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HYDROTHERMAL SYNTHESIS OF KNN-BASED PIEZOELECTRIC CERAMIC POWDERS

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The phase evolution of pure KNN powders during hydrothermal reaction was systematically studied by investigating the effect of KOH:NaOH molar ratio of the starting alkaline solution, reaction time, and reaction temperature on the phase, chemical composition, and morphology of synthesized particles. As the starting KOH:NaOH molar ratio was changed from 8.0:2.0 to 7.0:3.0, the phase of KNN particles synthesized by the hydrothermal reaction at 220 °C for 24 h was changed from K-rich KNN single phase to Na-rich KNN single phase, via two-phase mixtures consisting of both phases. In the cases of the starting KOH:NaOH molar ratio of between 7.0:3.0 and 7.6:2.4, K-rich KNN crystals firstly nucleated and grew during the hydrothermal reaction at 220 °C. As the reaction time increased, K-rich KNN particles became unstable and started to dissolve, and simultaneously, the stable Na-rich KNN particles started to precipitate. Therefore, the morphology of KNN crystals and their chemical composition were found to be dependent on the progress of the dissolution-precipitation process.

Keywords: Hydrothermal synthesis, KNN piezoceramics, Powder, Morphology of crystals

ELECTRIC PROPERTIES OF $BiFeO_3$-MODIFIED $Bi_4Ti_3O_{12}$ CERAMICS

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The aim of the present research was to fabricate bismuth layer structured ferroelectrics (BLSF) known also as the Aurivillius phases, and to study their electric properties. If modified appropriately, BLSFs may exhibit novel physical properties which enrich their functionality. The present study was focused on ceramics of the $Bi_4Ti_3O_{12}$-$BiFeO_3$ (BTO-BFO) system.

The general formula of BTO-BFO compounds is $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$. These compounds have layered perovskite-like structures, in which fluorite-like bismuth-oxygen layers of composition $\{(Bi_2O_2)^{2+}\}_\infty$ alternate with (001) perovskite-like slabs of composition $\{(Bi_{m-1}Fe_{m-3}Ti_3O_{3m+1})^{2-}\}_\infty$. The values of m indicates the number of perovskite-like layers per labs, and may take integer or fractional values.

The mixed oxide method was employed for fabrication of $Bi_9Fe_5Ti_3O_{27}$ ceramics (m = 8) from simple oxide powders Bi_2O_3, TiO_2 and Fe_2O_3. Stoichiometric mixtures of the powders were thermally analyzed with a Netzsch STA-409 system, so parameters of thermal treatment were determined. Pressureless sintering was used for final densification of the ceramic samples. It was found by the X-ray diffraction method that the compound crystallized in a tetragonal symmetry with the following parameters of the elementary cell: $a = b$ = 6.122(8) Å and c = 67.843(1) Å. Broadband dielectric spectroscopy was utilized to characterize the ac response within the temperature range ΔT = 130-600 K and the frequency range from nearly DC up to 10 MHz. Room-temperature Mössbauer spectra of $Bi_9Ti_3Fe_5O_{27}$ ceramics made it possible to determine the hyperfine structure of the BFTO compound.

The present research was supported by University of Silesia in Katowice, Poland from the funds for science – research potential (NO 1S-0800-001-1-05-01).

Keywords: BLSF, Aurivillius phase, $Bi_4Ti_3O_{12}$, Electrical properties, Perovskite

CURRENT STATUS AND FUTURE PROSPECTS OF HIGH PERFORMANCE PIEZOELECTRIC SINGLE CRYSTALS: "LEAD-BASED" AND "LEAD-FREE"

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Recently (Ba,Ca)(Zr,Ti) [BCZT] and (Ba,Ca)(Sn,Ti) [BCST] ceramics have been reported to offer high piezoelectric coefficients (d_{33} > 600 pC/N) which are comparable to those of PZT ceramics and are much higher than those of presently existing lead-free systems such as KNN and NBT-BT [1]. And the high values of piezoelectric coefficients are also known to be attributed to the presence of phase co-existence of rhombohedral and tetragonal phases at room temperature.

Most of the previous studies about the BCZT solid solutions are on the polycrystalline ceramics. In contrast to polycrystalline ceramics, single crystals have better piezoelectric properties as well as are considered as standard materials to certain the structure-property relations. However, so far only a few attempts to grow single crystals of BCZT were reported [2].

