Sr and Mn co-doped LaCuSO: a wide band gap oxide diluted magnetic semiconductor with \( T_C \) around 200 K

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Here we report the synthesis of a bulk oxide diluted magnetic semiconductor (DMS) system \( \text{La}_{1-x}\text{Sr}_x\text{Cu}_{0.925}\text{Mn}_{0.075}\text{SO} \) \((x = 0, 0.025, 0.05, 0.075 \text{ and } 0.1)\). As a wide band gap p-type oxide semiconductor, LaCuSO satisfies all the conditions forecasted theoretically to be a room temperature DMS. The Curie temperature \((T_C)\) is around 200 K as \( x \geq 0.05 \), which is among the highest \( T_C \) record of known bulk DMS materials up to now. The system provides a rare example of oxide DMS system with p-type conduction, which is important for formation of high temperature spintronic devices.

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The discovery of ferromagnetism in Mn-doped GaAs has drawn researchers to the field of Diluted Magnetic Semiconductor (DMS), which makes it possible to examine tremendous phenomena such as quantum Hall effects, semiconductor lasers and single-electron charging, and could bring about numerous applications in sensors and memories as well as computing with electron spins. However, the most applications are restricted by the low ferromagnetic transition temperature of III-V semiconductor based DMS. Followed by the observation of ferromagnetism in dilutely cobalt doped TiO$_2$, much attention was paid to oxide DMS systems, and room-temperature ferromagnetism was realized in oxide DMS systems, though the field has not yet reached the same level of maturity and clarity about the attendant phenomena as the III-V semiconductor based DMS. Owing to a limited number of p-type oxide systems are available and the difficulties encountered in converting natural n-type oxides such as ZnO to p-type conduction by doping, there have been only a limited number of studies on p-type oxide DMS systems. More work on p-type materials should be interesting, and p-type wide band gap oxide DMS systems are important for formation of spintronics devices.

Due to the limitation of the chemical solubility of Mn, most of the DMS systems are chemically metastable, and available only as thin films. Accordingly, the quality of the thin film material depends sensitively on the preparation methods and heat treatments. Only the bulk crystalline specimens make it possible to perform muon spin relaxation ($\mu$SR), nuclear magnetic resonance (NMR) and even neutron scattering. Therefore the bulk DMS materials are highly required to obtain more reliable results. Recently, a Mn doped pnictide Li(Zn,Mn)As was reported to be a bulk DMS material with a Curie temperature ($T_C$) of about 50 K. Layer-structured pnictides thus become a promising avenue for exploring bulk DMS materials.

LaCuSO was initially prepared through oxidation of LaCuS$_2$, and its crystal structure was determined as the tetragonal ZrCuSiAs-type (also called 1111 type), which is identical to that of LaFeAsO, a typical parent compound of the 1111 type iron-based pnictide superconductor. LaCuSO is a wide band gap (3.1eV) p-type conductive oxysulfides semiconductor and it can become metallic with Sr doping. Apparently, as a wide band gap p-type oxide semiconductor, LaCuSO is an attractive candidate for p-type oxide DMS. There are a few theoretical studies on Mn doped LaCuSO, but only the samples with low Mn doping level were experimentally synthesized, and no ferromagnetism was found.
which should be due to the low Mn concentration and low charge carrier density. Moreover, LaCuSO is important to transparent p-n junctions and optoelectronic devices.\textsuperscript{24,25}

