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### X-ray Diffraction Study of Thermal Properties of Titanium Oxide

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Temperature dependence of microstructure of titanium oxide, $TiO_2$, and the phase transition of anatase (**A**) to rutile (**R**) were studied by *in situ* X-ray powder diffraction and Raman spectroscopy, as well as by TEM and SAED techniques. The as-synthesized $TiO_2$ p.a. showed a gradual transition **A** → **R** during the temperature increase from ≈1200 K to ≈1570 K and during the temperature decrease to ≈600 K. High-energy ball-milling at room temperature induced a partial transition **A**→**R**. The transition continued during the temperature increase to ≈1370 K and during the temperature decrease, and is accompanied by sharpening of diffraction lines. Anisotropy of thermal expansion was noticed for both **A** and **R**. In the transition **A**→**R**, the nuclei of **R** are formed either throughout the **A** crystallites ( in case of as-synthesized $TiO_2$ p.a.) or mainly in the interior of the **A** crystallites ( in case of milled $TiO_2$ p.a.). These nuclei grow in number and size with a prolonged time of thermal agitation.

**Keywords: titanium oxide, phase transition, thermal expansion**

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### Influence of Grinding and Atmosphere on the Crystallization of $ZrO_2$ Gel

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The influence of the grinding and the surrounding atmosphere on the thermal decomposition of zirconia gel has been studied. The XRPD analysis of the products obtained by thermal decomposition of zirconia gel at 500ºC has shown that pure tetragonal phase is obtained if the gel decomposition is carried out under high vacuum or dry inert atmosphere. However, monoclinic zirconia results from the decomposition of the zirconia gel either under air or inert gas saturated with water vapor. A mechanism for the thermal decomposition of zirconia gel has been proposed from the study of the variation of the crystal size of the monoclinic and tetragonal zirconia phases formed as a function of the temperature and the surrounding atmosphere.

The thermal decomposition of the zirconia gel previously ground during two hours in a centrifugal mill leads to the formation of $ZrO_2$ with a percentage of tetragonal phase higher than 80% irrespective of the surrounding atmosphere. The stabilization of the tetragonal phase by grinding seems to be connected with the formation of tiny cubic or tetragonal zirconia crystals that cannot be observed by XRPD. The results obtained by DSC supports this conclusion. Thus, the crystallization enthalpy determined for the as prepared gel was equal to -128± 7 J/g, in good agreement with literature, while the crystallization enthalpy for the ground gel amounted only -12±2 J/g.

**Keywords: zirconia gel, crystallization mechanism, crystal size**

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### Magnetic Study of Intermetallic $Ce_{1-x}Tb_xMn_2Ge_2$ ($0 \le x \le 1$) Compounds

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In this study[a], the crystal structure and magnetic properties of $Ce_{1-x}Tb_xMn_2Ge_2$ ($0 \le x \le 1$) compounds have been investigated by means of x-ray powder diffractions and magnetization measurements. X-ray diffraction patterns at room temperature indicated that all compounds are single phase and crystallize in the $ThCr_2Si_2$ type structure with space group I4/mmm. With increasing $x$, lattice parameters and unit cell volume have decreased linearly, obeying the Vegard`s law. The magnetic properties of $Ce_{1-x}Tb_xMn_2Ge_2$ were investigated by means of field-cooled and zero-field-cooled magnetization measurements in the temperature range $5\ K \le T \le 600\ K$. In $CeMn_2Ge_2$[1] and $TbMn_2Ge_2$[2], the interlayer magnetic coupling in the Mn sublattice is, respectively, ferromagnetic and antiferromagnetic below about 350 K. At low temperatures, Tb sublattice orders and reconfigures the ordering in the Mn sublattice while Ce does not order at any temperature. In this study, we investigated the variations in the magnetic properties of $Ce_{1-x}Tb_xMn_2Ge_2$ as a function of rare earth concentration by examining the evolution of the features in the temperature dependence of the magnetization. The results are summarized in the magnetic phase diagram.

