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Effect of doping by transitional elements on properties of chalcogenide glasses

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Abstract

In present work, the results on the influence of doping by transitional elements on thermal, optical, structural and magnetic properties of chalcogenide glasses are presented.

Thermal properties (T_g values for undoped and doped glasses) were studied using differential scanning calorimetry technique. Activation energy of glass transition was estimated with the use of Kissinger's expression. Structural studies were carried with the use of Raman and infrared spectroscopy and X-ray diffraction. Radial electron distribution functions in doped and undoped bulk glasses were obtained and analyzed. In Raman spectra, main observed effect under the introduction of dopants was the change of relative concentration of main and non-stoichiometric structural units characteristic for As_2S_3 glasses. Investigation of influence of transition metals Mn-dopants on the optical properties of As_2S_3 glass was studied in mid-IR region. Pure chalcogenide glasses are diamagnetics. Introduction of transitional and rare earth impurities changes the magnetic properties of investigated chalcogenide glasses.

Keywords: B. Spectroscopy; B. X-ray methods; C. Magnetic properties; C. Thermal properties; D. Glass

1. Introduction

Chalcogenide glasses (ChGs) exhibit a number of interesting optical properties with various potential applications as reviewed in, for example [1–5], etc. As frequently pointed out by various researchers, ChGs are promising materials for various applications because they are transparent over a wide range of wavelengths in the infrared (IR) region, they possess high refractive indices, low phonon energies and are easy to fabricate. Chalcogenide glasses can be used in applications in sensorics, infrared optics and optoelectronics. The glasses can be used for the preparation of optical fibers both for passive and active applications. Developments in photonics applications have highlighted the chalcogenide glass as a host for rare-earth elements.

The refractive index and its wavelength dependence, other optical properties are among important parameters that determine the suitability of materials as optical media. Refractive and absorption indexes, optical band gap of chalcogenide glasses can be changed by doping of different elements [3–6].

Special interest for applications is related with chalcogenide glasses doped with optically active rare-earth and transition metal ions, because they alter electrical, thermophysical, mechanical, magnetic and optical properties of the host material due to structural and electronic changes of the glass network [6–8].

The present work was devoted to studies of the influence of doping by transitional elements (Mn) on thermal, optical, structural and magnetic properties of As_2S_3 chalcogenide glasses.

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2. Experimental

The As_2S_3 glasses with manganese concentration from 0 up to 5 wt% Mn were prepared by standard melt-quenching technique using constituent elements of 6 N purity in vacuum-sealed silica ampoules. Ampoules were heated at 80 K/h rate, melt was hold at 1010 K during 80 h with subsequent quenching in the air at 10 K/h rate. Glass samples were obtained in the form of bar with 10 mm diameter. The prepared bulk glasses were cut into plates of 1 mm in thickness and polished to yield samples with high quality flat surfaces suitable for optical measurements.

X-ray diffraction measurements (XRD) were carried out using ARL X'tra (Thermo scientific) installation. Cu K_λ radiation (λ=0.154 nm) was used. Diffraction spectra were recorded by θ–θ-scanning in 2–140° range at room temperature. Measurements were carried out in step regime with scanning step 0.2° and point acquisition time 5 s.

Room temperature Raman spectra were recorded using Fourier spectrophotometer Bruker IFS-55 Equinox with FRA-106 attachment (with measurement step 1 cm^1). Nd:YAG laser light at 1.06 μm wavelength was used for excitation.

The positron annihilation lifetime spectrum was taken by conventional fast–fast coincidence method using plastic scintillators coupled to Phillips XP2020 photomultipliers with a ^{22}Na source placed between two sandwiched samples. The time resolution (FWHM) was about 320 ps, measured by defect free Al sample with 3 Gaussian approximation of resolution function. A total number of coincidences in analyzed time spectrum overreach 1×10^6 counts. Analysis of lifetime spectrum was carried out using the LT-9.0 program of Kansy [9].

Room temperature transmission spectra in the 700–4000 cm^{-1} region were recorded using an FT spectrometer "Perkin Elmer" Spectrum BXII.

