ordered manner. Raman and infrared spectra were recorded and assignments of the stretching and bending vibrations of the AsO_4^{3-} tetrahedra were made. The number of the peaks observed is in good agreement with that predicted by the factor group analysis of the R-3 space group. The high value of the optical absorption gap observed for $Sr_{0.5}Zr_2(AsO_4)_3$ (5.39 eV), greater than that of ZrO_2 (4.77 eV), is due to the presence of the covalent As – O bonds around Zr^{4+}.

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Keywords: nasicon; arsenate; crystal structure

FA2-MS04-P06

Magnetocaloric Properties of the $Gd_5Si_{2-x}Ge_{2-x}Mn_{2x}$ Compounds. <u>Yalcin Elerman</u>[a], Ercument Yuzuak[a], Ilker Dincer[a]. *[a]Department of Engineering Physics, Ankara University, Ankara Turkey.*
E-mail: elerman@ankara.edu.tr

Magnetic Magnetic refrigeration is based on the magnetocaloric effect and was discovered by Warburg in 1881 [1]. Magnetocaloric effect is the isothermal magnetic entropy change or the adiabatic temperature change in magnetic material when it is subjected to a change in external magnetic field. For a long time, the main application of the magnetocaloric effect had been to attain very low temperatures.refrigeration has drawn increasing attention due to numerous. Recently, magnetic refrigeration in the temperature range between 250 and 300 K is of particular interest because of potential impact on energy savings and environmental concerns [2]. To improve the magnetocaloric properties of the $Gd_5Ge_2Si_2$ compound with alloying Mn using heat treatment and low-purity Gd.

The influence of the manganese-alloying on the structure and magnetocaloric properties of the $Gd_5Si_{2.05}Ge_{1.95}$ compound has been studied by x-ray powder diffraction and magnetization measurements. The $Gd_5Si_{2.05-x}Ge_{1.95-x}Mn_{2x}$ (2x=0, 0.03 and 0.08) compounds crystallize in the $Gd_5Si_2Ge_2$-type monoclinic structure. In all x-ray powder diffraction patterns, a minor hexagonal Gd_5Si_3 phase is observed as a second phase. With Mn doping, the unit cell parameters increase. For the compounds with x=0, 0.03 and 0.08, the first order phase transition is observed. The maximum entropy change of the $Gd_5Si_{2.05-x}Ge_{1.95-x}Mn_{2x}$ compound with 2x=0.03 at 275 K is found to be -11.6 J/ kg.K in an applied field of 5 T. X-ray diffraction and magnetic measurements show that the annealing is very important to improve the magnetocaloric properties of the $Gd_5Si_2Ge_2$ and alloying $Gd_5Si_2Ge_2$ compounds.

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Keywords: magnetocaloric effect; magnetic measurements; X-ray powder diffraction

FA2-MS04-P07

Multinary Layered Tellurides with Almost Homometric Structures. <u>Matthias N. Schneider</u>[a], Oliver Oeckler[a]. *[a]Department of Chemistry and Biochemistry, LMU Munich.*
E-mail: matthias.schneider@cup.uni-muenchen.de

Layered multinary chalcogenides with long translation periods and a certain degree of disorder probably exhibit low thermal conductivity in combination with tunable electrical properties, which is required for promising thermoelectrics. [1] In the system Ge-Sb-Te, metastable long-periodic phases can be obtained by partial spinodal decomposition and subsequent annealing. They exhibit combinations of building blocks found in the series of stable compounds $(GeTe)_n(Sb_2Te_3)_m$ and $(Sb_2Te_3)_m(Sb_2)_k$ and can occasionally be stabilized by doping with additional elements. Some of these compounds, e.g. $Ag_xSb_{3-x}Te_4Sb_8$ (x = 0.24; $P\bar{3}m1$, a = 4.282 Å, c = 28.64, $R1$ = 0.054), have been characterized by single-crystal X-ray diffraction.[2] Hexagonal atom layers are periodically stacked with varying transition vectors, so that e.g. A7-type Sb or GeTe layers are formed. Interestingly, we have found that ambiguities concerning X-ray structure analysis can arise due to almost homometric but clearly incongruent structures. Crystals of $Sb_{10}Te_3$, $(Sb,Pb)_8Te_3$, $Ge_2Sb_2Te_5$ and $GeSb_4Te_4$ yield diffraction patterns that allow the refinement of alternative incongruent structure models (in addition to the trivial ambiguity of Sb/Te distribution!). If atom assignments are derived from interatomic distances, the wrong structure models are reasonable and exhibit almost the same R values as the correct ones but correspond to a different stoichiometry. For example, $Ge_2Sb_2Te_5$ exhibits rocksalt-like blocks built up from 9 atom layers that are separated by van der Waals gaps, whereas in $GeSb_4Te_4$ rocksalt blocks comprising 7 atom layers ($GeSb_2Te_4$) alternate with A7-type Sb nets (Sb_2). Both compounds do exist and both structure models can be reasonably refined on either dataset. Structure solution by direct or Patterson methods as well as by charge flipping frequently affords the wrong solutions. These findings strongly affect structure analyses of such thermoelectrics and stress the necessity of accurate chemical analyses. Although the problem of homometric structures has been discussed since the early days of X-ray crystallography,[3] it occurs very seldom during practical structure determination. Although the examples presented here are only approximately homometric, the wrong structure models can be refined on calculated data of the correct models with R values < 0.01. As all layers are primitive 2D hexagonal nets, the problem is reduced to 1D and can be understood with the help of cyclotomic sets.