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**Keywords: magnetic transitions, layered magnetic structures, rare earth compounds**

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### Phase Transitions and Crystal Dynamics at Low Temperature of Alpha-U and $^4He$

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Uranium metal includes temperature dependent elastic constants with the occurrence of a charge-density wave (CDW). At $T_0 < 43$ K (lower limit of stability of the structure) a transition involving modes for which $\mathbf{q_{CDW}} = <q_x, q_y, q_z>$ occurs. Domains are formed in different parts of the crystal in relation with the lowering of symmetry. The electronic instability which causes Kohn anomaly also triggers the displacive (Peierls) transition. The band gap created at the Fermi surface geometry determines the wave vector of the Kohn anomaly and of the incommensurable distortion. Inelastic neutron scattering1) has confirmed the existence of a transition to the incommensurate low-temperature condensing soft mode with a modulation wave vector $\mathbf{q}_{min}$ = [0.497 (1), 0.13 (1), 0.21 (1)]. The helicoidally motion of $\mathbf{q_{CDW}}$ (43 → 20 K) to the clock-side around $\mathbf{a}^*$(measured by Laue elastic diffraction) has been observed in continuity of the variation of $\mathbf{q}_{min}$ (65 → 44 K) (recently measured inelastic scattering with three–axis spectroscopy) and $\mathbf{q}_{min} \cong \mathbf{q_{CDW}}$ at $T_0 = 43$ K.

In situ phase transition from solid α (hcp) –to– solid γ (bcc) occurring in pure $^4He$ has been investigated in (P, T) plane at 27.5 bar, 1.65 K, by neutron three–axis spectrometer and Laue diffraction. Dynamic solid – solid transformation2) of mosaic crystal grains were clearly observed with the two techniques continuously followed in time and observed as motion of macroscopic small angle grain boundaries of quantum crystal.

[1] Marmeggi J.- Cl., et al., *J. Phys. Soc. Jpn*, 2001, A**70**, 22-24 [2] Pelleg O., et al., *submitted for publication.*

**Keywords: phase, transitions, in solids**

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### Phase Transition of $C_2H_5NH_2CH_2CH_2NH_3Zr[N(CH_2COO)_3]_2 \cdot 4\ H_2O$

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In the course of our investigations on zirconium-nitrilotriacetates of alkyldiamines we found in the title compound, 2-ethylammonium-ethylammonium-zirconium bis(nitrilotriacetato)-tetrahydrate, anomalous thermal and elastic properties between 288 und 293 K. Above 293 K, this species exhibits space group $P2_1/n$ with lattice parameters $a_1$ = 10.534(2), $a_2$ = 11.683(2), $a_3$ = 20.407(4)Å, $\alpha_2$ = 93.33(3)°. When lowering the temperature from 293 K, a strong attenuation of certain ultrasonic resonances occurs reaching a maximum at 288.4 K. Below this temperature the attenuation of ultrasonic waves, in which the elastic constants $c_{11}$, $c_{22}$, $c_{12}$ and $c_{66}$ are involved, is drastically reduced. If the low temperature phase is heated to room temperature, the attenuation reaches a maximum at 291.5 K indicating a hysteresis. This hysteresis is confirmed in DSC measurements, where a transition enthalpy of 2 J/g is observed. In the low temperature phase, domains with several mm thickness parallel to (001) are formed. In the direction [010] the angle of optical extinction of these domains deviates by about ± 6° from the extinction in the high temperature phase. Both phases exhibit a topotactic structural relation, which however, does not prevent the single crystalline state of the mother crystal to be maintained after the transition. The phase transition is considered to be of weakly first order.

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**Keywords: nitrilotriacetates, elasticity, phase transition**

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### Thermal Transformations of Some Alicyclic β-amino Acid Hydrates

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Alicyclic β-amino acids were recently used for the construction of two-dimensional hydrogen-bond grids that link molecules into bilayer structures [1]. While the crystallization of several β -amino acids yielded the expected bilayer type structures, others (*cis*-2-hydroxycyclohex-4-ene-1-carboxylic acid, all-*cis*-amino-4-hydroxy-cyclohexanecarboxylic acid, *trans*-2-aminocyclopentane-carboxylic acid and 3-*exo*-aminobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid) crystallized as hydrates and did not form the expected grid pattern. These hydrates were analysed by thermogravimety, differential scanning calorimetry, powder and single crystal X-ray diffraction in an attempt to prepare and characterize their anhydrous crystal forms. The results show that each powder loses the hydrogen-bonded solvent before decomposition. The powder patterns of the solvent-free forms show similarity to those of the bilayer structures.

[1] Fábián L., Kálmán A., Argay Gy., Bernáth G., Gyarmati Zs. Cs., *Cryst. Growth Des.*, 2005, **5**, *in press*.

