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Structure and magnetic properties of C-type doped rare earth oxides $\text{Er}_{2-x}\text{Mn}_x\text{O}_3$ and $\text{Er}_{2-x}\text{Ni}_x\text{O}_3$

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Doped rare earth oxides are potential materials not only due to expected applications taking advantages of their properties, but also because of the interesting physics in this class of materials. The structure and magnetic properties of the two systems $\text{Er}_{2-x}\text{Mn}_x\text{O}_3$ and $\text{Er}_{2-x}\text{Ni}_x\text{O}_3$ have been investigated. The two systems with the composition $x=0.0, 0.05, 0.10$ and 0.15 were prepared with the sol gel technique. Single phase solid solution is formed up to $x=0.2$ for $\text{Er}_{2-x}\text{Mn}_x\text{O}_3$, while for $\text{Er}_{2-x}\text{Ni}_x\text{O}_3$ single phase is obtained only for $x=0.05$. All structural parameters including the cation distribution between the non-equivalent sites 8b and 24d have been determined applying Rietveld method. In spite of the smaller ionic radii of Mn^{+3} and Ni^{+3} than that of Er^{+3} , substituting the later by one of the formers is found to increase the lattice parameter (a) of the cubic bixbyite structure. For the system $\text{Er}_{2-x}\text{Mn}_x\text{O}_3$, preferential cationic distribution is found for $x=0.05$ & 0.15 with different preferred site, and random for $x=0.1$. For $\text{Er}_{2-x}\text{Ni}_x\text{O}_3$, slight preferential distribution is found for $x=0.05$ and 0.1 and random for 0.15 . Magnetic susceptibility measurements were done in the temperature range $5-300$ K and a behavior in accordance with Curie-Weiss law was found. The Curie's constants, the Curie-Weiss paramagnetic temperature and effective magnetic moments μ_{eff} were determined for all samples. For the system $\text{Er}_{2-x}\text{Ni}_x\text{O}_3$, μ_{eff} is found to decrease linearly with composition parameter x . For $\text{Er}_{2-x}\text{Mn}_x\text{O}_3$, interesting behavior is obtained where μ_{eff} increases for $x=0.05$ and decreases for $x=0.1$ & 0.15 with a bigger value for the later. The Curie-Weiss paramagnetic temperatures indicated antiferromagnetic interaction. These magnetic results are discussed in view of the cationic distribution and magnetic ions clusterisation.

Keywords: Magnetic measurements, Cation distribution, rare earth sesquioxides

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Mossbauer and neutron diffraction study of polycrystalline GaFeO_3

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Gallium iron oxide (GaFeO_3) is a member of a multiferroic family which exhibits ferrimagnetic and piezoelectric properties below room temperature [1-2]. This material has orthorhombic crystal structure with space group $Pc2_1n$ with four different cation sites labeled Ga1, Ga2 (mostly occupied

by gallium) and Fe1, Fe2 (mostly occupied by iron) [3-5]. Polycrystalline GaFeO_3 materials have been prepared by a traditional solid state reaction (SR) and sol-gel (SG) methods. The Curie temperature (T_C) for GaFeO_3 (SR) is about 190K and increases or reaches room temperature when the temperature of preparation is decreased from 1400°C to 900°C . The dielectric constant and dielectric loss are temperature and frequency independent for both samples. Mossbauer analysis shows that at least two different assignment of the EFG and IS for the main Fe1 and Fe2 sites are possible. Both assignments results in similar site occupancies. It follows from the neutron powder diffraction that GaFeO_3 exhibits a ferrimagnetic order with spins parallel to c -axis. Also Mossbauer indicates for higher temperature of magnetic order in SG sample, in agreement with magnetization and neutron data.

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Magnetic and nuclear structure of orthorhombic and monoclinic polymorphs of CoGeO_3 pyroxene.

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Pyroxenes have gained vivid interest in solid state science due to their low temperature magnetic properties and the discovery of multiferroic behaviour in some members of this well known mineral group [1]. As a continuation of our ongoing research in crystal-chemistry and crystal-physics of pyroxenes [2-4 and references therein] we here report on the synthetic pyroxene-type material CoGeO_3 . The title compound was synthesized at 1273K and 1448K using ceramic sintering techniques in the monoclinic and orthorhombic modification respectively. The two compounds were analysed by magnetic susceptibility measurements and neutron diffraction in order to study magnetic ordering and spin structures at low temperature. The monoclinic form of CoGeO_3 has $C2/c$ symmetry and orders magnetically below 36K with a small negative paramagnetic Curie temperature $\theta_p = -4.6(2)\text{K}$. The magnetic structure can be described with $\mathbf{k} = (1, 0, 0)$ in the magnetic space group $C2'/c'$ having a ferromagnetic spin arrangement within the chains of M1 sites, but a dominating antiferromagnetic coupling between the chains. At the M1 sites the magnetic spins are aligned within the $a-c$ plane forming an angle of 120° with the $+a$ -axis and they are not parallel to the spins at M2. Here spins are also ferromagnetically coupled within, but anti-ferromagnetically coupled between the M1/M2 site bands. The orthorhombic phase of CoGeO_3 displays $Pbca$ symmetry

and transforms to an anti-ferromagnetically ordered state ($\theta_p = -18.6(2)$ K) below 33 K. The magnetic spin structure can be described with $k = (0, 0, 0)$ in space group $Pbca'$ and it is similar to the one of the $C2/c$ phase except that it is non-collinear in nature, i.e. there are components of the magnetic moment along all three crystallographic axes. Small magneto-elastic coupling is observed in the orthorhombic phase. More details are reported in [5].