Thermal properties were studied using differential scanning calorimetry (DSC) technique, T_g values for undoped and doped glasses were obtained. NETZSCH DSC 404 (with accuracy ± 0.5 K) calorimeter was used in DSC measurements. Calorimetric measurements were carried out using powder samples ($m \sim 20$ mG) in argon atmosphere under temperature changes within 40–250 °C. Heating rate consisted $q = 10$ K/min. Calibration of calorimeter was carried out by melting of pure metals In, Sn, Bi, Pb, Al, Cu with known values of temperature and enthalpy of melting.

Magnetizations of samples were measured with Cryogenic S600 Super-conducting Quantum Interference Device (SQUID) magnetometer in the temperature range of 5–400 K and in magnetic fields up to 6 T. A cryogenic system is completed with automated instrument control, data acquisition and analysis using the National Instrument's LabVIEW software.

3. Results and discussion

3.1. XRD measurements

X-ray diffraction patterns (Fig. 1) confirm the amorphous nature of the bulk samples of chalcogenide glasses. Radial electron distribution functions (Fig. 2) in doped and undoped bulk glasses were obtained and analyzed [10].

3.2. Raman spectra

From Fourier Raman spectra information (Fig. 3) on the structural changes in As–S glasses doped with transitional metals was obtained. Introduction of such dopants leads to the concentration increase of non-stoichiometric molecular fragments (such as As_4S_4, etc.).

Introduction of manganese leads to the intensity increase of 192, 227, 236, 365 cm^{-1} bands that correspond to the vibrations of non-stoichiometric molecular fragments As_4S_4. Intensity of band near 496 cm^{-1}, characteristic for vibrations of S–S bonds is decreasing. In 130–190 cm^{-1} range bands appear, that can be connected with the creation of new sulphur containing structural units, similar to MnS molecular fragments [6,11]. The main feature of Raman spectra under the introduction of manganese

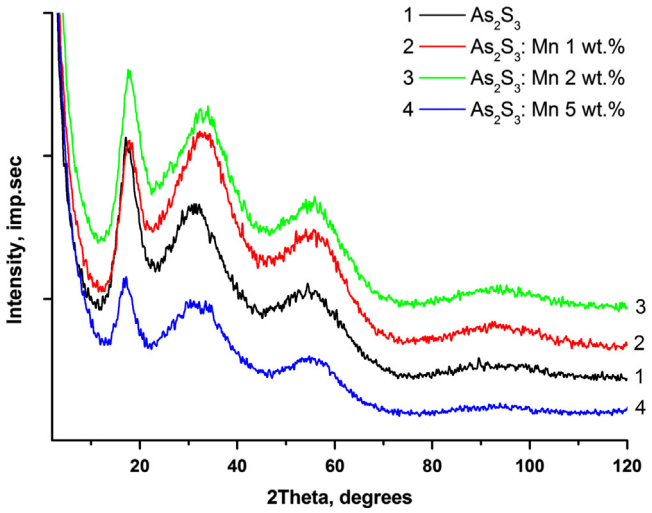

Fig. 1. X-ray diffraction patterns of As_2S_3 doped by Mn. Spectra are shifted on equal distance in order of appearance.

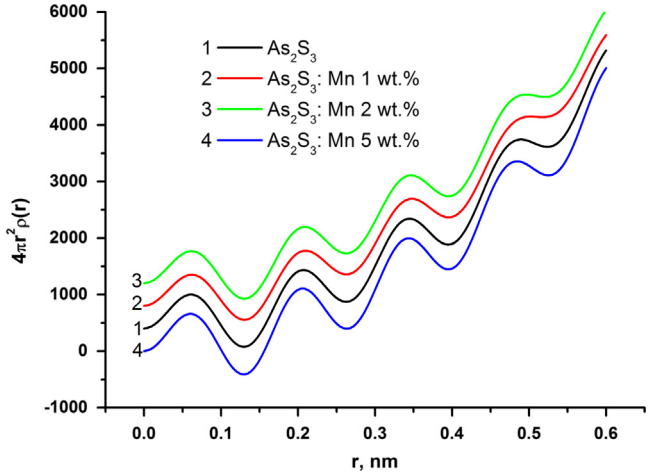

Fig. 2. Curves of radial electron distribution function of As_2S_3 doped by Mn. Curves are shifted on equal distance in order of appearance.

