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Nanohardness change of silicon and sapphire substrates by TiC/VC multilayers. Peter Paufler^a, Andre Belger^b, Marianne Reibold^c, ^aTU Dresden, FR Physik, Inst.f. Strukturphysik. ^bOn leave of^a. ^cTriebenberg Laboratory, TU Dresden.
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The nanohardness of multilayer specimens TiC/VC @Si und TiC/VC @Sapphire prepared by Pulsed-Laser-Deposition (Nd-YAG laser 355nm) has been investigated to check the existence of a supermodule effect similar to that reported by [1] with TiN/VN. The multilayer period thickness λ varied between 1.34nm and 24.8nm (total layer thickness ~200nm). Nanohardness H was improved, regardless of t , by covering Si as well as sapphire with the TiC/VC multilayer. The maximum value of H obtained was 38 GPa for TiC/VC @Sapphire. Individual hardness of the multilayer and the substrate could be separated by extrapolation the dependence on λ . The results are $H(\text{ML on Si}) = 32.9$ GPa, $H(\text{ML on sapphire}) = 41.5$ GPa, $H(\text{Si}) = 13$ GPa, $H(\text{sapphire}) = 30$ GPa. The multilayer on Si substrate carries 45% of the total load whereas the same layer on sapphire carries only 5%. The rest is due to the substrate. A maximum of H was observed for a multilayer thickness of $\lambda = 10$ nm for both substrates, i.e., a superlattice hardening effect has been detected. Young's modulus E_r , however, did not exhibit a pronounced maximum as function of λ . The beginning of plastic deformation during indentation manifested itself by pop-ins along the force-penetration curve. The critical load was higher for the pop-in registered with the multilayer on sapphire than for sapphire without layer. High-resolution transmission electron microscopy showed that the multilayers are nanostructured. Hardness obeys, as a function of λ , a Hall-Petch relation $H = 35.3 + 6.9 \lambda^{-0.5}$ (H in GPa und λ in nm). Obstacles for dislocation movement are boundaries between nanocrystalline particles, the size of which depends on the annealing history.

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Keywords: multilayers; nanohardness; nanostructure

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Transmission electron microscopy on stable and metastable Ge/Sb/Te phases. Tobias Rosenthal, Matthias Schneider, Oliver Oeckler Department of Chemistry, LMU Munich, Germany.
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Metastable crystalline phases are crucial in the read-erase cycle of GST (Ge/Sb/Te) phase-change materials (PCMs). Whereas they seemingly exhibit strongly disordered rocksalt-type structures, [1] the corresponding stable phases [2] are characterized by layer-like cation defect ordering. This involves the relaxation of Te atoms in a fashion that means the formation of van der Waals gaps rather than that of defect layers in an undistorted matrix. The thermodynamically stable layered phases can be gradually approached by annealing processes, especially if the rocksalt-type phase is stable at high temperatures and metastable states are accessible by quenching. The partially ordered phases thus obtained are

interesting model systems for PCMs but in addition exhibit remarkable thermoelectric properties.

The real structure of such metastable compounds $(\text{Sb}_2\text{Te}_3)_n(\text{GeTe})_m$ ($4 < n < 20$) has been investigated by electron diffraction and microscopy. HRTEM and STEM-HAADF clearly reveal both the extension, relative orientation and frequency of defect layers as well as the local relaxation of atoms near them. Whereas the Te atom positions of the rocksalt-type phase are approximately retained near the limits of defect layers and throughout defect layers that extend over just few unit cells of the basic structure, Te-Te contacts form whenever the cation defect layers extend over larger areas. The frequency of defect layers is determined by the stoichiometry. If the GeTe content is low, the structure contains numerous defect layers which are perpendicular to all $\langle 111 \rangle$ directions of the cubic basic structure, however, their 2D extension is very limited. This results in a parquet-like domain structure. If there are less defect layers, they tend to arrange in a parallel fashion that is similar to the block structures of the thermodynamically stable phases but involves blocks or irregularly varying thickness. At very high GeTe contents, the defect layers again lead to domain structures. In these cases, the cation defect layers (with van der Waals and partially covalent Te-Te bonding) can be viewed as boundaries between rhombohedrally distorted GeTe-like twin domains. These microstructures are due to the very long diffusion pathways that would be necessary to reach the stable superstructure with regularly spaced parallel van der Waals gaps. The influence of both the stoichiometry and the annealing-quenching process on the microstructure is very pronounced and can be tuned well. Its effect on thermoelectric properties will also be discussed.

