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Magnetic properties of the In-doped $MnWO_4$-type solid solutions $Mn_{1-3x}In_{2x}\square_xWO_4$ [$\square$ = vacancy; $0 \le x \le 0.11$]

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ABSTRACT

Polycrystalline $Mn_{1-3x}In_{2x}\square_xWO_4$ ($\square$ = vacancy; $0 \le x \le 0.11$) solid solutions synthesized via solid state reactions were characterized by means of magnetic ac susceptibility (χ_{AC}) and specific heat (C). The effect of this substitution on the magnetic transition temperatures give rise to three consequences: (1) the disappearance of the basic antiferromagnetic (AFM) phase AF1 when exceeding the doping concentration $x = 0.03$; (2) the phase transition of the paramagnetic phase (PM) to the sinusoidal AFM phase AF3 at the Neel temperature (T_N) is shifted toward lower temperatures with respect to pure $MnWO_4$. This is valid also for the transition of AF3 to the cycloidal AFM phase AF2; (3) a systematic lowering of the effective magnetic moment with increasing In-doping. These substantial changes are attributed to the weakened overall magnetic interaction and a strong spin–lattice coupling due to the static disorder of Mn^{2+} with the nonmagnetic species, i.e. In^{3+} and vacancy.

1. Introduction

$MnWO_4$ (mineral name: huebnerite) crystallizes in wolframite structure (space group $P2/c$) and is paramagnetic (PM) at room temperature (RT). At low temperatures three antiferromagnetic (AFM) phases are observed in zero magnetic field. These AFM phases labeled as AF1, AF2, and AF3 are formed below their respective magnetic transition temperatures at $T_1 = 7.6$ K, $T_2 = 12.7$ K, and $T_N = 13.5$ K [1]. The basic AFM phase AF1 shows a commensurately modulated collinear spin order with the propagation vector $k = (\pm 0.25, 0.5, \text{and } 0.5)$ [2]. The phases AF2 and AF3 exhibit an incommensurately modulated cycloidal and sinusoidal spin wave, respectively, with their common propagation vector $k = (-0.214, 0.5, \text{and } 0.457)$ [2]. The magnetic phase diagram of $MnWO_4$ contains further multiple high-field phases at magnetic fields higher than 14 T in the low temperature range below 12 K [3–7]. Among those diverse magnetic phases, only the phase AF2 features non-inversion symmetry in its nuclear structure as a result of a cycloidal spin order in the *ac*-plane. The resulting extremely small displacement of Mn^{2+} could be proven only indirectly by detecting ferroelectric polarization (P_y) induced parallel to the crystallographic *b*-axis [8,9]. The maximum P_y ($\sim 50\ \mu C/m^2$) was measured right before the first order transition AF2 → AF1 at T_1. The coercivity field to reverse the spontaneous polarization is about 600 kV/m at 10 K [8].

The origin of such an interesting magnetoelectric coupling is to be subtle handled as MF properties are driven by competition of several interactions, e.g. spin–orbital, spin–lattice, and magnetic anisotropy. From this point of view $MnWO_4$-type materials belong to the most studied MF families [1–9]: the creation of P_y in AF2 can be explained by superexchange interaction between Mn atoms over bridging oxygens [10]. Another plausible explanation is the spin-induced degeneracy of dipole displacements of two symmetrically equivalent Mn atoms at their hidden polar atomic sites C_2 in the inversion-symmetric space group **P**2/c [11]. Both models can be combined to elucidate and manipulate short- and long-range order lattice distortions correlated with spiral spin order in $MnWO_4$ modifications. Accordingly several studies were addressed to structural and magnetic properties of $Mn_{1-x}A_xW_{1-y}B_yO_4$ (A = Ni, Co, Fe, Zn, and Mg; B = Mo) solid solutions in order to find better performing $MnWO_4$-type MFs applicable under ambient conditions [12–19]. As summarized in Table 1, the replacement of Mn^{2+} by Co^{2+} increases the Neel temperature T_N, but decreases the transition to the AF2 phase T_2 [15–18]. By substituting Fe^{2+} for Mn^{2+} both T_N and T_1 increase, which unfortunately impedes the formation of the MF phase AF2 [16]. Doping with non-magnetic Zn^{2+} and Mg^{2+} stabilizes AF2 merely toward low temperatures, and both T_2 and T_N are lowered [16,17]. For easy application of MF

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Table1
Magnetic phase transitions in $Mn_{1-x}A_xW_{1-y}B_yO_4$ (A=Ni, Co, Fe, Zn, and Mg; B=Mo) solid solutions previously studied by other research groups.