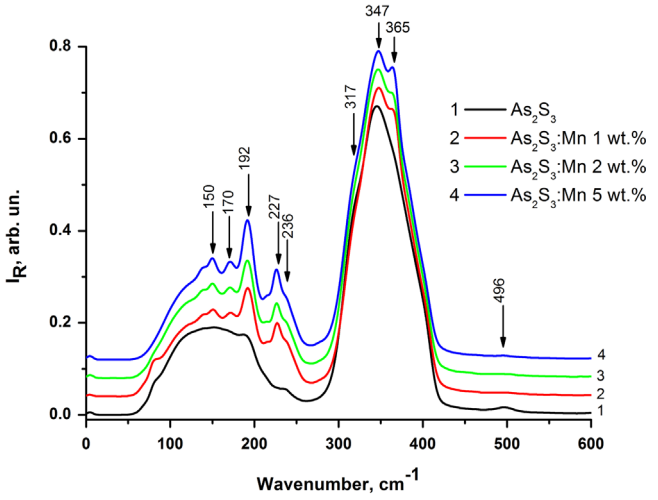

Fig. 3. Raman spectra of Mn doped As_2S_3 glasses. Spectra are normalized on intensity at value 347 cm^{-1} and shifted on equal distance in order of appearance.

Table 1
Positron annihilation lifetimes and corresponding intensities for As_2S_3–Mn glasses (the shortest lifetime component is fixed, $\tau_1 = 0.20$ ns).

PALS parameters	τ_1 (ns)	I_1	τ_2 (ns)	I_2	τ_3 (ns)	I_3	FIT
As_2S_3	0.20	0.14	0.36	0.84	2.4	0.02	1.25
As_2S_3:Mn 1 wt%	0.20	0.33	0.36	0.65	2.6	0.02	1.05
As_2S_3:Mn 5 wt%	0.20	0.46	0.36	0.51	2.7	0.03	1.01

Note: Lifetime τ_3 and intensity I_3 are due to the source contribution but not the sample.

into As_2S_3 glass matrix is in the change of relative concentration of the main and non-stoichiometric structural elements typical for As_2S_3 glasses [12].

3.3. Positron annihilation spectroscopy

Two-state positron trapping model [13] was used for analysis. Positron lifetime is sensitive to the defects and structural non-uniformities which are present in vitreous matrix. Thermalized positrons can be trapped and annihilate on vacancies (free volume) which gives information on the local electronic environment around defect.

Data presented in Table 1 shows the following:

- Defect related component τ_2 is found to be independent on Mn content within experimental uncertainties. It means that the size of voids, which serve as trapping centers for positrons, is the same to be independent on Mn additives into As_2S_3 host.
- At the same time, the intensity I_2 shows changes with Mn content. Namely, I_2 decreases with Mn additives into As_2S_3. Intensity I_2 is not directly proportional to concentration of voids, but decreasing of I_2 may indicate on some rearrangement of voids in the course of the reduction of their concentration.

3.4. Optical properties in mid-IR

Investigation of influence of transition metals (Mn) dopants on the optical properties of As_2S_3 glass was studied in mid-IR region. Room temperature IR impurity absorption spectra in 700–4000 cm^{-1} region for chalcogenide As_2S_3 glasses of doped with manganese (1, 2, 5 wt%) have been studied. Intensity of the vibrational absorption bands of various structural molecular fragments essentially depends on the chemical composition of glasses. The observed changes upon doping with Mn in the mid-infrared region are most likely related to interactions of a portion of the introduced metal ion impurities with the inherent impurities of the host glass, such as hydrogen and oxygen atoms. It has been established that As atoms are responsible for absorption of molecular water H_2O, whereas S atoms—for hydrogenous groups (OH). The $-S-H$ and $-S-OH$ are stabilized in the glass structural network as the products of closing of S "dangling" bonds and $-S-H$ groups are formed on the internal surfaces of microvoids, created technologically during samples preparation. The observed absorption bands [14] in Fig. 4 were identified using previous experimental results (Table 2).

3.5. DSC measurements

As–S chalcogenide glasses doped with Mn (1, 2, 5 wt%) have been investigated by differential scanning calorimetry. The glass transition temperature T_g was determined for all compositions. Data are presented in Table 3. Thermograms for As_2S_3 with different content of Mn dopants (heating rate—10 K/min) are shown in Fig. 5. With the increase of heating rate T_g value is shifted towards higher temperatures.

