal to the GB plane of a dense $\Sigma3(111)$ twist/tilt GB and some compression for the rather open $\Sigma3(110)$ twist configuration. These results are discussed in the context of atomistic simulations which suggest that higher energy GBs generally have larger volume expansion normal to the GB plane. H in a $\Sigma3(111)$ GB reduces Fe-Fe bonding strength by ~3% within a 0.25 nm spherical volume around the H site, associated with reduction of the 4s and 4p occupancy of the nearest neighbor Fe. Since these orbitals contribute mainly to metallic bonding, the action of H atoms as an embrittlement inducer can be understood.

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A new design of tungsten carbide tools with diamond coatings

V. Weihnacht*, W.D. Fan*, K. Jannadham*, J. Narayan*, C-T. Liu+

*(*North Carolina State University, +Oak Ridge National Laboratory)*

We have designed tungsten carbide tools with a new binder, which makes them suitable for advanced diamond tool coatings. The new tool substrates, made of tungsten carbide and nickel aluminide as binder phase, are produced by sintering and hot isostatic pressing, and also by combustion synthesis. The high temperature strength of nickel aluminide is key to superior tool performance at elevated temperatures. More importantly, nickel aluminides reduce the formation of graphite and promote diamond growth during chemical vapor deposition. Diamond films are deposited on the new tool substrates to investigate the nucleation density, adhesion and wear resistance. The diamond coatings are characterized by scanning electron microscopy and Raman spectroscopy. The graphitizing tendency due to cobalt in the tungsten carbide tools was found to be a limitation to improve adhesion of diamond films. The new tool substrates with nickel aluminide binder have been found to exhibit good adhesion and wear resistance. The implications of these results in advanced cutting tools are discussed.

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TiC/metal nacrous structures and their fracture toughness increase

C.H. Liu, W-Z. Li, H-D. Li

(Tsinghua University)

Multilayers of TiC and a series of metals have been fabricated by ion beam sputtering deposition to simulate nacre. The individual layer thickness varies from 1 to 10 nm, and the total thickness of the multilayers is about 1 micron. TEM, LXRD and HREM show their periodicity and lattice images. A particular method is devised to evaluate the relative toughness of this artificial pearlite. It is shown that the toughness of these nanocomposite materials can be tremendously improved. A maximum of toughness appears at certain modulation. Metals with high plasticity such as Al and Cu can produce particularly spectacular effects upon increasing the toughness of these multilayers.

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Influence of in-process copper incorporation on the quality of diamond-like carbon films deposited by pulsed laser deposition technique

S.J. Dikshit*, P. Lele*, S.B. Ogale*, S.T. Kshirsagar+

*(*University of Poona, +National Chemical Laboratory)*

Copper incorporated carbon films have been prepared on Si(100) and corning(7059) glass substrates by pulsed excimer laser deposition technique using KrF radiation (λ = 248 nm). Cold pressed composite pellets, having compositions from 2 at.% to 11 at.% copper in carbon, were used as targets for ablation. Good quality scratch proof films were obtained at laser energy density of 2–3 J/cm^2 and a substrate temperature of 50°C. The films were characterized by x-ray diffraction (XRD), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), UV-visible spectrometry, ellipsometry and four point probe resistivity measurements. Under similar deposition conditions, films obtained from composite targets of lower copper concentration are seen to have better diamond-like character as compared to those obtained from a pure graphite target. At such low concentrations, copper is seen to cluster in the form of nanoparticles. As the copper concentration increases in the films, they tend to acquire disordered graphitic network with degraded DLC characteristics and the size of copper agglomerates increases from about 5 nm (for 2 at.% case) to 85 nm (for 11 at.% case). It is seen that increase in the copper content leads to modifications in the carbon network, additional interband transitions, and reduction of the band gap.