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Keywords: pyroxene, neutron diffraction, magnetism

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Magnetostructural and magnetocaloric properties of $Ni_{50-x}Cu_xMn_{36}Sn_{14}$ by magnetic measurements and neutron diffraction experiments. Ilker Dincer^a, Yalcin Elerman^a, Ercüment Yüzüak^a, Markus Hölzel^b, Anatoliy Senyshyn^b, Eyüp Duman^a, Thorsten Krenke^c,

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Compared with conventional refrigeration, magnetic refrigeration technology has many advantages, such as the absence of harmful gas, less noise, low cost and high efficiency. Since the discovery of martensitic transformation with both phases magnetically ordered in Heusler alloys Ni-Mn-Z (Z: Ga, In, Sn and Sb) increasing attention has been paid to study the change in magnetic and electrical properties associated to the first-order reversible magnetostructural transition that originates valuable functional properties such as magnetic superelasticity, large inverse magnetocaloric effect, and large magnetoresistance change [1 and the references therein]. The reversibility and irreversibility of the magnetostructural transition is very important for magnetic actuator materials such as magnetic shape memory alloys. The austenite phase induced by the magnetic field is able to transform back to the initial martensite phase when the magnetic field is removed. A complete recovery of the initial martensite state may bring about magnetoelasticity (two-way magnetic shape memory effect), while the irreversible magnetostructural transition would result in magnetoplasticity (one-way magnetic shape memory effect).

We showed that the effects of the irreversibility of the magnetostructural transitions on magnetocaloric effect in the (Ni-Cu)-Mn-Sn compounds was very important by magnetic and resistance measurements under magnetic field [1]. The magnetic entropy change of the $Ni_{50-x}Cu_xMn_{36}Sn_{14}$ ($x=2$ and 4) compounds are estimated by using Maxwell equation and the $M(H)$ curves obtained from noncontinuous heating method. These compounds show the magnetostructural phase

transition from cubic to orthorhombic structure with decreasing temperature at around 218 and 168 K, respectively. To see better the type of the magnetostructural transition, we perform the neutron diffraction experiments for these compounds at the different temperatures and under different magnetic fields. According to the neutron diffraction experiment near A_S (A_S : Austenite start temperature), the Martensite phase of these compounds transforms to Austenite phase with increasing the magnetic field from 0 to 5 T, while these compounds remains in the Austenite phase with decreasing the magnetic field to zero Tesla. This is the evidence of the irreversible magnetostructural transition occurred in these compounds. Because of that, the determination of the magnetic entropy change in alloys which show the irreversible magnetostructural transition has carefully been studied [2].

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Structural, magnetic and magnetocaloric effect in the off-stoichiometric $Gd_5Ge_{2.05-x}Si_{1.95-x}Mn_{2x}$ alloys
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Magnetic refrigeration based on MCE of solid-state working substances have attracted tremendous attention in recent years due to its energy efficient and environment friendly properties as compared with the gas compression refrigeration technology that is used currently. Practical applications of the MCE, therefore, have the potential to reduce the global energy consumption and eliminate or minimize the use of ozone-depleting alloys, greenhouse gases, and precarious. After the discovery of the giant magnetocaloric effect in the $Gd_5Si_2Ge_2$ alloy, there has been much interest in the $Gd_5(Si_xGe_{1-x})_4$ family alloys [1]. As seen in earlier studies, the stoichiometric $Gd_5Si_2Ge_2$ with doping alloys have not won with the appropriate of magnetocaloric features. For this reason, we attempt to improve the magnetocaloric properties of the off-stoichiometric $Gd_5Ge_{2.05}Si_{1.95}$ alloy by replacing non-magnetic Ge/Si atoms by a small amount of magnetic Mn atom. We have investigated the structural, magnetic and magnetocaloric properties of the $Gd_5Ge_{2.05-x}Si_{1.95-x}Mn_{2x}$ ($2x=0.02, 0.06$) alloys using scanning electron microscopy, x-ray powder diffraction, DSC and magnetic measurements. According to DSC and magnetic measurements, the both alloys exhibit a structural phase transition (the first order phase transition) around room temperature. The Curie temperatures of these alloys are around 295 K. We determine the magnetic entropy changes near the transition temperatures using Maxwell relation and magnetization data. The maximum values of isothermal magnetic entropy change of the $Gd_5Ge_{2.05-x}Si_{1.95-x}Mn_{2x}$ alloy with $2x = 0.02$ that occurred is found to be $-12.1 \text{ J.kg}^{-1}.\text{K}^{-1}$ and $-19.8 \text{ J.kg}^{-1}.\text{K}^{-1}$ around 268 K in an applied field of 2 T and 5 T, respectively. The magnetic entropy changes are also estimated from DSC analysis for each alloy. The values of the magnetic entropy change of the $Gd_5Si_{2.05-x}Ge_{1.95-x}Mn_{2x}$ ($2x=$