Here we report the synthesis of a bulk p-type oxide DMS in the Sr and Mn co-doped La\textsubscript{1-x}Sr\textsubscript{x}Cu\textsubscript{0.925}Mn\textsubscript{0.075}SO (\(x = 0, 0.025, 0.05, 0.075\) and 0.1) system. The La\textsubscript{1-x}Sr\textsubscript{x}Cu\textsubscript{0.925}Mn\textsubscript{0.075}SO (\(x = 0, 0.025, 0.05, 0.075\) and 0.1) system exhibits ferromagnetic order with \(T_C\) around 200 K, which is among the highest \(T_C\) record of known bulk DMS materials up to now.\textsuperscript{7–11,26–28} By contrast, due to the low solubility limit of Mn (<0.5 mol %), Mn doped LaCuSeO does not exhibit intrinsic ferromagnetism\textsuperscript{13}. As a wide band gap p-type conductive oxysulphide semiconductor, LaCuSO satisfies all the conditions forecasted by Dietl \textit{et al.} to be a room temperature DMS.\textsuperscript{3,13} We expect that the solubility of Sr and Mn can be raised to a higher level with epitaxy and/or nanotechnology, and a room temperature p-type oxide DMS may be realized in thin films and/or nanostructured materials. Our discovery makes the formation of high temperature spintronics p-n junction devices become possible.

The polycrystalline samples with nominal formula La\textsubscript{1-x}Sr\textsubscript{x}Cu\textsubscript{0.925}Mn\textsubscript{0.075}SO (\(x = 0, 0.025, 0.05, 0.075\) and 0.1) were synthesized by solid state reaction method.\textsuperscript{29} All the starting material, La ingot, the powders of La\textsubscript{2}O\textsubscript{3}, Cu, Mn, S and SrS are of high purity (99.9%). First, the La ingot was grounded to powder by hand. The powders of these materials were weighted according to the stoichiometric ratio, and then thoroughly mixed in an agate mortar. The mixtures were pressed into pellets under a typical pressure of 2000 kg cm\textsuperscript{-2}. All these processes were operated in a glove box filled with high-purity argon. The pellets were put into crucibles and sealed in evacuated quartz tubes, then heated up with a ramping rate of 0.5 K/min to 1223 K and kept at that temperature for 2000 min, and finally furnace cooled to room temperature.

Powder x-ray diffraction (XRD) was performed at room temperature using a PANalytical x-ray diffractometer (Model EMPYREAN) with a monochromatic CuK\textsubscript{a1} radiation. The XRD diffractometer system was calibrated using standard Si powders. The detailed structural parameters were obtained by Rietveld refinement using step-scan (4 s/step) data. The dc magnetization measurement was carried out on a Quantum Design magnetic property measurement system (MPMS-5) employing both zero-field-cooling (ZFC) and field-cooling (FC) protocols. For the measurement of isothermal magnetization, the magnetic field was applied in a field sweep mode. The thermopower was measured by a steady-state technique. Figure 1(a) displays the X-ray diffraction patterns of La\textsubscript{1-x}Sr\textsubscript{x}Cu\textsubscript{0.925}Mn\textsubscript{0.075}SO for \(x =\)
FIG. 1. (a), (color line) Room-temperature XRD patterns of La$_{1-x}$Sr$_x$Cu$_{0.925}$Mn$_{0.075}$SO ($x = 0$, 0.025, 0.05, 0.075 and 0.1) compounds. *, † and ‡ denote the minor peaks due to impurity phases SrS, (La,Sr)MnO$_3$ and MnS (Alabandite), respectively. The impurity phase of (La,Sr)MnO$_3$ can only be detected for $x = 0.1$ sample (indicated by †). Inset of (a) exhibits the variation of lattice constants $a$ (squares) and $c$ (circles) with Sr doping content ($x$). (b), Rietveld refinement of the powder X-ray diffraction for the $x = 0.05$ sample. Inset of (b) shows the crystal structure of (La,Sr)(Cu,Mn)SO belonging to the tetragonal ZrCuSiAs-type structure.