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X-ray absorption near edge structures in cobalt oxides

T. Jiang, D.E. Ellis

(Northwestern University)

Theoretical studies have been made of K-edge x-ray absorption near edge structure (XANES) of Co in CoO, Co(OH)$_2$, CoTiO$_3$, Co$_3$O$_4$ and CoAl$_2$O$_4$. Correlations of experimental near edge features with site symmetry, local geometry, local electronic structure, i.e., atomic configuration, charge transfer, and backscattering from neighboring atomic potentials are interpreted. The self-consistent discrete variational X$_\alpha$ method (DV-X$_\alpha$) within an embedded cluster technique has been used to generate the crystal potential. A multiple scattering (MS) approach is then used to solve for the final state wave function. The ground state DV wave functions are analyzed in terms of the projected density of states, whereas the final state MS continuum wave functions are analyzed through the concept of photoelectron trapping time.

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Microstructure, electrical properties, and thermal stability of Al ohmic contacts to n-GaN

L.L. Smith*, R.F. Davis*, M.J. Kim+, R.W. Carpenter+, Y. Huang#

*(*North Carolina State University, +Arizona State University, #Argonne National Laboratory)*

As-deposited Al contacts were ohmic with a room-temperature contact resistivity of 8.6 x 10^{-5} $\Omega \cdot$cm^2 on Ge-doped, highly n-type GaN (n = 5x10^{19} cm^{-3}). They remained thermally stable to at least 500°C, under flowing N$_2$ at atmospheric pressure. The specific contact resistivities (ρ_c) calculated from TLM measurements on as-deposited Al layers were found to range from 8.6x10^{-5} $\Omega \cdot$cm^2 at room temperature and

6.2×10^{-5} $\Omega \cdot cm^2$ at 500°C. Annealing treatments at 550°C and 650°C for 60 s each under flowing N_2 resulted in an overall increase of contact resistivity. Cross-sectional, high-resolution electron microscopy (HREM) revealed that interfacial secondary phase formation occurred during high-temperature treatments, and coincided with the degradation of contact performance. Electron diffraction patterns from the particles revealed a cubic structure with lattice constant a = 0.784 nm, and faceting occurring on the {100} faces. Spectroscopic analysis via EELS revealed the presence of nitrogen and small amounts of oxygen in the Al layer, but no appreciable amounts of Ga. The results of microstructural and crystallographic characterization indicate that the new interfacial phase is a type of spinel Al nitride or Al oxynitride.

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Characteristics of conductive SrRuO₃ thin films with different microstructures

Q.X. Jia, F. Chu, C.D. Adams, X.D. Wu, M. Hawley, J.H. Cho, A.T. Findikoglu, S.R. Foltyn, J.L. Smith, T.E. Mitchell
(Los Alamos National Laboratory)

Conductive $SrRuO_3$ thin films were epitaxially grown on (100) $LaAlO_3$ substrates by pulsed laser deposition over a temperature range from 650°C to 825°C. Well-textured films exhibiting a strong orientation relationship to the underlying substrate could be obtained at a deposition temperature as low as 450°C. The degree of crystallinity of the films improved with increasing deposition temperature as confirmed by x-ray diffraction, transmission electron microscopy, and scanning tunneling microscopy. Scanning electron microscopy revealed no particulates on the film surface. The resistivity of the $SrRuO_3$ thin films was found to be a strong function of the crystallinity of the film and hence the substrate temperature during film deposition. A residual resistivity ratio (RRR = $\rho_{300K}/\rho_{4.2K}$) of more than 8 was obtained for the $SrRuO_3$ thin films deposited under optimized processing conditions.

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Spectroscopic characterization of annealed Si₁₋ₓCₓ films synthesized by ion implantation

G. Compagnini*, L. Calcagno*, G. Foti*, G. Baratta+
*(*Corso Italia, +Osservatorio Astrofisico-Citta' Universitaria)*

Amorphous hydrogenated silicon carbon alloys were synthesized by C_2H_2 ions implantation in a silicon substrate at different fluences to obtain samples with different carbon atomic concentrations (10–50 at.%). As implanted and subsequently annealed samples were investigated by using Rutherford backscattering, infrared and Raman spectroscopies were used in order to follow the crystallization process. It was found that crystallization of stoichiometric SiC phase starts at 1000°C both in low and high containing carbon films, while at the stoichiometric composition silicon (or carbon) was found to clusterize into homonuclear islands even at lower temperatures. The analysis of the fundamental absorption edge reveals the presence of an optical energy gap of about 1.3 eV independently on the film composition in the as implanted samples, while after thermal process at 1000°C it increases to 2.2 eV for a carbon concentration below 0.5 and up to 1.8 eV for all those samples with a carbon excess.