In this presentation the effort on developing BCZT single crystals with high piezoelectric constants (d_{33} > 600 pC/N) as well as electromechanical coupling coefficient (k_{33} > 0.85) is introduced. The solid-state single crystal growth (SSCG) technique is applied for fabrication of BCZT single crystals. Their dielectric and piezoelectric properties, the temperature dependence of their piezoelectric/electromechanical properties, and their ferroelectric fatigue effect are characterized and compared with those of BCZT polycrystalline ceramics.

Keywords: Piezoelectric single crystals, BCZT, BCST, Dielectric properties, Piezoelectric properties

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HYBRID NANO-TiC/ZrO_2-ALUMINA COMPOSITES – MODELING OF RESIDUAL THERMAL STRESSES AND MANUFACTURE PRACTICE

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A detailed investigation and analysis of the usability of hybrid nano-TiC/ZrO_2 particles for the development of alumina matrix particulate composites of improved hardness and wear resistance were performed, focusing the study on modeling thermal mismatch stresses, producing first composite materials and determining their properties. Hybrid nano-TiC/ZrO_2 particles were composed of nano-TiC inclusions embedded in polycrystalline zirconia s.s. microparticles. Hybrid, multiphase particles are not commercially produced, and are a non-explored class of reinforcing inclusions for ceramic and metal matrix composites. The finite element method was used for modeling. The composites were produced by using mixtures of a commercially available α-alumina nano-powder and hybrid nano-TiC/ZrO_2 one which was laboratory manufactured by the *in-situ* method. The method takes advantage of the reaction between TiO_2 dissolved in a zirconia solid solution and carbon which comes from an external source. The mixtures were high temperature consolidated for 7 min at 1400 °C under 35 MPa in argon by SPS. The powders were characterized with respect to the phase composition, crystallite sizes and particle size distributions. A state of densification, microstructural features, hardness, fracture toughness and wear resistance were determined for the composites.

FEM simulations showed fine effects of hybrid nano-TiC/ZrO_2 inclusions on residual thermal stresses in alumina and tetragonal zirconia grains of ZTA composites, and more significant effects were predicted for TiC particles of hybrid nano -TiC/ZrO_2 polycrystalline areas. It is suggested that the detected effects can affect both the transformability of tetragonal zirconia polymorph and the crack propagation. A difficulty to save the microstructure of hybrid nano-TiC/ZrO_2 particles during high temperature consolidation has been stated and attributed to grain growth and chemical instability of TiC particles.

The work was financially supported by the statutory means of AGH WIMiC nr 11.11.160.617 in 2015.

Keywords: Hybrid particle, Al_2O_3, ZrO_2, Thermal stresses, FEM simulation

UBIQUITOUS MAGNETO-MECHANO-ELECTRIC GENERATOR

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Magnetoelectric (ME) composites exploit the product property of magnetostriction and piezoelectricity. The ME effect is the result of multiple energy transduction starting from magnetic energy to mechanical energy and finally to electrical energy, i.e. magneto-mechano-electric (MME) transduction.

In this presentation we report the energy harvesting performance of self-biased ME laminate composite with anisotropic piezoelectric single crystal fiber composites (SFC) and magnetostrictive Ni plate. The flexibility of SFC represents high compliance of the sample and it is ideal for achieving low resonance frequency in cantilever structure. Flexibility also imparts durability and ability to apply increased strain magnitudes. Ni can be easily self-biased and generates linear strain response in low level magnetic field environment. ME properties and MME generator performance were evaluated under 60 Hz low level magnetic noise to clarify the performance metrics and illustrate the uniqueness of this architecture. In addition, we demonstrate the energy harvesting from the real power line for vacuum pump and 60 LEDs lighting under the weak magnetic field of 700 μT at 60 Hz. Furthermore, this MME harvester can operate wireless sensor networks (WSN) composed of TI-MSP430-CC2500 module.

Keywords: Magneto-mechano-electric generator, Magnetoelectric composite, Energy harvesting, Magnetoelectric properties, Ni plate

COMPOSITES IN THE ALUMINUM OXYNITRIDE – MeN (Me = Ti, Ta, Nb, Cr) SYSTEMS PREPARED FROM SHS-DERIVED POWDERS

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Aluminium oxynitride, γ-alon, is a spinel-type structure solid solution of Al_2O_3 and AlN. Due to its good mechanical and chemical properties γ-alon has a great potential of application in high-performance structural ceramics. Much attention has been focused on developing alon-based composites to improve its properties and performance. Additions of different types of hard ceramic phases such as Al_2O_3, AlN, SiC, ZrN, TiN and TiC have been investigated. Formation of such composites enhanced aluminium oxynitride hardness, flexural strength, toughness and especially wear resistance.