0, 0.025, 0.05, 0.075 and 0.1, respectively, and Fig. 1(b) shows a representative Rietveld refinement of the sample with $x = 0.05$. All the peaks are assigned the same as those for the LaCuSO phase and can be well indexed based on the P4/nmm (No. 129) space group with tetragonal ZrCuSiAs-type structure, except a few minor peaks assigned as impurity phases, which indicates that the samples are mostly composed of single phases (more than 99%). For $x = 0.1$, a trace of (La,Sr)MnO$_3$ can be detected (indicated by † in Fig.1(a)). More information on the solubility of Mn in LaCuSO can be found in the supplementary material. The lattice parameters of the samples were obtained by Rietveld refinement, as shown in the inset of Fig. 1(a), both the $c$-axis and $a$-axis expand slightly with increasing
Sr content ($x$). This should be due to the slightly larger ionic radius of Sr$^{2+}$ compared with La$^{3+}$. The Rietveld refinement of $x = 0.05$ sample based on the ZrCuSiAs-type structure shows that the calculated profile well matches the experimental data. The weighted reliable factor $R_{wp}$ and the goodness of fit $S$ are 9.04% and 1.34, respectively, indicating a good refinement. The inset of Fig. 1(b) exhibits the crystal structure of LaCuSO which belongs to tetragonal ZrCuSiAs-type structure.

The temperature dependence of electrical resistivity of La$_{1-x}$Sr$_x$Cu$_{0.925}$Mn$_{0.075}$SO ($x = 0, 0.025, 0.05, 0.075$ and $0.1$) specimens is shown in Fig. 2(a). We used bar-shaped samples of typical sizes $2 \times 1 \times 0.5$ mm for transport property measurements. At least two sets of samples were checked for each doping level, and the results are consistent with each other within an error of 10%. The $x = 0$ sample is highly insulating, whose electrical resistivity ($\rho$) is as large as $2.8$ M$\Omega$ cm in the room temperature, and it increases drastically with decreasing temperature (it increases beyond our measurement limitation below 260
K). Other transport properties such as Hall and Seebeck coefficients are also difficult to measure due to the extremely low carrier density. With Sr doping, hole-type charge carrier can be introduced and resistivity decreases rapidly. Electrical resistivity of all the $x = 0.05, 0.075$ and 0.1 samples exhibits typical semiconductor behavior as well, i.e., it increases rapidly with decreasing temperature. As it will be shown below, the samples with a higher Sr doping level exhibit ferromagnetism with $T_C$ as high as 199 K. Namely, the $x = 0.05, 0.075$ and 0.1 samples are p-type oxide DMS. Fig. 2(b) displays the thermopower of $x = 0.05, 0.075$ and 0.1 samples. The positive thermopower indicates that p-type electrical conduction is dominant in these samples. The thermopower of $x = 0.05$ samples increases with decreasing temperature, consistent with the typical behavior of a semiconductor. With more Sr doping, the thermopower decrease drastically. The thermopower of $x = 0.075$ and 0.1 samples decreases with decreasing temperature, which deviates from the typical semiconductor behavior.

Figure 3 (a) shows the temperature dependence of dc magnetic susceptibility in zero-field-cooling (ZFC) and field-cooling (FC) procedures under $H = 1$ kOe for La$_{1-x}$Sr$_x$Cu$_{0.925}$Mn$_{0.075}$SO ($x = 0, 0.025, 0.05, 0.075$ and 0.1) samples, with solid symbols standing for FC and open ones for ZFC. Apparently the samples become ferromagnetically ordered. Denoted by arrows, the Curie temperatures ($T_C$), which are defined as the x-axis intercept of the linear fitting curves of the temperature dependence of inverse magnetic susceptibility $1/\chi$ (see the inset of Fig. 3(b)), are 92, 130, 180 and 199 K for $x = 0, 0.025, 0.05$ and 0.075 samples, respectively. When the Sr doping level ($x$) reaches 0.1, a long tail above 200 K can be observed, which may result from a tiny impurity phase (La,Sr)MnO$_3$. The Rietveld analysis shows that the impurity phase (La,Sr)MnO$_3$ is less than 0.3%. (La,Sr)MnO$_3$ is a ferromagnetic compound with $T_C$ of about 300 K. This impurity phase cannot be detected in the XRD patterns of the La$_{1-x}$Sr$_x$Cu$_{0.925}$Mn$_{0.075}$SO samples with low Sr content ($x < 0.1$). But it can be clearly found in the samples with either high Sr content or high Mn doping level (such as 0.1) specimens. $T_C$ of the $x = 0.1$ sample appears to be over 200 K. As shown in the inset of Fig. 3(b), a small deviation of linearity in $1/\chi$ above 280 K is probably due to the presence of trace amount of ferromagnetic (La,Sr)MnO$_3$ impurity. The $T_C$ increases with the Sr doping level ($x$), which should be proportional to the carrier density, indicating that the induction of hole-type charge carriers by Sr doping is crucial to the enhancement of FM order and that is consistent with the carrier-induced origin of the ferromagnetism.
FIG. 3. (a), Temperature dependence of dc magnetic susceptibility measured under $H = 1$ kOe for the La$_{1-x}$Sr$_x$Cu$_{0.925}$Mn$_{0.075}$SO ($x = 0, 0.025, 0.05, 0.075$ and $0.1$) specimens, with solid symbols standing for field-cooling (FC) and open ones for zero-field-cooling (ZFC). (b), Field dependence of magnetization measured at $T = 10$ K for La$_{1-x}$Sr$_x$Cu$_{0.925}$Mn$_{0.075}$SO ($x = 0, 0.025, 0.05, 0.075$ and $0.1$) samples. Inset: Plot of $1/\chi$ vs. $T$ and the determination of the Curie temperature $T_C$ is shown.