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Formation of SrBi₂Ta₂O₉: Part I. Synthesis and characterization of a novel "sol-gel" solution for production of ferroelectric SrBi₂Ta₂O₉ thin films

T.J. Boyle*, C.D. Buchheit*, M.A. Rodriguez*, H.N. Al-Shareef*, B.A. Hernandez*, B. Scott+, J.W. Ziller#
*(*Sandia National Laboratories, +Los Alamos National Laboratories, #University of California-Irvine)*

We have developed a simple and rapid method for the synthesis of a precursor solution used in the production of SBT powders and thin films of the layered perovskite phase $SrBi_2Ta_2O_9$ (SBT). Precursor solution preparation takes less than 30 minutes and involves the generation of two solutions: (a) $Bi(O_2CMe)_3$ dissolved in pyridine, and (b) $Ta(OCH_2Me)_5$ added to $Sr(O_2CMe)_2$ and then solubilized by HO_2CMe. After stirring separately for 10 minutes, these solutions are combined, stirred for an additional 10 minutes, and used without any further modifications. The individual solutions and ternary mixture were studied using a variety of analytical techniques. Films of the layered perovskite phase were formed at temperatures as low as 700°C. Ferroelectric testing of SBT films, fired at 750°C, reveals standard hysteresis loops with no fatigue for up to 4×10^9 cycles.

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Formation of SrBi₂Ta₂O₉: Part II. Evidence of a bismuth-deficient pyrochlore phase

M.A. Rodriguez, T.J. Boyle, B.A. Hernandez, C.D. Buchheit, M.O. Eatough
(Sandia National Laboratories)

A bismuth-deficient pyrochlore phase has been observed in both powder and film samples fired at 775°C. The estimated stoichiometry of this pyrochlore (based on calculated diffraction patterns) was $Sr_{0.2}(Sr_{0.5}Bi_{0.7})Ta_2O_{6.75}$. This bismuth-deficient pyrochlore phase may be considered deleterious to the formation of the $SrBi_2Ta_2O_9$ "SBT" ferroelectric compound since a significant presence of this pyrochlore compound implies a large deviation from the desired cation ratios. Additionally, films prepared on platinized silicon substrates indicate the SBT phase formation may be encouraged by the substrate; there appears to be some 00*l* preferential orientation for stoichiometric SBT thin films.

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Structural and dielectric properties of Bi₂NbₓV₁₋ₓO₅.₅ ceramics

K.B.R. Varma, K.V.R. Prasad
(Indian Institute of Science)

$Bi_2V_{1-x}Nb_xO_{5.5}$ ceramics with x ranging from 0.01 to 0.5 have been prepared. The crystal system transforms from an orthorhombic to tetragonal at $x \geq 0.1$ and it persists until $x = 0.5$. Scanning electron microscopic (SEM) investigations carried out on thermally etched $Bi_2Nb_xV_{1-x}O_{5.5}$ ceramics confirm that the grain size decreases markedly (18 μm to 4 μm) with increasing x. The shift in the the Curie temperature (725 K) towards lower temperatures, with increasing x, is established by differential scanning calorimetry (DSC). The dielectric constants as well as the loss tangent (tan δ) decrease with increasing x at room temperature.

