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Preparation and characterization of $(CuInTe_2)_{1-x}(TaTe)_x$ solid solutions (0<x<1)

P. Grima-Gallardo [a, b, *], O. Izarra [a], L. Méndez [b], S. Torres [b], M. Quintero [a], H. Cabrera [c, d], E. Pérez-Cappé [e], I. Zumeta-Dubé [f], A. Rodríguez [f], J.A. Aitken [g], D.P. Rai [h]

[a] Centro de Estudios en Semiconductores (CES), Departamento de Física, Facultad de Ciencias, Universidad de Los Andes (ULA), Mérida, Venezuela
[b] Centro Nacional de Tecnología Óptica (CNTO), Mérida, Venezuela
[c] SPIE-ICTP Anchor Research in Optics Laboratory, International Centre for Theoretical Physics (ICTP), Trieste, Italy
[d] Centro Multidisciplinario de Ciencias, Instituto Venezolano de Investigaciones Científicas (IVIC), Mérida, Venezuela
[e] Instituto de Ciencia y Tecnología de Materiales (IMRE), Universidad de La Habana, Vedado, Cuba
[f] Instituto Politécnico Nacional, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Unidad Legaria, México D.F, Mexico
[g] Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, USA
[h] Department of Physics, Pachhunga University College, Aizawl, 796001, India

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ABSTRACT

Polycrystalline samples of the $(CuInTe_2)_{1-x}(TaTe)_x$ alloys system were prepared by the melt and anneal technique in the composition range $0 < x < 1$. Products were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Thermal Analysis (DTA) and SQUID techniques. From XRD and SEM, it was found that the solubility of TaTe in $CuInTe_2$ is around 10%; however, samples up to $x = 2/3$ are composed by a mean tetragonal $CuInTe_2$-like phase with traces of Ta_2Te_3. Samples with $x > 2/3$ show diffraction patterns with several phases with poor crystallization. In addition, the tetragonal $CuInTe_2$-like phase shows spinodal decomposition i.e. there are two phases, one Ta-rich and the other Ta-poor, with the same crystal structure and very close lattice parameters. SEM measurements also show up to six different phases, although they do not produce observed diffraction line in powder XRD patterns.

DC magnetic susceptibility measurements as a function of temperature using the ZFC-FC protocol were performed in samples with $x \leq 2/3$. With the exception of $x = 2/3$, all samples show a similar behavior in the ZFC and FC curves which are typical of a system with a distribution of magnetic cluster sizes. Sample $x = 2/3$ shows ferromagnetic behavior with $T_c = 50$ K. For sample $x = 1/4$, measurements of the magnetization as a function of the applied magnetic field and temperature were performed. From the analysis of the curves it was found that the clusters contain 10^5 Ta-atoms and a coercitive field of 0.22 kOe at $T = 5$ K.

1. Introduction

Spintronics exploits the spin of the electron rather than its charge to create a new generation of devices, which will be smaller, more versatile and more robust than those currently making up silicon chips and circuit elements [1,2]. Due to these great advantages, intensive attention has been paid to semiconductors with potential room temperature ferromagnetism (RT-FM), including $A^{II}B^{IV}C^{V}_2$ and $A^{I}B^{III}C^{VI}_2$ chalcopyrite semiconductors, doped or alloyed with transition metals (TMs). Most of the experimental and theoretical investigations has been based on the use of Mn as TM since the electronic structure of this element ([Ar] $3d^5\ 4s^2$) looks very appropriate for the substitution of cations in the ternary matrix of chalcopyrite compounds [3–19]. Additionally, in particular for $A^{I}B^{III}C^{VI}_2$ compounds, substitution with other TMs, such as Fe, Cr, Co, Ni and Ta has been also investigated [13,20–26]. Details about alloy system investigated, included composition, preparation and magnetic behavior are show in Tables 1 and 2.