[3] Different sets of stacking vectors give non-congruent sets of interatomic distances which yield almost the same Patterson function and hence similar diffraction patterns.

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Keywords: thermoelectrics; homometry; tellurium compounds [1]

FA2-MS04-P08

Temperature- and Concentration-induced Structural Transitions in $Pr_{1-x}R_xAlO_3$. Leonid Vasylechko[a], Tetyana Basyuk[a], Anatoliy Senyshyn[a,b], Dmytro Trots[b], Rainer Niewa[c], Stefan Hoffmann[d]. [a]Department of Semiconductor Electronics, Lviv Polytechnic National University, Lviv, Ukraine. [b]TU Darmstadt, Germany. [c]TU Munich, Germany. [d]MPI CPfS, Dresden, Germany. E-mail: crystal-lov@polynet.lviv.ua

The pseudo-binary systems $PrAlO_3$—$RAlO_3$ (R = rare earth metals) display complex phase and structural behaviours. Seven different types of crystal structures ranging from the ideal cubic perovskite to its triclinic derivative are found among $Pr_{1-x}R_xAlO_3$ solid solutions, depending on composition and temperature [1]. In this work, the influence of both "chemical pressure" and temperature on the crystal structures of $PrAlO_3$-based perovskites and on the character of structural phase transformations occurring in the pseudo-binary systems $PrAlO_3$—$RAlO_3$ is discussed on the basis of *in situ* high resolution powder diffraction applying synchrotron radiation and differential thermal analysis.

At room temperature (RT), continuous solid solutions $Pr_{1-x}R_xAlO_3$ with rhombohedral perovskite structures are formed in the La and Nd systems, whereas in the systems with Sm, Eu and Gd, the phase separation in two solid solutions with $LaAlO_3$ and $GdFeO_3$ types of structures occurs. One more kind of solid solution with orthorhombic structure (*Imma*) at RT has been observed in the systems with Ho—Er and Y. At elevated temperatures, orthorhombic and rhombohedral $PrAlO_3$-based perovskites undergo structural phase transitions *Pbnm*—*R-3c* and *R-3c*—*Pm-3m*, respectively. Similar to the "pure" aluminates, both transitions can be parameterized in the terms of Goldschmidt tolerance factor. The transitions temperatures increase linearly with decreasing average R-cation radii in $Pr_{1-x}R_xAlO_3$ solid solutions.

Much intricate relationship was observed between the cationic substitution and low-temperature (LT) structural transformations *R-3c*—*Imma* and *Imma*—*I2/m* in the $PrAlO_3$—$RAlO_3$ systems. In the systems with La and Nd, the temperatures of both transitions decrease with decreasing Pr content, whereas in the systems with Sm—Tm and Y a decrease of the *Imma*—*I2/m* and an increase of the *R-3c*—*Imma* transition temperatures are observed. The range of existence of the orthorhombic (*Imma*) phase expands in these systems with decreasing Pr content, thus explaining an appearance of this phase in the Ho—Er and Y systems

at RT. Unexpectedly, in the $PrAlO_3$—$NdAlO_3$ system a rare triclinic structure has been found below 70 K, which is the first repesentative among the perovskites with a single *B*-cation.

A complicated character of electron-phonon and phonon-phonon coupling is evidently the reason of the anomalous thermal behaviour recently observed in the majority of $RAlO_3$ perovskites (R=Eu—Dy, Er, Tm, Y) [1]. However, in contrast to $PrAlO_3$ and $CeAlO_3$, in which such a coupling leads to the change of crystal structures at LT, the present anomalies are reflected in the different deviations of the lattice expansion from the "normal" trends.

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Keywords: perovskite oxides; structural transitions; phase diagrams

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Hydrogen Storage Materials Studied at Neutron Powder Diffractometer SPODI. Markus Hoelzel[a], Eveline Weidner-Ronnefelder[b], Fransceco Dolci[c], Jianjiang Hu[c], Norbert Juenke[d], Hartmut Fuess[a]. [a]Fachbereich Material- und Geowissenschaften, Technische Universität Darmstadt, Germany. [b]Institute for Energy, Joint Research Centre Petten, Netherlands. [c]Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Germany. [d]Insititut für Physikalische Chemie, Universität Göttingen, Germany. E-mail: markus.hoelzel@frm2.tum.de

The structure and phase transformation behaviour of promising hydrogen storage materials has been investigated by neutron powder diffraction. In this contribution, we report on measurements carried out at the high-resolution neutron powder diffractometer SPODI (FRM II / Garching n. Munich, Germany) [1]. The instrument provides diffraction patterns with excellent profile shape and high resolution over a wide 2θ scattering angular range. Thus it suited for structure refinement on complex systems, in particular phase mixtures. On the other hand, the stepwise movement of the detector array limits the possibilites for kinetic studies.

Fully deuterated samples of the system $LiD/Mg(ND)_2$ have been studied after desorption and re-deuteration at 220 °C and different pressures up to 70 bar to analyse the phase transformation behaviour. The measurements were carried out using a wavelength of 2.536 Å. The analysis of diffraction patterns collected at different deuterium pressure levels revealed that the deuteration occures via intermediate reaction steps. Corresponding intermediate phases could be identified and analysed by Rietveld refinement.

A sample of $Li_4(NH_2)_3(BD_4)$ was studied at ambient conditions using a wavelength of 1.548 Å. The compound was synthesized by mixing a 1:3 stoichiometric ratio of