

phase transition to lower temperatures and modify the hysteresis loop. The tetragonal form is thus strongly stabilized via the addition of dopants. The tetragonal c/a ratio also increases with doping at 3% mol. An analysis of the isotropic atomic displacement parameters for the tetragonal phase indicates that in the case of oxygen the values are greater for doped samples. These higher values are most probably linked to additional static disorder resulting from modifications to the oxygen sublattice as a consequence of doping. It can be noted that doping had already resulted in an increase in B_{iso} for oxygen of 0.2-0.3 Å² at ambient temperature in the monoclinic phase. There are no significant effects of doping on the B_{iso} of Zr. The results, in particular the possible increase in static disorder, are linked to changes in electrical conductivity measured under the same conditions by complex impedance spectroscopy. Thus, structure-property relationships can be developed in order to optimize these materials for high-temperature refractory applications.

Keywords: zirconia; neutron powder diffraction; high-temperature crystallography

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Magnetic and Magnetocaloric Result of Magnetic Field-induced Transitions in $\text{La}_{1-x}\text{Ce}_x\text{Mn}_2\text{Si}_2$. Baris Emre^a, Ilker Dincer^a, Yalcin Elerman^a. ^a*Department of Engineering Physics, Ankara University, Ankara Turkey.*

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Rare earth-based intermetallic compounds are having great attention due to their potential for various applications. Among ternary intermetallic compounds, the RMn_2X_2 compounds (R=rare-earth, X=Si or Ge) have been extensively studied because of their interesting physical properties ranging from superconductivity to heavy fermion behavior [1]. Ternary RMn_2X_2 compounds crystallize in the body-centered tetragonal ThCr_2Si_2 -type structure (space group: $I4/mmm$), which is characterized by stacked R–X–Mn–X–R layers along the c axis. Magnetic structure of these compounds contains two interacting magnetic subsystems: One of them is composed of rare-earth atoms and the other one is manganese atoms. The magnetic ordering of the Mn sublattice can take up various configurations, as a result the nature of the magnetic ordering is closely related to the Mn–Mn separation. Since, the magnetic ordering of Mn sublattice is very much dependent on the lattice parameters, the overall magnetic state of these compounds is quite sensitive to temperature, due to the thermal variation of lattice parameters. In this study we investigate the $\text{La}_{1-x}\text{Ce}_x\text{Mn}_2\text{Si}_2$ ($x=0.35$ and 0.45) where we expect a variety of magnetic structures to appear in these compounds since they may exhibit quite interesting magnetic and magnetocaloric properties. Among this series LaMn_2Si_2 is ferromagnetic with $T_C=310$ K and CeMn_2Si_2 is a mixed valent compound with $T_N=376$ K [2]. All compounds investigated crystallize in the ThCr_2Si_2 -type structure with the space group $I4/mmm$. Substitution of Ce instead of La leads to a linear decrease in the lattice constants and the unit cell volume.

Magnetic properties have been examined between 5 and 350 K in 50 Oe. In both samples shows multiple AF-FM state transitions and field-induced transition from the AF to the FM state. The isothermal magnetic entropy change is found and both samples show inverse and conventional magnetocaloric effect around transition temperature. Finally we have used Landau theory on magnetic entropy changes around magnetic transitions.

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Synthesis, Crystal Structure and Vibrational and Optical Spectra of $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$. Abdelaziz El Jazouli^a, Abderrahim Jirifi^a, Jean Pierre Chaminade^b, Michel Couzi^c. ^a*LCMS, Université Hassan II-Mohammedia, Faculté des Sciences Men M'Sik, Avenue Idriss El Harti, Casablanca, Maroc.* ^b*CNRS, Université Bordeaux, Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), 87 avenue Albert Schweitzer, 33608 Pessac, France.* ^c*Institut des Sciences Moléculaires, Université Bordeaux 1, CNRS UMR 5255, Batiment A12, 351 cours de la libération, 33405 Talence cedex, France.*

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Nasicon-type materials have been extensively studied as solid electrolytes, ionic conductors, electrode materials, low thermal expansion ceramics, sensors, etc. In contrast to the extensive studies of the Nasicon-type phosphates and silicates, only few investigations have been reported for the arsenates analogues [1-8]. We described in a previous work the structure of $\text{NaZr}_2(\text{AsO}_4)_3$ [9]. Substitution of Na^+ by divalent ions in $\text{NaZr}_2(\text{AsO}_4)_3$ led to the synthesis of new arsenates $\text{M}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ ($\text{M} = \text{Ca}, \text{Cd}, \text{Sr}, \dots$). The present paper reports on the synthesis, crystal structure and vibrational and optical spectra of $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$. Crystalline powder of $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ was prepared from solutions of SrCO_3 (or $\text{SrCl}_2 \cdot \text{H}_2\text{O}$), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{H}_2\text{AsO}_4$. Stoichiometric proportions of these reagents were dissolved in dilute nitric acid solution (6M) for the carbonate and in distilled water for the other reagents. The mixture of these solutions was heated at 60°C until complete evaporation. The white solid obtained was successively sintered at 100, 300, 500 and 700°C, for 24 hours with intermediate grinding, to obtain microcrystalline powder of $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$. Its structure, which belongs to the Nasicon-type family, was refined by the Rietveld method in the R-3 space group, from X-ray powder diffraction data. The hexagonal unit-cell parameters were determined to be $a_h = 8.965(2)$ Å, $c_h = 23.955(6)$ Å, $V = 1667.43(6)$ Å³, and $Z = 6$. The structure is formed by an ionic three-dimensional network of AsO_4 tetrahedra and ZrO_6 octahedra linked by corners with Sr^{2+} ions occupying half of the M1 sites in an

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 $\text{Sr}_{0.5}\text{Zr}_2(\text{AsO}_4)_3$ (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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Magnetocaloric Properties of the $\text{Gd}_5\text{Si}_x\text{Ge}_{2-x}\text{Mn}_{2x}$ Compounds. Yalcin Elerman^a, Ercument Yuzuak^a, Ilker Dincer^a. ^aDepartment of Engineering Physics, Ankara University, Ankara Turkey.
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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 $\text{Gd}_5\text{Ge}_2\text{Si}_2$ 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 $\text{Gd}_5\text{Si}_{2.05}\text{Ge}_{1.95}$ compound has been studied by x-ray powder diffraction and magnetization measurements. The $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Mn}_{2x}$ ($2x=0, 0.03$ and 0.08) compounds crystallize in the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -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 $\text{Gd}_5\text{Si}_{2.05-x}\text{Ge}_{1.95-x}\text{Mn}_{2x}$ 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 $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and alloying $\text{Gd}_5\text{Si}_2\text{Ge}_2$ compounds.

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Multinary Layered Tellurides with Almost Homometric Structures. Matthias N. Schneider^a, Oliver Oeckler^a. ^aDepartment of Chemistry and Biochemistry, LMU Munich.

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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 $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ and $(\text{Sb}_2\text{Te}_3)_m(\text{Sb}_2)_k$ and can occasionally be stabilized by doping with additional elements. Some of these compounds, e.g. $\text{Ag}_x\text{Sb}_{3-x}\text{Te}_4\text{Sb}_8$ ($x = 0.24$; $P \bar{3}m1$, $a = 4.282$ 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 $\text{Sb}_{10}\text{Te}_3$, $(\text{Sb,Pb})_8\text{Te}_3$, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ 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, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ 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 $(\text{GeSb}_2\text{Te}_4)$ 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.