The aim of the present work is to show a new idea of producing CMC composed of aluminium oxynitride matrix and tantalum nitrides particle reinforcement. The precursor powders were formed in a single step process using the SHS synthesis. Starting powder mixtures were composed of aluminium oxide, aluminium, and titanium, tantalum niobium or chromium powders. Al_2O_3 and Al powders remained a ratio of 4:1, when adding other metals powder. The powder mixtures were subjected to self-propagating high-temperature synthesis (SHS) in nitrogen atmosphere under a pressure of 3 MPa. The SHS-derived powders were ground and hot-pressed for 1 h at 1750-1850 °C under 25 MPa. The dense samples were composed of γ-alon, small amount of aluminium nitride and respective nitrides: MeN and Me_2N. An increase of the nitri-

des content in the composites improved significantly their mechanical properties. The samples prepared from the powder, containing formally 30 mol% of the metals, showed Vicker's hardness over 16 GPa, fracture toughness about 7 MPa·$m^{0.5}$ and wear resistance three orders of magnitude larger than the dense corundum material.

This work was performed within statutory activities of Department of Ceramics and Refractory Materials, Faculty of Materials Science and Ceramics, AGH University of Science and Technology under the contract no. 11.11.160.617.

Keywords: Aluminium oxynitride, MeN, Me_2N, SHS, Mechanical properties,

IMPROVEMENT OF UNIFORMITY IN SiC-CVD PROCESS BY COMPUTATIONAL FLUID DYNAMICS

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Recently, there has been a fierce competition for market share in the global semiconductor market, and the studies on high integration of semiconductors and large diameter wafer has been carried out vigorously, which is focused on achievement of cost competitiveness. Despite the difficulty in manufacturing process, the jigs used in semiconductor devices are produced by coating graphite or RBSC (Reaction Bonded Silicon Carbide) with silicon carbide, which is carried out in order to remedy the shortcomings of the existing quartz and graphite products. In the process of deposition of silicon carbide (SiC), the reactions between raw gases containing Si and C sources occur from gas phase to solid phase, so that the merit of CVD technology is that it can provide high purity SiC in relatively low temperature in comparison with other sintering methods. The thermodynamic interpretation of the SiC-CVD processes in CH_3SiCl_3-H_2 systems has been recently suggested with the pressure, the composition of H/Si and the temperature as variables. In this study, not only the experimental verification of thermodynamic prediction but also computational fluid dynamic simulations on the CVD process were carried out in order to increase the computational fluid dynamic uniformity of silicon carbide in CH_3SiCl_3-H_2 system.

Keywords: SiC-CVD process, CH_3SiCl_3-H_2, Computational fluid dynamic simulations, Thermodynamic prediction, SiC

NANOPOWDERS OF TiO_2 FOR GAS SENSORS

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An increasing interest in nanomaterials for gas sensing has its beginning in 1990s, when it was demonstrated that nanocrystalline SnO_2 reveals improved gas sensing performance. Since that time we can observe growing research in different nano-sized metal oxides, among others TiO_2, for gas detection. Titanium dioxide is a well-known and extensively examined gas sensing material. Resistive gas sensors based on TiO_2 emerged thanks to promising features such as: reversible and large changes in the electrical resistance along with the exceptional chemical stability of titania. The motivation for this study is to decrease the temperature of hydrogen detection, and to investigate the size effect with respect to gas sensing properties. Well-crystallized TiO_2 nanopowders with a specific surface area, ranging from about 37 m^2/g to 121 m^2/g, and of the anatase form in majority have been successfully synthesized from metal-organic precursor by means of flame spray synthesis (FSS). The positive influence of decreasing particle diameter manifests itself in an increase of electrical conductivity and sensor response while lowering operating temperature.

Project for Science (Ministry of Science and Higher Education no. 11.11.160.438) at the Faculty of Materials Science and Ceramics.

