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+}.

[1] M. El Brahimi and J. Durand, *Z. Anorg. Allg. Chem.,* **1990**, 584(1), 178-184. [2] J. M. Winand, A. Rulmont and P. Tarte, *J. Solid State Chem,* **1990**, 87(1), 83-94. [3] A. Yaakoubi, T. Jouini, and N. Jouini, *C. R. Acad. Sci. Paris,* **1991**, 312(5), 451-453. [4] C. Masquelier, F. d'Yvoire and G. Collin, G. *J. Solid State Chem.,* **1995**, 118(1), 33-42. [5] S. Khorari, A. Rulmont and P. Tarte *J. Solid State Chem.,* **1997**, 134(1), 31-37. [1] K. Lii and H. Ye, *J. Solid State Chem.,* **1997**, 131(1), 131-137. [6] D. Mazza, M. Lucco-Borlera and S. Ronchetti, *Powder Diffraction,* **1998**, 13(4), 227-231. [7] C. Masquelier, A.K. Padhi, K.S. Nanjundaswamy and J.B. Goodenough, *J. Solid State Chem.,* **1998**, 135(2), 228-234. [8] W.T.A. Harrison and M.L.F. Philips, *Acta Cryst. C,* **2001**, 57, 2-3. [9] M. Chakir, A. El Jazouli and D. de Waal, *Mat. Res. Bull,.* **2003**, 38(13), 1773-1779.

Keywords: nasicon; arsenate; crystal structure

FA2-MS04-P06

Magnetocaloric Properties of the $Gd_5Si_{2-x}Ge_{2-x}Mn_{2x}$ Compounds. Yalcin Elerman[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.

[1] E. Warburg, *Ann. Phys.*, **1881**, 13, 141. [2] Pecharsky, V.K.; Gschneidner, K.A.; *Phys. Rev. Lett.*, **1997**, 78, 4494.

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

FA2-MS04-P07

Multinary Layered Tellurides with Almost Homometric Structures. Matthias N. Schneider[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.