Material	T_1	T_2	T_N	Remarks
$MnWO_4$	7.6 K	12.7 K	13.5 K	[1]
$Mn_{1-x}Co_xWO_4$	–	Decreasing	Increasing	AF1 suppressed [13–16]
$Mn_{1-x}Fe_xWO_4$	Increasing	–	Increasing	AF2 suppressed [16]
$Mn_{1-x}Zn_xWO_4$		Decreasing	Decreasing	AF1 suppressed [16,17]
$Mn_{1-x}Mg_xWO_4$		Decreasing	Decreasing	AF1 suppressed [17]
$Mn_{0.93}Ni_{0.07}WO_4$	T_1 not observed and T_2 =13.1 K or T_1=13.1 K; T_2=Not observed;		13.9 K	AF1 or AF2 suppressed [19]
$MnW_{0.70}Mo_{0.30}WO_4$	11 K	14 K	15 K	[18]

properties, however, it is necessary to increase T_N and T_2. These magnetic transition temperatures can be elevated only about a few Kelvin when substituting Mo^{6+} for W^{6+} or Ni^{2+} for Mn^{2+} in $MnWO_4$ [18,19].

All of the attempts afore mentioned are based on the isovalent substitution, i.e. introduction of divalent cations for Mn^{2+}. In order to investigate the influence of aliovalent substitution on structural distortion we have synthesized a series of $Mn_{1-3x}In_{2x}{}^{\square}{}_xWO_4$ solid solutions [$\square$=vacancy; $0 \le x \le 0.11$] (hereafter denoted as In:$MnWO_4$) [20]. Despite of the presence of smaller In^{3+} replacing larger Mn^{2+}, the In-rich compound $Mn_{0.71(2)}In_{0.19(1)}{}^{\square}{}_{0.10}WO_4$ undergoes a bulk volume expansion of 0.4% with respect to $MnWO_4$ due to a local space expansion of 0.13% around bridging oxygen sites. Even though the bulk symmetry of In:$MnWO_4$ materials maintain the centrosymmetric space group $P2/c$ the presence of a high amount of defects at Mn sites up to 11 at% indicates a strong distortion of the local Mn–O–Mn configuration, as confirmed by Raman spectroscopy [20]. Concerning the influence of local perturbations such as defects and strains in MFs on their dielectric and magnetic responses [21–24], the current study reports results from magnetic a.c. susceptibility, specific heat, and high-resolution neutron powder diffraction (HRNPD) to show the changes of the magnetic behavior in highly defective In:$MnWO_4$ materials.

2. Methods

Powder samples of In:$MnWO_4$ synthesized by solid state reactions out of the stoichiometric mixtures of MnO, WO_3, and In_2O_3 are listed in Table 2. Electron micro probe analyses (EMPA) combined with micro-Raman spectroscopy and X-Ray powder diffraction (XPD) could confirm the maximal 33 at% Mn replacement by 22 at% In, creating 11 at% vacancies at Mn sites [20]. Details of results from synthesis and structural characterization of In:$MnWO_4$ are given in Ref. [20].

Magnetization (M) and a.c. susceptibility (χ_{AC}) were acquired in a Quantum Design Physical Properties Measurement System (PPMS) at the excitation frequency and amplitude 911 Hz and 1 mT, respectively. Temperature sweeps were performed in zero magnetic field from 2 K to 350 K for the pure $MnWO_4$ sample (Labcode: **In0**) and for In-doped samples in a narrow temperature range of 2–20 K. Field sweeps were performed at 2 K between −14 T and 14 T for the undoped sample (**In0**), and between 0 T and 9 T for several In-doped samples. Magnetic phase transition temperatures were determined by intersections of linear approximation functions. The specific heat (C) of the samples **In0** and **In19** was measured in the PPMS with a large pulse method from 2 K to 290 K. The heat pulse size was 30% of the current temperature, further experimental principles can be found in Ref. [25].