By inspection of Tables 1 and 2, it can be noted that RT-FM has only been observed in several $A^{II}B^{IV}C^{V}_2$ compounds doped with Mn, whereas for $A^{I}B^{III}C^{VI}_2$ doped or alloyed with any TMs there are no

* Corresponding author. Centro de Estudios en Semiconductores (CES), Departamento de Física, Facultad de Ciencias, Universidad de Los Andes (ULA), Mérida, Venezuela.
E-mail address: peg@ula.ve (P. Grima-Gallardo).

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Table 1
Chalcopyrite compounds doped or alloyed with Mn.

Alloys	Magnetic element composition	Synthesis method	Magnetic behavior	T_c [K]	Reference
$A^{II}B^{IV}C^{V}_2$					
$Cd_{1-x}Mn_xGeP_2$	$x = 0.2$	SSR	FM	300	[3]
$Zn_{1-x}Mn_xGeP_2$	$x = 0.056$	SSR	FM	312	[4]
$(ZnGe)_{1-x}Mn_xAs_2$	$x = 5$ mass %	BM	FM	333	[5]
$(ZnSn)_{1-x}Mn_xAs_2$	$x = 1.2$ mass %			329	
$(CdGe)_{1-x}Mn_xAs_2$	$x = 6$ mass %	SSR	FM	355	[6]
$(ZnGe)_{1-x}Mn_xAs_2$	$x = 3.5$ mass %	SSR	FM	367	[7]
$(ZnSi)_{1-x}Mn_xAs_2$	$x = 1$ mass %	SSR	FM	325	[8]
	$x = 2$ mass %			337	
$Zn_{1-x}Mn_xGeAs_2$	$x = 0.078$	SSR	FM	320	[9]
$(Zn_{0.9}Cd_{0.1})_{1-x}Mn_xGeAs_2$	$x = 1.13$ mass %	SSR	FM	349	[10]
	$x = 2.65$ mass %			351	
AIBIIICVI2					
$Cu_{1-x}Mn_xInTe_2$	$x = 0.03$ and 0.06	SSR	PM	–	[11]
	$x = 0.09$ and 0.12		AFM		
$(CuIn)_{1-x}Mn_{2x}Te_2$	$0.010 \leq x \leq 0.101$	BM	SG	–	[12]
$CuIn_{1-x}Mn_xS_{2-x}$	$x = 0$, 0.05, 0.1 and 0.2	SSR	AFM	–	[13]
$Cu_{x/2}In_{x/2}Mn_xS_2$	$x = 0.1$				
$CuIn_{1-x}Mn_xS_2$	$x = 0–0.2$	SSR	PM	–	[14]
$Cu_{1-x}Mn_xInS_2$	$x = 0–0.1$				
$Cu_{1-x}Mn_xInS_2$	$x = 0–0.20$	SSR	PM	–	[15]
$Cu_{0.95-x}Mn_{0.05}InSe_2$					
$CuIn_{1-x}Mn_xSe_2$	$x = 0.0125–0.2$	SSR	PM	–	[16]
$Cu_{1-y}In_{1-y}Mn_{2y}Se_2$	$2y = 0.0125–0.6$				
$Cu_{x/2}Ga_{x/2}Mn_xTe_2$	$x = 0.2$	SSR	SPM	–	[17]
$Cu_{1-x}Mn_{2x}InS_2$	$x = 0.03$	SSR	PM + FM	–	[18]
$Cu_{1-x}Mn_{2x}AlS_2$	$x = 0.01$				
$CuGa_{1-x}Mn_xTe_2$	$x = 0.004$, 0.008, 0.010 and 0.012	SSR	SPM	–	[19]

T_c: critical temperature (magnetic transition temperature from paramagnetic to ferromagnetic).
SSR: Solid State Reaction; BM: Bridgman Method; PM: Paramagnetic; AFM: Antiferromagnetic; SG: Spin Glass; SPM: Superparamagnetic; FM: Ferromagnetic.

Table 2
$A^{I}B^{III}C^{VI}_2$ compounds doped or alloyed with TMs different than Mn.

