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### Photoemission studies of $Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.5-x}Si_x$ bulk compounds exhibiting giant magnetocaloric effect

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Magnetocaloric materials exhibiting large magnetocaloric effect (MCE), due to their possible application in magnetic cooling devices, have been recently widely studied. [1] Prominent advantages of magnetocaloric materials over the currently used vapor compression-expansion technique results from its high efficiency and environmental compatibility.

An interesting group of compounds exhibiting giant MCE are compounds belonging to the large  $MM'X$  family of materials (M and M' - 3d/4d/5d transition metal and X - p-block element). The  $MM'X$  group of compounds shows large entropy changes in a wide temperature range near room temperature [2, 3]. Our studies are focused on compounds from the  $MnFe(As,P,Si)$  system exhibiting giant MCE.

The electronic structure of obtained with the use of Spark Plasma Sintering (SPS) technique bulk compounds  $Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.5}$ ,  $Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.4}Si_{0.1}$  and  $Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.45}Si_{0.05}$  was studied with the use of X-ray photoelectron spectroscopy. Obtained results have been confronted with the magnetic and structural properties of the compounds.

The X-ray diffraction studies showed single phase structure of the  $Fe_2P$  type.

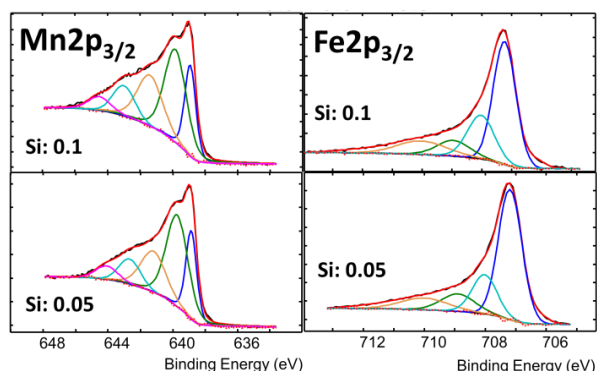


Figure 1. Mn2p and Fe2p high resolution photoemission spectra.

The atomic concentrations of both samples indicate that the iron content in the samples is undervalued in relation to nominal composition. High resolution photoelectron spectra of Fe2p, O1s, Mn2p, Si2p, As3d, P2p and valence band have been collected from fractured in UVH sample surfaces. The analysis was focused on determination of chemical states of sample components; it indicates that iron and manganese are in metallic state, however in case of manganese some traces of oxides have been observed (see Fig. 1).

Further structural characterization was realized with the use of Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS, ION OTF TOF.SIMS5 spectrometer). In this part of our studies we focused on microstructure of the compounds investigating the distribution of the  $[Mn, Fe, P, Si, As]^{+/-}$  ions. Analysis of the microstructure (TOF-SIMS) revealed inhomogeneity within the distribution of Mn, Fe, Si, P ions (see. Fig 2). On both samples Si exhibit tendency to segregation in the form of ~1-2micron precipitates.

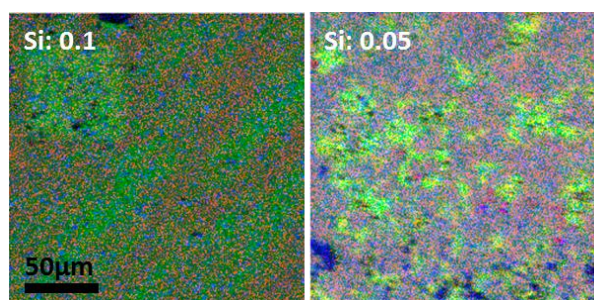


Figure 2. Overlay of distribution maps Fe2+ (red), Mn+ (green), Si+ (blue). Particular distribution maps were normalized.

The highest MCE exhibit undoped  $Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.5}$  sample, it shows adiabatic temperature change of about 4 K at field of 1.7 T. However Si-doped samples prepared by the SPS method also exhibit high MCE for the Si=0.1 adiabatic temperature change of about 3.8K and for the Si=0.05 of about 3K. Partial oxidation of manganese and nonuniformity in the distribution of particular elements affects MCE properties of Si doped samples; however the MCE effect still remains giant.

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