For the analysis of T_g dependence on heating rate α two approaches were used. First—empirical relation:

$$T_g = A + B \times \log \alpha, \quad (1)$$

where A and B—constants. Values of A and B for different glasses are presented in Table 4.

Dependence of T_g on $\log\alpha$ is shown in Fig. 6. A value equals glass transition temperature value at 1 K/min., and B—constant which characterize glass composition, frequently B slope is

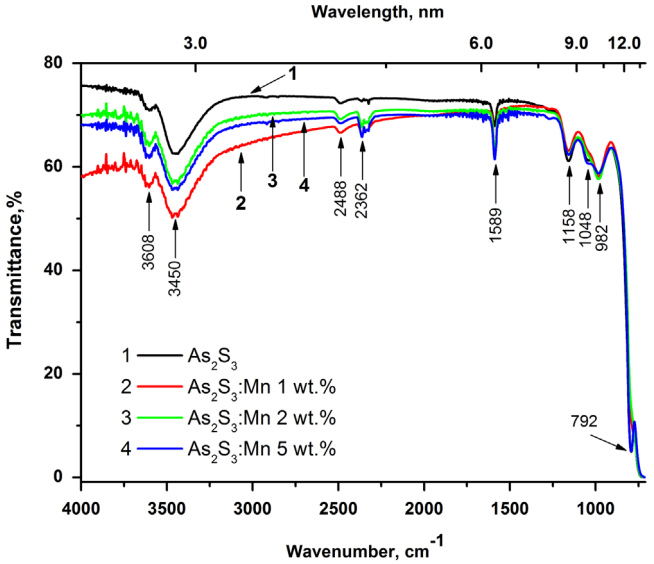

Fig. 4. Mid-infrared transmission spectra of As_2S_3 doped by Mn.

Table 2
Assignments of characteristic vibrational bands for vitreous As_2S_3 doped by Mn.

Glass composition	Infrared frequency (cm^{-1}) and assignments										
	O–H	H_2O	S–H	CO_2	CO_2	H_2S or CO_2	H_2O	SO_2	As–O	As–O As–H or As–S S–S	AsO_4
As_2S_3	3601	3450	2488	–	2346	2323	1589	1158	1048	982	792
As_2S_3:Mn 1 wt%	3608	3450	2487	2361	2342	–	1587	1159	–	981	–
As_2S_3:Mn 2 wt%	3605	3451	2486	2361	2343	2324	1588	1158	–	982	–
As_2S_3:Mn 5 wt%	3607	3451	2488	2362	2343	2324	1588	1157	1048	981	792

Table 3
Glass transition temperature dependence T_g of As_2S_3 glasses doped by Mn on manganese concentration.

Mn content (wt%)	1	2	5
Glass transition temperature T_g (K)	471	468.5	465

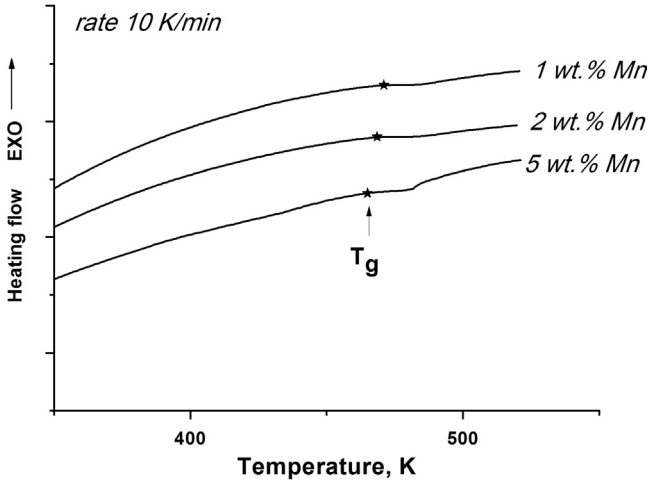

Fig. 5. Thermograms for As_2S_3 with different Mn content. Heating rate—10 K/min.

Table 4
Kinetic parameters of glass transition.

Composition of glasses	Parameters of Eq. (1)		Parameter of Eq. (2)
	A (K)	B (min)	E_a (kJ/mol)
As_2S_3	178.9	29.8	142
As_2S_3:Mn 1 wt%	175.6	22.2	141
As_2S_3:Mn 2 wt%	172.8	22.9	140
As_2S_3:Mn 5 wt%	171.1	21.1	130

connected with melt cooling rate: the slower cooling rate the smaller B value.