Keywords: TiO_2, Nanopowder, Hydrogen detection, Flame spray synthesis, Electrical properties

TRANSPARENT YTTRIUM OXIDE CERAMICS FOR APPLICATION IN OPTICAL ISOLATORS

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Due to the extremely rapid development in the field of optoelectronics and laser techniques, efforts are being made to design new materials which can be used to produce optical isolators for application in optical devices that transmit light only in one direction. Studies on optical isolators utilize the Faraday effect, in which the plane of light polarization undergoes rotation when light travels through a medium placed in a magnetic field. When choosing a material suitable for this purpose, the main criterion is a sufficiently high Verdet constant, i.e. the optical constant of a material, named after the French physicist Èmile Verdet.

The objective of the present study was to investigate the usefulness of transparent yttria sintered polycrystals as optical isolators. The examined materials included pure yttria and yttria doped with lanthanum and neodymium. Micropowders obtained by means of EDTA gel processes were used to produce sintered materials with a density close to the theoretical one and the composition of $La_{0.1}Nd_{0.1}Y_{1.8}O_3$ via 2 hrs of hot isostatic pressing (HIP) in argon at 1250°C. To obtain an unmodified yttria sample, a commercially available Y_2O_3 powder (4N, Metall Rare Earth Ltd.) was sintered for 2 hrs in argon at 1300°C under 30 MPa in a device designed by Astro Thermal Technology. A number of sintered materials with different microstructures and visible and infrared light transmittance were obtained.

Based on the spectrophotometric measurements of absorption and the Verdet constant, performed in a wavelength range of 500-1000 nm, the possibility of applying sintered Y_2O_3 as an optical isolator was demonstrated. Doping Y_2O_3 with lanthanum and neodymium is recommended in order to increase the value of the Verdet constant.

This work was done as part of the statutory activities of the Department of Physical Chemistry and Modeling, Faculty of Materials Science and Ceramics, AGH University of Science and Technology (contract No. 11.11.160.257).

Keywords: Y_2O_3, $La_{0.1}Nd_{0.1}Y_{1.8}O_3$,Transparent yttria, Optical properties, Optical isolator,

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FABRICATION OF TRANSPARENT $MgAl_2O_4$ SPINEL BY MICROFLUIDIZATION AND SINTER-HIP PROCESS

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In this study, a transparent magnesium aluminate ($MgAl_2O_4$) spinel prepared by homogeneous green compaction and sinter-HIP processes was investigated. The uniformity of the particle configuration in a green body could be improved by both the wet shaping via slip casting and a microfluidization process, which effectively disintegrates particle agglomerates in aqueous slurry by passing the material through a narrow channel with a high shear stress. The relation between the green body state and the sintering behaviour showed that the densification during pre-sintering was accelerated by reducing the mean pore size in the green body, which resulted in a finer microstructure. After post-HIP processing, the final grain size and the in-line transmittance was found to be significantly affected by the pre-sintered state. A high in-line transmittance (ILT = 79.3% at λ = 550 nm) was achieved in the specimen fabricated via microfluidization and slip casting. The effect of Ca addition on the sintering activity and in-line transmittance of $MgAl_2O_4$ will be discussed.

Keywords: Transparent $MgAl_2O_4$, HIP, Microfluidization, Microstructure, Optical properties

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SINTERING AND PROPERTIES OF MAX SINTERS PREPARED WITH POWDERS ACHIEVED BY SHS METHOD

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The presentation describes the processing of interesting novel group of advanced ceramics composed of ternary carbides and nitrides which have layered structures and are called MAX phases, H-phases or nanolaminates. Their layered structure is in a nanoscale with heterodesmic covalent chemical bonds, when compare to natural silicates, graphite or graphene. These compounds have a $M_{n+1}AX_n$ formula, where: M is early transition metal, A is an element of A groups (mostly IIIA or IVA) and X is carbon and/or nitrogen. They have the highly anisotropic and unique properties, laying between ceramics and metals, with high elastic modulus, low hardness and very high fracture toughness and energy. The unique electrical, magnetic and chemical properties, including superconductivity, are also reported and predicted. These make MAX phases ones of the most interesting and perspective novel materials.

The results of original works made by AGH UST research group on the preparation of different composites based on the MAX compounds such as Ti_3SiC_2, Ti_3AlC_2, Ti_2AlN and others are presented. The self-propagating high-temperature synthesis (SHS) was used for obtaining precursor powders. Next the powders were milled and sintered into fully dense polycrystals based on ceramic nanolaminates. The properties of MAXs and their application are discussed.

Keywords: MAX phase, Ti_3SiC_2, Ti_3AlC_2, Ti_2AlN, SHS, Ceramic nanolaminate