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Domain structure-property relations in lead lanthanum zirconate titanate

M.A. Akbas, I.M. Reaney, W.E. Lee
(The University of Sheffield)

The domain structure and dielectric properties as a function of lanthanum concentration and Zr/Ti ratio have been investigated in rhombohedral and tetragonal lead lanthanum zirconate titanate (PLZT) ceramics. Transmission electron microscopy revealed that, with increasing lanthanum concentration and Zr/Ti ratio, the long-range-ordered domains (macrodomains) reduced in width, initially being fine scale (20 nm) striations but eventually forming a "mottled" contrast (5 nm), characteristic of a relaxor. Relative permittivity measurements as a function of temperature revealed a correlation between broadening of the dielectric maxima and the onset of relaxor-type behavior with the appearance of the striations and mottled (relaxor) contrast, respectively.

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Affect of A-site vacancy order-disorder states on diffuse phase transition of the morphotropic phase boundary of $Pb_{1-x}Ba_xNb_2O_6$ ferroelectrics

X. Xiao, Y. Xu, Z. Zeng, Z. Gui, L. Li, X. Zhang
(Tsinghua University)

Affect of A-site vacancy order-disorder states on diffuse phase transition (DPT) of tungsten bronze $Pb_{1-x}Ba_xNb_2O_6$ (PBN) ferroelectrics has been investigated. The A-site vacancy disordered PBN ceramics exhibit remarkable variations of the Curie temperatures (i.e., the temperatures at the dielectric maximum permittivities) up to 12°C in response to frequency changed from 0.1 KHz to 100 KHz. The largest frequency dispersion occurred at the morphotropic phase boundary of $1-x = 0.63$, accompanying with the lowest Curie point. In contrast, the A-site vacancy ordered PBN ceramics present little frequency dispersion in the range of 2°C from 0.1 KHz to 100 KHz. Dielectric constants of the disordered PBN ceramics were generally higher than those of the ordered ones. Compared with the ordered PBN ceramics, the Curie points of the disordered ceramics were shifted from lower to higher temperature sides as the Pb^{2+} cation percentage was decreased, i.e., the Curie temperatures of the disordered PBN ceramics were lower than those of the ordered ones when $1-x \geq 0.70$, but higher when $1-x \leq 0.65$. These differences are suggested to be inherently resulted from the A-site vacancy order-disorder states. The relationship between the A-site vacancy order-disorder states and the dielectric properties has also been confirmed with the studies of thermal hysteresis.

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Microstructure and 90° domain assemblages of $Pb(Zr,Ti)O_3$ // RuO_2 capacitors as a function of Zr to Ti stoichiometry

B.A. Tuttle, T.J. Headley, H.N. Al-Shareef, J.A. Voigt, M. Rodriguez, J. Michael, W.L. Warren
(Sandia National Laboratories)

Planar microstructure, 90° domain configurations and cross-sectional perovskite grain morphology were characterized for a series of $Pb(Zr,Ti)O_3$ // RuO_2 thin film capacitors. Perovskite grain size increased substantially with increasing Zr concentration of the $Pb(Zr,Ti)O_3$ (PZT) films, being on the order of 0.15 μm for PZT 20/80 films and 2.5 μm for PZT 50/50 films. While PZT 20/80 and PZT 30/70 films were single phase perovskite, the PZT 40/60 and 50/50 films contained a second phase with fluorite structure. The second phase matrix consisted of two nanophases, one having fluorite structure while the other was amorphous. Both the amorphous nanophase and the fluorite nanophase were Pb deficient compared to the perovskite phase. Differences in cross-sectional perovskite grain morphology were substantial for these materials, with the PZT 40/60 film being almost entirely columnar and the PZT 20/80 film exhibiting almost entirely granular morphology. Differences in 90° domain wall density were essentially negligible among the films, suggesting that if 90° domains were responsible for the differences in electrical properties, it is not due to 90° domain population.