Physical essence of B is in response of configuration changes in temperature range of glass transition and means that at different B values glasses undergo different structural configurations. The other approach for T_g analysis is using

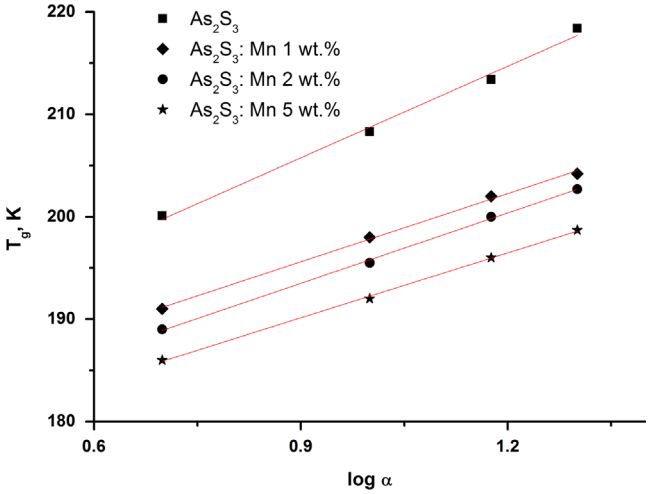

Fig. 6. T_g vs. logα for As_2S_3 glasses with different content of Mn.

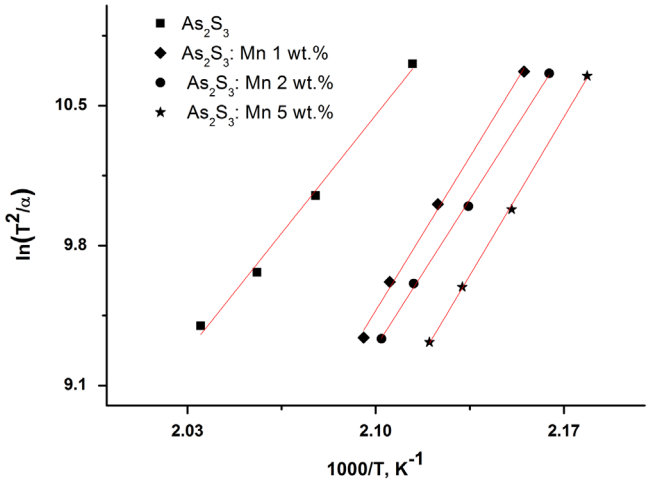

Fig. 7. Dependence of $\ln(T_g^2/\alpha)$ vs. $(1000/T_g)$ for As_2S_3 glasses with different content of Mn.

Kissinger's formula:

$$\ln\left(\frac{T_g^2}{\alpha}\right) = \frac{E_a}{RT_g + \text{const}}, \quad (2)$$

where E_a—activation energy of glass transition. Dependence of $\ln(T_g^2/\alpha)$ on $(1000/T_g)$ for As_2S_3 glasses with different level of Mn content is presented in Fig. 7. From data of Fig. 7. it is possible to estimate activation energy of glass transition. E_a

values are presented in Table 4. As can be seen from the obtained data with the increase of Mn doping level of As_2S_3 glasses glass transition temperature is decreased and also activation energy of glass transition is decreased. That can be connected with structural changes due to interaction of Mn with As_2S_3 glass matrix which was considered using data of Raman and X-ray diffraction measurements [11].

3.6. Magnetic properties

Chalcogenide glasses are diamagnetics, in particular glass of As_2S_3 composition (Fig. 8). Introduction of Mn dopant changes magnetic properties of glasses. Thus in constant magnetic field ($B=6$ T) dependence of mass magnetization $M=M(T)$ is observed which is characteristic for paramagnetics and ferromagnetics in paramagnetic region of temparature (Fig. 9) and described by Curie–Weiss law [15]. Differences between the $M(T)$ dependences for ZFC and FC curves [8] remain up to the value of the external field $B=468\times10^{-4}$ T, and this difference disappears in a field $B=197\times10^{-3}$ T. This gives a possibility to consider that influence of the external field on the orientation of the intrinsic magnetic moments of the dopant atoms in the energy value exceeds the energy of their thermal movement. At $T=5$ K the differences in the values of the specific magnetic moment for ZFC and FC branches depend on the magnitude of magnetic field (Table 5).

