

MS14-05 Diffusion processes in $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)$ ($4?n?12$) crystals investigated by synchrotron radiation.

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Stable $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)$ ($3 < n < 12$) phases exhibit disordered rocksalt-type high temperature (HT) modifications with $1/(n+3)$ cation vacancies per anion [1]. At room temperature (RT), they form trigonal long-periodically ordered layered structures [2] with rocksalt-type slabs separated by van der Waals gaps. Quenching the cubic HT phases yields metastable pseudocubic domain structures [3]. The phase transitions involve cation diffusion, which was investigated by time and space resolved white-beam (Laue) diffraction at beamline BM32 (ESRF). The diffraction patterns of quenched crystals with $n = 6$ and 12 reveal a pseudocubic compound with asymmetrically broadened reflections interconnected by diffuse streaks along o^* _{cubic}. These indicate stacking disorder involving vacancy layers. Upon heating, superstructure reflections appear at moderate temperatures (250 – 300 °C), indicating a fourfold twin of a long-range ordered trigonal phase. At ~ 500 °C, the rocksalt-type HT phase with random vacancy distribution is formed. In contrast, crystals with $n > 15$ exhibit significant deviations from the cubic metrics at RT, but no pronounced diffuse scattering [4]. They resemble GeTe itself but form the cubic HT phase in a first order phase transition after a certain degree of vacancy ordering (formation of finite vacancy layers) has taken place at intermediate temperatures. The qualitative information from the diffuse intensity distribution of the Laue patterns was supplemented by precise monochromatic-beam data obtained at ID 11 (ESRF) at various temperatures (cf. Fig. 1). They allow one to derive the atomic structure of ordered domains as well as the stacking sequences in disordered ones, where the intensity distribution along diffuse streaks yields reliable information concerning the average defect layer spacing (which depends on the chemical composition), its variance and the structural distortion around the defect layers. For low n , the defect layers resemble the van der Waals gaps in the stable RT phases, whereas for high n the fcc Te atom arrangement remains little distorted.

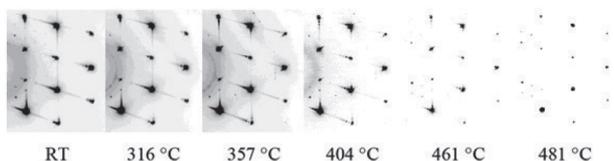


Fig. 1: rotation images ($\Delta\phi = 10^\circ$) of $(\text{GeTe})_{12}(\text{Sb}_2\text{Te}_3)$

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Keywords: in situ diffraction; diffuse scattering; phase transitions

MS15-01 Mullite-type dibismuth-nonaoxometallates-(III): The effects of strontium doping. Th. M. Gesing,^{a,b} M. Schowalter,^c C. Weidenthaler,^d M. M. Murshed,^a G. Nénert,^c C. B. Mendive,^f M. Curti,^f A. Rosenauer,^c H. Schneider,^{b,g} R. X. Fischer,^b ^aSolid state chemical crystallography, Inorganic Chemistry, University Bremen, Germany, ^bCrystallography, FB5 Geoscience, University Bremen, Germany, ^cSolid state physics, University Bremen, Germany, ^dMax-Planck-Institut für Kohlenforschung, Mülheim, Germany, ^eInstitut Laue Langevin, Grenoble, France, ^fDepartamento de Química, Universidad Nacional de Mar del Plata, Argentina, ^gCrystallography, University Cologne, Germany.

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Strontium doped dibismuth-nonaoxometallate-(III) phases were produced at 1023 K. Partial substitution of bismuth by strontium in the $(\text{Bi}_{1-x}\text{Sr}_x)_2\text{M}_4\text{O}_{9-x}$ structure ($\text{M} = \text{Al}, \text{Ga}$) yields oxygen vacancies for charge balance. Introducing oxygen vacancies into the structure causes the rearrangement of associated M_2O_7 double-tetrahedra forming “ M_3O_{10} ” tri-clusters which were identified by multi-quantum MAS NMR. Both STEM-EDX and XPS showed a homogeneous distribution of strontium in the bulk and on the surface, respectively. Moreover, XPS confirms the trivalent state of bismuth after doping. The orientations of bismuth $6s^2$ lone electron pairs were calculated using DFT methods. Additionally, while replacing half of the bismuth atoms by strontium (Fig. 1) the resulting structural distortions were calculated taking different possibilities into account. The amount of strontium in the crystal structure of the aluminum containing phase was further confirmed from the decomposition product SrAl_2O_9 formed during the temperature-dependent X-ray powder diffraction. Thermal expansion coefficients were calculated out of these evaluated data. The crystal structural proof was carried out refining $(\text{Bi}_{0.94}\text{Sr}_{0.06})_2\text{Al}_4\text{O}_{8.94}$ combined from powder neutron and X-ray diffraction data. Rietveld refinements clearly showed that partial occupation of one oxygen site and the simultaneous shift of two aluminum atoms from the double-tetrahedra to two tri-cluster sites occurred. Thermal expansion and high-temperature neutron diffraction powder data analysis confirms the thermal stability of the Sr-doped phases up to 1250 K.

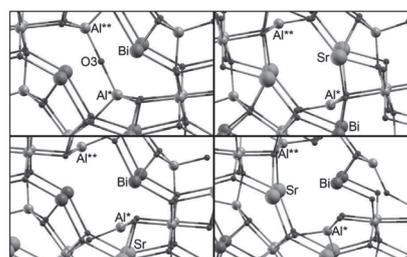


Fig. 1 Al_2O_7 double-tetrahedra configuration with bridging O3 atom in undoped mullite-type $\text{Bi}_2\text{Al}_4\text{O}_9$ (top left) and the structural effect of three possibilities of strontium doping: 1,2 (top right), 3,4 (bottom left) and 1,4 (bottom right) in $(\text{Bi}_{1-x}\text{Sr}_x)_2\text{M}_4\text{O}_{9-x}$ for $x = 0.5$.

Keywords: mullite-type; structure; properties