**Keywords: thermal analysis, hydrates, hydrogen bonding**

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### X-ray Diffraction Study on the Phase Transitions of Barium Titanate

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Structural phase transitions in as-grown single crystal of $BaTiO_3$ were studied by X-ray precession method in the temperature range between 420 K and 90 K. It was found that high temperature cubic phase, designated here as cubic I, is transformed into the room temperature phase (RTP at $T_1$=403 K), and further into the low temperature phase (LTP at $T_2$=278 K), in both of which closely related two structures coexist to form domains with a shape of multi-domain 'hybrid' structure. In RTP the coexisting structures are tetragonal I and monoclinic I and in the LTP tetragonal Ⅱ and monoclinic Ⅱ. On the other hand, the lowest temperature phase (below $T_3$=183 K) is in a single domain of a tetragonal Ⅲ form. These observations are in disagreement with the phase transition sequence, proposed by previous studies, cubic→tetragonal→orthorhombic→rhombohedral. The lattice constants of the tetragonal I form are $a_{\mathrm{TI}}$=0.4009(10) nm and $c_{\mathrm{TI}}$ =0.4048(10) nm, and those of the monoclinic I form are $a_{\mathrm{MI}}$=0.4059(10), $b_{\mathrm{MI}}$=0.4009(10), $c_{\mathrm{MI}}$=0.5700(10) nm and $\beta_{\mathrm{MI}}$=135.33(10)°at room temperature. Those of the tetragonal Ⅱ form are $a_{\mathrm{TII}}$=0.4027(10) and $c_{\mathrm{TII}}$=0.3996(10) nm, and those of the monoclinic Ⅱ form are $a_{\mathrm{MII}}$=0.3994(10), $b_{\mathrm{MII}}$=0.4027(10), $c_{\mathrm{MII}}$=0.5678(10) nm and $\beta_{\mathrm{MII}}$=134.77(10)°at 233 K. Evolution and crystallographic relationship of the four phases forming the multi-domain 'hybrid' structures are presented.

**Keywords: $BaTiO_3$, phase transitions, 'hybrid' structure**

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### X-ray and Neutron Scattering Study of *as-grown* $Pb(In_{1/2}Nb_{1/2})O_3$ Single Crystals

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Characters of static and dynamic structures of *as-grown* $Pb(In_{1/2}Nb_{1/2})O_3$ (PIN) at room temperature (RT) have been investigated by a complementary use of x-ray and neutron scatterings. The PIN crystal has different chemical ordering ($S_2$ = 0 ~ 1) in the arrangement of $In^{3+}$ and $Nb^{5+}$ on the B-site by a different thermal treatment.

The diffuse scatterings showing the relaxor state have been observed in the outer-layer of the crystals, while *h/4 k/4 0* reflections showing the long-range antiferroelectric (AFE) state in the inside [1,2]. Phonon dispersion of the as-grown PIN crystals has also been measured, which is the first time for the PIN series. We have measured two transverse optic modes (TO1 and TO2) at zone center and concluded that the major part of the as-grown crystal at RT is ferroelectric(FE). This is consistent with the dielectric measurement performed on the as-grown PIN crystal [3].

These results show that the degree of B-site order $S_2$ is widely distributed in the as-grown PIN crystal from $S_2$ = ~ 0 to ≥ 0.7. That is, the AFE grain locates in the FE matrix, while the outer-layer is Relaxor in the as-grown PIN.

[1] Nomura K., et al., *J. Phys. Soc. Jpn*., 1999, **68**, 39. [2] Nomura K., et al., *J. Phys. Soc. Jpn*., 1997, **66**, 1856. [3] Ohwa H., et al., *J. Phys. Soc. of Jpn*., 2000, **69**, 1533.

**Keywords: ferroelectric properties, neutron and X-ray scattering, phase transitions**

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### Phase Relationship of Two Polymorphs of a Diaminodicyanopyrazine Dye

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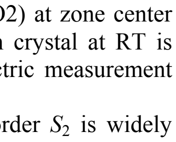

2,5-Diamino-3,6-dicyanopyrazine dyes are novel fluorescent dyes for opto-electronic applications [1]. These dyes have been found to have crystal polymorphs with different colours depending on the amino substituents. The colour difference is considered to be ascribed to the different molecular conformation among the polymorphs. In this study, the stability relationship of two polymorphs (red and yellow) of **1** were determined by melting data and correlated with their molecular and crystal structures.

The red phase was found to transform to the yellow phase at room temperature. DSC measurement showed that the yellow phase has a higher melting point than that of the red phase. The heat capacities were also determined by DSC measurement. These results suggest that the red phase and the yellow phase are a monotropic relationship. The phase relationship will be also discussed on the basis of their