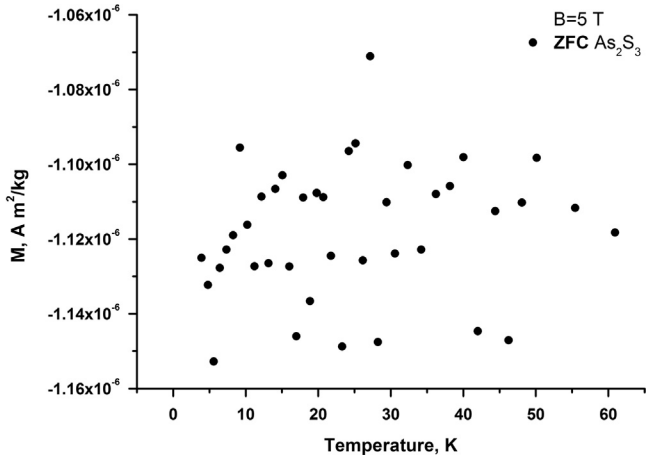

Fig. 8. Dependence of mass magnetization M vs. T of As_2S_3. in magnetic field 5 T.

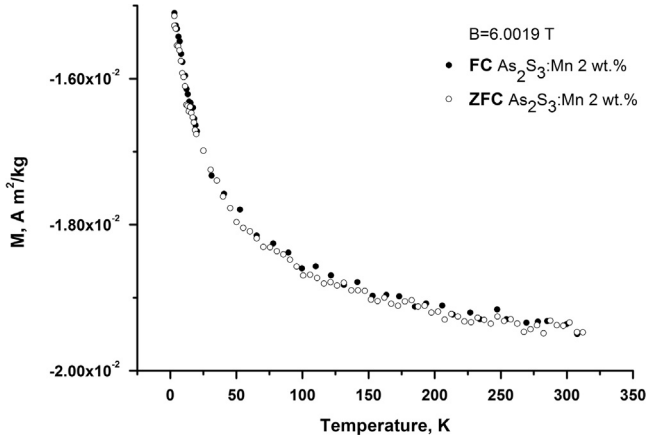

Fig. 9. Dependence of mass magnetization M vs. T of As_2S_3: Mn 2 wt% in magnetic field 6 T.

Measurements of magnetic properties (temperature dependence of the specific magnetic moment) were performed under the different conditions of sample cooling. A sample was cooled in zero external magnetic field; then, the magnetic-field with specified magnitude was set. In the following, the magnetic-field was maintained constant during the sample heating. The interval of temperature variation was chosen in such a way that the maximal value of temperature exceeded the temperature of transition into the paramagnetic state. Hereinafter, such dependences are denoted as ZFC. Further, the sample was cooled in the magnetic field and $M=M(T)$ was obtained, denoted as FC in figures.

4. Conclusions

Optical, thermal and magnetic properties of chalcogenide glasses can be changed by doping of transitional metals. This can be used for the creation of nanocomposites on the base of chalcogenide glasses with new properties, optimization of sensitivity, stability improving of registering media on their base, etc. Perspective direction of application is sensor technique and fabrication of optical elements with the use of registering media on the base of such glasses for optics, optoelectronics and integrated optics.

Acknowledgements

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Table 5
Dependence of mass magnetization on the magnetic field.

Mass magnetization M (A m^2/kg)	Magnetic field B, $\times10^{-4}$ T				
	5	10	80	468	1970
FC As_2S_3:Mn 2 wt%	8×10^{-5}	1×10^{-4}	1.6×10^{-4}	1.6×10^{-4}	1.6×10^{-4}
ZFC As_2S_3:Mn 2 wt%	2×10^{-5}	2.5×10^{-5}	8×10^{-5}	1.4×10^{-4}	1.6×10^{-4}
FC As_2S_3:Mn 5 wt%	3.8×10^{-4}	5.8×10^{-4}	4.5×10^{-3}	3.5×10^{-3}	4.7×10^{-3}
ZFC As_2S_3:Mn 5 wt%	1.2×10^{-4}	1.5×10^{-4}	6.27×10^{-4}	2.7×10^{-3}	4.7×10^{-3}

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