Alloys	Magnetic element composition	Synthesis method	Magnetic behavior	T_c [K]	Ref.
$CuIn_{1-x}Fe_xS_2$	$x = 0.1$	SSR	AFM	–	[13]
$(CuIn)_{1-x}Fe_xTe_{2-x}$	$x = 0.5$	SSR	SPM	–	[20]
$(CuGa)_{1-x}Fe_xTe_{2-x}$					
$(CuIn)_{1-x}Fe_xSe_{2-x}$	$x = 0.5$	SSR	SPM	–	[21]
$(CuAl)_{1-x}Cr_xS_{2-x}$	$x = 0.1$ and 0.2	SSR	AFM	–	[22]
	$x = 0.33$				[23]
$(CuIn)_{1-x}Co_xTe_{2-x}$	$x = 0.67$	SSR	SPM	–	[24]
$(CuIn)_{1-x}Ni_xTe_{2-x}$			DM + FM		
$(CuIn)_{1-x}Ta_xTe_{2-x}$	$x = 0.25$	SSR	SPM	–	[25]
$(CuIn)_{1-x}Ta_xSe_{2-x}$	$x = 0.25$	SSR	SG	50	[26]
$(CuIn)_{1-x}Ta_xTe_{2-x}$	$x = 2/3$		FM		

SSR: Solid State Reaction; DM: Diamagnetic; AFM: Antiferromagnetic; SG: Spin Glass; SPM: Superparamagnetic; FM: Ferromagnetic. T_c: critical temperature (transition temperature from paramagnetic to ferromagnetic).

reports of RT-FM.

RT-FM is thought to arise from the interaction of holes (created by substitution of B^{IV} or B^{III} cations) with the local moment of the *d* electrons of TMs^{2+} [27,28]; however it is also argued that it is due by the presence of magnetic secondary phases such as MnP and MnAs [28–32]. Kochura et al. (2013), in samples prepared by solid state reaction under the condition of fast cooling, found that there exist three types of magnetic species in $A^{II}B^{IV}C^{V}_2$: Mn alloys: a) substitution of Mn ions making Mn complexes (especially dimers), b) MnAs micro-precipitates and c) MnAs nanosize precipitates (clusters with a mean diameter of 3 nm) [29].

Although the origin of RT-FM is until now under investigation, it seems well established that the magnetic behavior in $A^{II}B^{IV}C^{V}_2$: Mn alloys is composition dependent: at low values of x, the alloy shows a typical paramagnetic behavior (or also superparamagnetic) [6,8] whereas for higher values of x, a critical x_c value is attained for which, the paramagnetic→ferromagnetic transition occurs. It is also worth to note here that T_c values are approximately the same for all $A^{II}B^{IV}C^{V}_2$: Mn alloys suggesting that this transition is related to Mn-based secondary phases more than substitution of cations for Mn^{2+} in the ternary matrix.

It is interesting to compare experimental results with those obtained by theoretical calculations. Katamani et al. (2003) [33,34] using KKR-CPA-LDA method predict that ferromagnetic states are stable in $(Cd_{1-x}V_x)GeP_2$ and $(Cd_{1-x}Cr_x)GeP_2$, alloys whereas $(Cd_{1-x}Mn_x)GeP_2$, $(Cd_{1-x}Fe_x)GeP_2$ and $(Cd_{1-x}Co_x)GeP_2$ alloys must show spinglass-like ground states (calculations were made using $x = 0.1$); Ti and Ni substitutions in $CdGeP_2$ could not have a net magnetic moment (the same are applicable to $ZnGeP_2$ and $CdSiAs_2$). On the other hand, the ferromagnetic state was found to be stable in $AgGaS_2$ ($CuAlS_2$) doped with Ti, V, Cr and Mn, whereas doping with Fe, Co and Ni must stabilizes a spinglass-like state. The work of Zhao et al. (2004) [35], using first principle calculations, coincides with Katamani and predicts that Mn doping at the III site in $A^{I}B^{III}C^{VI}_2$ compounds provides holes that must stabilize ferromagnetic coupling between Mn ions. The predictions of both works