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Synthesis of yttria-stabilized zirconia nanoparticles by decomposition of metal nitrates coated on carbon powder

S. Jiang, G.C. Stangle, V.R.W. Amarakoon, W.A. Schulze
(New York State College of Ceramics at Alfred University)

Weakly agglomerated nanoparticles of yttria-stabilized zirconia (YSZ) were synthesized by a novel process which involved the decomposition of metal nitrates that had been coated on ultrafine carbon black powder, after which the carbon black was gasified. The use of ultrafine, high-surface-area carbon black powder apparently allowed the nanocrystalline oxide particles to form and remain separate from each other, after which the carbon black was gasified at a somewhat higher temperature. As a result, the degree of agglomeration was shown to be relatively low. The average crystallite size and the specific surface area of the as-synthesized YSZ nanoparticles were 5~6 nm and 130 m^2/g, respectively, for powder synthesized at 650°C. The as-synthesized YSZ nanoparticles had a light brown color and were translucent, which differs distinctly from conventional YSZ particles which are typically white and opaque. The mechanism of the synthesis process was investigated, and indicated that the gasification temperature had a direct effect on the crystallite size of the as synthesized YSZ nanoparticles. High-density and ultrafine-grained YSZ ceramic articles were prepared by fast-firing, using a dwell temperature of 1250°C and a dwell time of two minutes or less.

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Influence of microstructure on indentation and machining of dental glass-ceramics

H.H.K. Xu, D.T. Smith, S. Jahanmir
(National Institute of Standards and Technology)

The influence of microstructure on the abrasive machining and indentation response for a series of dental glass ceramics was characterized. The experimental materials prepared for this study contained crystalline mica platelets that ranged in diameter from about 1 μm to 15 μm, while the volume fraction of mica remained essentially constant. Damage formation and material removal behavior were studied as a function of mica platelet size using Vickers indentation, Berkovich instrumented indentation, and abrasive machining. In the instrumented indentation experiments, the energy absorbed in indentation decreased with increasing platelet size when indentations of equal penetration depth are made in each material. To characterize the grinding response, the normal and tangential forces for each material were measured as a function of the depth of cut in surface grinding. The grinding forces and the specific grinding energy at fixed depths of cut decreased with increasing the mica platelet size following the same trend observed in the fixed displacement indentation tests. Since the same microfracture process was observed to occur in both indentation and grinding, the absorbed indentation energy is proposed as a quantity for predicting the machining response of these glass-ceramics.

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Microstructure development in furfuryl alcohol-derived microporous glassy carbons

K.P. Constant, J-R. Lee, Y-M. Chiang
(Massachusetts Institute of Technology)

The processing of microporous glassy carbon derived from furfuryl alcohol and ethylene glycol mixtures has been studied, with emphasis on understanding and controlling microstructure development. It is shown that this system exhibits a polymerization-dependent miscibility gap, and that the carbon microstructure is determined by phase separation in the liquid state. Variations in carbon microstructure with composition and thermal history can be understood in terms of the time dependent immiscibility and resulting phase separation.

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Reactive-infiltration processing of SiC-metal and SiC-intermetallic composites

L. Hozer, Y-M. Chiang
(Massachusetts Institute of Technology)

Liquid-phase reactive infiltration is a rapid and net-shape method of synthesizing silicon carbide composites. We use reactive infiltration of carbon with Si-Al and Si-Cu melts to prepare composites consisting of interpenetrating networks of β-SiC and a secondary phase

assemblage containing ductile metal (Al-Si) or a metal silicide (Si-Cu). The mechanisms of phase formation have been characterized. It is shown that a rapid initial reaction upon infiltration forms a largely stationary SiC network, within which the secondary phase constitution evolves due to solute rejection and liquid phase diffusion processes. Both homogeneous composites and those with controlled composition gradients have been synthesized.

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An elastic-plastic indentation model and its solutions

W. Yu, J.P. Blanchard
(The University of Wisconsin at Madison)

An analytical model of hardness has been developed. Four major indentation tests, namely indentation by cones, wedges, spheres, and flat-ended, axisymmetric cylinders have been analyzed based on the model. Analytical relationships between hardness, yield stress, elastic modulus, Poisson's ratio and indenter geometries have been found. These results enable hardness to be calculated in terms of uniaxial material properties and indenter geometries for a wide variety of elastic and plastic materials. These relationships can also be used for evaluating other mechanical properties through hardness measurements and for converting hardness from one type of hardness test into those of a different test. Comparison with experimental data and numerical calculations is excellent.