HRNPD was performed at the instrument SPODI (Forschungs-Neutronenquelle Heinz Maier-Leibnitz) subsequently at 3.5, 20, and 300 K. All data sets were collected in a 2θ-range of 0.95–151.90° with a step size of 0.05° using a constant wavelength λ=1.54830(2) Å (Ge(551) monochromator at 155° take-off angle). The detector zero shift $2\theta_0$=0.022(3)° was determined by a Si SRM standard. The Rietveld method was applied for structure refinements with HRNPD data using the program package *FullProf Suite* [26]. Phase identification was done using the data bank *Inorganic Crystal Structure Database* on the interface *FindIt* [27].

3. Results and discussion

We start the presentation of our results with the zero field susceptibility of the natural sample huebnerite originated from Peru. As shown in Fig. 1a, the real part of $\chi_{AC}(Re\chi_{AC})$ in zero field increases with decreasing temperature toward the peak at 13.5 K (T_N) and decreases upon further cooling. This corresponds to the typical magnetic behavior of $MnWO_4$ [1]. The inverse magnetic susceptibility $Re\chi_{AC}{}^{-1}$ obeys a Curie–Weiss law above T_N, as highlighted in the inset of Fig. 1a. The susceptibility of In:$MnWO_4$ samples show their respective maximum at T_N below 20 K, followed by a small plateau between T_N and T_2 in the low temperature region (Fig. 1b). Only the undoped $MnWO_4$ (both natural and synthetic) samples display a third kink at T_1. For all In-doped samples, the imaginary part of $\chi_{AC}(Im\chi_{AC})$ shows no anomalies corresponding to the AF2–AF1 transition. The observed transition temperatures T_1=8.2 K, T_2=12.6 K, and T_3=13.7 K of the synthetic pure $MnWO_4$ sample (**In0**) are similar to the respective values determined for huebnerite. The transition temperatures T_N and T_2 of In:$MnWO_4$ decrease with increasing the In content. The temperature difference between T_2 and T_N is about 1 K and constant for all samples. These observations point that the substitution of vacancies and In^{3+} for Mn^{2+} stabilizes the cycloidal spin order (AF2) at the expense of the basic collinear spin order (AF1).

Table 2
Composition of In:$MnWO_4$ samples based on one WO_4 per formula unit. Quantitative phase analyses were made by Rietveld calculations [20].

Lab code	Atomic ratios		Ideal chemical formula[a]	Phases present in the sample (wt%)
	Mn	In		
In0	1.000(1)	0.000(1)	$MnWO_4$	$MnWO_4$ (100)
In4	0.93(5)	0.04(5)	$Mn_{0.93(5)}In_{0.04(5)}{}^{\square}{}_{0.02}WO_4$	$MnWO_4$ (96.2)+Mn_3O_4 (2.4)+In_2O_3 (1.4)
In6	0.91(2)	0.06(1)	$Mn_{0.91(2)}In_{0.06(1)}{}^{\square}{}_{0.03}WO_4$	In:$MnWO_4$ (100)
In14	0.80(2)	0.14(1)	$Mn_{0.80(2)}In_{0.14(1)}{}^{\square}{}_{0.06}WO_4$	In:$MnWO_4$ (100)
In19	0.71(2)	0.19(1)	$Mn_{0.71(2)}In_{0.19(1)}{}^{\square}{}_{0.10}WO_4$	In:$MnWO_4$ (100)
In22	0.67(2)	0.22(1)	$Mn_{0.67(2)}In_{0.22(1)}{}^{\square}{}_{0.11}WO_4$	In:$MnWO_4$ (90.0)+$In_2W_3O_{12}$ (10.0)

[a] Obtained from Rietveld analysis.