The magnetic hysteresis loop $M(H)$ curves of La$_{1-x}$Sr$_x$Cu$_{0.925}$Mn$_{0.075}$SO ($x = 0, 0.025, 0.05, 0.075$ and $0.1$) specimens at $T = 10$ K are shown in Fig. 3(b). Although the ferromagnetic hysteresis is small, the $M(H)$ curves exhibit typical FM behavior. The saturating magnetic moments reach $0.52, 0.30, 0.73, 0.65$ and $1.17 \mu_B$ per Mn atom at $H = 50$ kOe, for $x = 0, 0.025, 0.05, 0.075$ and $0.1$ samples, respectively, which are comparable with those in (Ga, Mn)As and Li(Mn, Zn)As. The observed magnetic moment strongly supports the bulk ferromagnetism and rules out the possibility that the magnetism is due to the impurity phase of (La, Sr)MnO$_3$, whose mass fraction is as small as $0.3\%$ (obtained by Rietveld refinement) for $x = 0.1$ and even undetectable for $x < 0.1$. For the sample with $x = 0.1$, the saturating magnetization is $0.13 \mu_B$/Mn at $T = 200$ K (not shown here) after subtracting the small $T$-linear contribution. The obtained saturating magnetic moments consistent with the fact
that the mass fraction of (La, Sr)MnO$_3$ is as small as 0.3%, assuming the ordered moment in (La, Sr)MnO$_3$ is $3 \sim 4 \mu_B$ per Mn atom.$^{31}$

A small $H$-linear component can be found in the $M(H)$ curves which may result from the remaining paramagnetic spins and/or field-induced polarization. Moreover, a divarication between the ZFC and FC curves is observed. Usually such a divarication can result from the magnetic hysteresis of FM ordered state. However, a magnetic glass state could have a similar divarication between the ZFC and FC curves.$^{32,33}$ The magnetic behavior demonstrated here should not result from the canonical spin glass (SG) systems since the samples still carry large magnetic moment down to 5 K.

In summary, a wide band gap p-type bulk oxide DMS system La$_{1-x}$Sr$_x$Cu$_{0.925}$Mn$_{0.075}$SO has been synthesized. The bulk specimens with suitable Sr and Mn doping (i.e., $x = 0.05, 0.075$) exhibit ferromagnetic order with $T_C$ around 200 K. The induction of hole-type charge carriers by Sr doping is crucial to the enhancement of FM order. LaCuSO satisfies all the conditions forecasted by Dietl et al.$^3$ for realizing room temperature DMS. It is expected that the solubility of Sr and Mn can be raised to a higher level with epitaxy and/or nanotechnology, and a room temperature DMS may be realized in thin films and/or nanomaterials. Our discovery makes the formation of high temperature spintronics p-n junction devices possible.

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30See supplementary material at [URL will be inserted by AIP] for the information on the solubility of Mn in LaCuSO.

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