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Maximum heating rates for producing undistorted glassy carbon ware determined by wedge shaped samples

H. Maleki*, L.R. Holland*, G.M. Jenkins*, R.L. Zimmerman*, W. Porter+
*(*Alabama Agricultural and Mechanical University, +Oak Ridge National Laboratory)*

Polymeric carbon artifacts are particularly difficult to make in thick section. Heating rate, temperature and sample thickness determine the outcome of carbonization of resin leading to a glassy polymeric carbon ware. Using wedge shaped samples, we found the maximum thickness for various heating rates during gelling (300 K–360 K), curing (360 K–400 K), postcuring (400 K–500 K), and precarbonization (500 K–875 K). Excessive heating rate causes failure. In postcuring the critical heating rate varies inversely as the fifth power of thickness; in precarbonization this varies inversely as the third power of thickness. From thermogravimetric evidence we attribute such failure to low rates of diffusion of gaseous products of reactions occurring within the solid during pyrolysis. Mass spectrometry shows the main gaseous product is water vapor; some carboniferous gases are also evolved during precarbonization. We discuss a diffusion model applicable to any heat treatment process in which volatile products are removed from solid bodies.

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Crystallization behavior of $Li_{1-5x}Ta_{1+x}O_3$ glasses synthesized from liquid precursors

J.A. Allemann*, Y. Xia*, R.E. Morriss*, A.P. Wilkinson*, H. Eckert*, J.S. Speck*, C.G. Levi*, F.F. Lange*, S. Anderson+
*(*University of California-Santa Barbara, +Westmont College)*

The crystallization of amorphous oxides synthesized by pyrolytic decomposition of mixed Li and Ta 2-ethylhexanoates and alkoxides has been investigated. The study was motivated by thermodynamic considerations that, in the light of experience in other systems, suggest the potential for metastable extension of the $LiTaO_3$ homogeneity range. Materials investigated are described by the general stoichiometry $Li_{1-5x}Ta_{1+x}O_3$ and include Li_2O contents from 0 to 70 mol% ($-0.18 \leq x \leq 0.2$). The samples were prepyrolyzed at 400°C and subsequently crystallized by heat treatments in air at 550–700°C for 0.1–100 h. The first product of crystallization for compositions from 30 to 65%Li_2O is always the $LiTaO_3$ phase. Extensive characterization by x-ray and neutron diffraction, as well as ^7Li-NMR spectroscopy, revealed that this phase evolves with a structure and stoichiometry close to equilibrium. For Li^+-deficient compositions, excess Ta^{5+} is rejected to the amorphous constituent during crystallization and eventually gives rise to the evolution of Ta_2O_5, with the $LiTa_3O_8$ phase suppressed in all cases. Similar observations were made for the Li^+-rich compositions, but the evolving second phase is the equilibrium Li_3TaO_4. The absence of solubility extension in $LiTaO_3$, which appears feasible from a thermodynamic viewpoint, is ascribed to the large differences in mobilities of the Li and Ta species in the parent amorphous oxide resulting from pyrolysis.

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Precipitation of bcc nanocrystals in bulk Mg-Cu-Y amorphous alloys

W. Liu, W.L. Johnson
(California Institute of Technology)

Coexistent amorphous and nanoscale bcc-Mg_7Li_3 phases were found in slowly quenched alloys of the $Mg_{65-x}Li_xCu_{25}Y_{10}$ system containing 3 to 15 at.% Li. The crystallization behavior of these alloys has been studied. The grain size of the nanocrystalline bcc phase which is formed ranges from 2 to 20 nm. The volume fraction of nanocrystalline phase as well as the grain size of the nanocrystals increase as the Li composition increases. Transmission electron microscopy studies suggest that the alloy exhibits phase separation in the undercooled liquid state and that the nucleation and growth of the bcc-nanocrystals is related to the phase separation. Some characteristic thermal properties of the glassy phase are presented and the composition dependence of Tg and Tx are discussed. It is concluded that the addition of a small amount of Li is essential for the production of a bcc nanocrystalline phase in Mg-Li-Cu-Y system.

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