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Resonant diffraction study of concentration gradients in multinary antimony tellurides. Matthias N. Schneider, Felix Fahrnbauer, Oliver Oeckler. Department of Chemistry, LMU Munich, Germany.
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In recent years, multinary antimony tellurides have gained interest as promising candidates for thermoelectrics and phase-change materials for data storage media. [1] Long-periodically ordered layered phases $(\text{MTe})_n(\text{Sb}_2\text{Te}_3)_m$, $(\text{Sb}_2\text{Te}_3)_m(\text{Sb}_2)_k$ and $(\text{MTe})_n(\text{Sb}_2\text{Te}_3)_m(\text{Sb}_2)_k$ ($M = \text{Ge}, \text{Sn}$) can be obtained by quenching and subsequent temperature treatment. They exhibit distorted rocksalt-type as well as A7-type building blocks as described for example for $9P\text{-GeSb}_4\text{Te}_4$ ($P-3m1$) or $51R\text{-Ge}_{2-x}\text{Sb}_{2+x}\text{Te}_5\text{Sb}_8$ ($x = 0.43$; $R-3m$). [2] $39R\text{-(Ge}_x\text{Sb}_{1-x})_2\text{Te}_3[(\text{GeTe})_y\text{Sb}_{1-2y}]_8$ ($x = 0.31$, $y = 0.033$; $R-3m$, $a = 4.266$, $c = 75.02$ Å) and $39R\text{-(Sn}_x\text{Sb}_{1-x})_2\text{Te}_3[(\text{SnTe})_y\text{Sb}_{1-2y}]_8$ ($x \approx 0.3$, $y \approx 0.03$; $R-3m$, $a = 4.292$, $c = 75.58$ Å), however, exhibit concentration modulations along the stacking direction, as shown by STEM-HAADF

investigations. Due to the similar electron count of Sn, Sb and Te, conventional X-ray diffraction does not allow to study the exact element distribution. We obtained high-resolution resonant scattering data at the Sn-, Sb- and Te-edges (29.20 keV, 30.49 keV, 31.81 keV) and at wavelengths far away of the edges which allow for a simultaneous refinement of mixed site occupancies with anisotropic displacement parameters. The enhanced scattering contrast clearly reveals the element distribution in long-periodically ordered structures. For 21R-SnSb₂Te₄, the structure of which has been controversially discussed, a joint refinement of all datasets ($R-3m$, $a = 4.292$, $c = 41.50$ Å, $R1 = 0.028$) including refined dispersion correction terms f' and f'' indicates no significant amounts of Sb-Te or Sn-Te anti-site defects, but mixed site occupancy of cation positions comparable to that in 21R-GeSb₂Te₄. [3] The optimized f' and f'' values were used for the determination of the concentration modulation of the elements in the much more complex 39R-type phases mentioned above. These show interdependent concentration modulations of the site occupancies of anion and cation positions accompanied by positional displacements. Thermoelectric properties of both phases can be correlated with the structural differences between the Ge and Sn containing materials.

Comparable structure-property relationships may be expected for crystalline phases of Ge-Sb-Te phase-change materials. Metastable GeTe-rich single crystals obtained by chemical transport exhibit a pseudocubic average structure with significant temperature-dependent changes of the diffuse intensities present. In situ temperature dependent single-crystal diffraction data obtained at the K-edges of Sb and Te promise further insight into the structural chemistry of this class of materials.

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SAXS INVESTIGATION OF THE SURFACE FRACTAL DIMENSION OF MnO₂ PYROLYTIC THIN FILMS. Skatkov^a, V.Gomozov^b. ^aPCB "Argo", 4/23 Shaul ha-Melekh Str., 84797 Beer Sheva, Israel ^bNTU "KhPI" 21 Frunze Str., 61002 Kharkov, Ukraine. E-mail: sf_lskatkov@bezeqint.net

MnO₂ films which have been prepared by the thermal deposition (pyrolysis) of Mn(NO₃)₂ are important semiconductor materials for application as semiconductor layer in metal (sintered Nb pellet) – dielectric (anodic Nb₂O₅)- semiconductor (MnO₂) MDS electrical capacitors.

Earlier reported significant influence of the fractal layer on electrical characteristics of MDS capacitors. This feature are responsible for the interest in investigating the fractal properties of this latter. The surface fractal dimension D have been investigated by small-angle X-ray scattering (SAXS). The theory of scattering by a porous solid was developed by Wong. The main formula of this theory is as follows:

$I(q) \sim \text{constant} \times q^{D-6}$ (1) Here $I(q)$ is the X-ray scattering intensity, q is the wave vector, and D is the surface fractal dimension. The scattered intensity vs wavevector relationship shows the fractal behaviour. Indeed, on the graph the coefficient of the slope of the curved part, which can be closely approximated by a line, is: $-\text{d} \ln I(q) / \text{d} \ln q = 2.87$

As report in [1] in case when $2 < \alpha < 3$, the scattering cause by the **whole volume** of subject and $D = \alpha = 2.87$. The obtained D value coincides with previously found value of surface fractal dimensionality in a sintered niobium powder pellet with high accuracy $D_{(Nb)} = 2.81$ (see formula (1) at $\alpha = 3.19$).

So far, authors are at loss and cannot say whether it is a mere coincidence or the result of some specific features of generation of the capacitor MDS structure. But it as should be noted in [2] in case when $2 < \alpha < 3$ scattering stipulate by the **surface** of sample.

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Structural, magnetic, electrical and magnetocaloric properties in Pr_{0.6}Sr_{0.4}MnO₃/BaTiO₃ composites. M. Triki^a, E. Dhahri^a, M.P.F. Graça^b, M.A. Valente^b.

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Composites with varying composition of ferromagnetic Pr_{0.6}Sr_{0.4}MnO₃ and ferroelectric BaTiO₃ have been prepared using a solid-state ceramic method (1-x)(Pr_{0.6}Sr_{0.4}MnO₃)/x(BaTiO₃), with x is the molar ratio and x = 0.0, 0.03, 0.05, 0.10 and 0.30 using conventional ceramic double sintering process. We report the structural, magnetic electrical and magnetocaloric properties of all samples. The presence of the two phases of Pr_{0.6}Sr_{0.4}MnO₃ (PSMO) and BaTiO₃ (BTO) was confirmed by X-ray diffraction (XRD) technique and the structural analysis. Magnetic measurements of magnetization versus temperature and applied field were performed. The temperature dependence of magnetization reveals that the composite samples show paramagnetic to ferromagnetic transition when the temperature decreases at the same Curie temperature as the parent PSMO compound ($T_c \approx 273$ K). The magnetic entropy change $|\Delta S_M|$ has been deduced from the

$M(H)$ data by the Maxwell relation. Close to T_c , large change in magnetic entropy has been observed in all samples. The maximum value of the magnetic entropy is $|\Delta S_M^{\max}|$ decreases

from 2.88 J.kg⁻¹.K⁻¹ for x = 0 to 1.86 J.kg⁻¹.K⁻¹ for x = 0.3 for an applied magnetic field of 2T. At this value of magnetic field the relative cooling power (RCP) decreases also from 63 J.kg⁻¹ for the parent sample to 38.3 J.kg⁻¹ for x = 0.3. The temperature dependence of the Landau coefficients have been deduced using the Landau expansion of the magnetic free energy, indicating the second order nature of the magnetic transition.

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