New oxide diluted magnetic semiconductor
La$_{0.75}$Ca$_{0.25}$Cu$_{0.75}$Mn$_{0.25}$SO with independent spin and charge
doping by first-principle study

Haoze Chen$^1$, Linxian Li$^1$, Sheng Wang$^1$, Yuke Li$^2$, Jianye Chen$^1$, Li Zhang$^1$, *

$^1$China Jiliang University, Hangzhou, 310018, China
$^2$Hangzhou Normal University, Hangzhou, 310018, China

E-mail: lzhang6688@sina.com

Abstract. Here we report the first-principle study of a bulk oxide diluted magnetic semiconductor (DMS) La$_{0.75}$Ca$_{0.25}$Cu$_{0.75}$Mn$_{0.25}$SO and its parent LaCuSO. As a wide band gap p-type oxide semiconductor, LaCuSO system satisfies all the conditions forecasted theoretically to be a room temperature DMS, which is important for formation of high temperature spintronic devices. Then we compare the band gap and optical properties (such as loss function, reflectivity, absorption, the real part and the imaginary part of dielectric function) among LaCuSO, (La$_{0.75}$Ca$_{0.25}$)(Cu$_{0.75}$Mn$_{0.25}$)SO, (La$_{0.75}$Ba$_{0.25}$)(Ag$_{0.75}$Mn$_{0.25}$)SO and (Y$_{0.75}$Sr$_{0.25}$)(Cu$_{0.75}$Mn$_{0.25}$)SO. The results show that the band gap of LaCuSO system decreases most drastically with co-doped Ca and Mn (from 2.1 eV to 1 eV). As for the optical properties, both the position and intensity of the peaks changed most drastically, too. It illustrates that the energy band structure influences the optical properties.

I. Introduction

Diluted magnetic semiconductors have both the spin and charge properties of electrons, which are the material basis for the preparation of spin-optical devices, and are of great significance for the transmission, processing and storage of information. The earliest dilute magnetic semiconductor was II-VI diluted magnetic semiconductor. Since then, people have successively studied group III-V, II-VI and IV-VI family of diluted magnetic semiconductors and oxide dilute magnetic semiconductors. Due to the limitation of the chemical solubility of Mn, most of the DMS systems are available only as thin films. However, only the bulk crystalline specimens make it possible to perform muon spin relaxation (µSR), nuclear magnetic resonance (NMR) and even neutron scattering. Therefore, the bulk DMS materials are highly required.

Recently, a few of Mn doped pnictides such as Li(Zn,Mn)As, (Ba,K)(Zn,Mn)$_2$As$_2$, and (La,Sr)(Zn,Mn)SO were reported to be a bulk DMS materials[1]. Among them, LaCuSO is expected to be one of the candidate materials for optoelectronic devices in ultraviolet and/or blue regions, since it has a wide band-gap energy of 3.1 eV with an intense photoluminescence due to the interband transition at room temperature [2,3]. Therefore, in this paper, bulk DMSs based on LaCuSO (LaAgSO, YCuSO)
have been investigated by first-principle calculation in order to combine electricity, light and magnetism together for synthesizing devices. The first paragraph after a heading is not indented.

II. Calculation method and model construction

The CASTEP module in Material Studio was selected for calculation. The valence electrons of O, S, La, Cu, Mn and Ca were selected as O2s2p4, S3s23p4, La5d16s2, Cu3d104s1, Mn3d54s2 and Ca4s2, respectively. The convergence criterion of the optimization parameters in the calculation is single atomic energy, $1.0 \times 10^{-5}$ eV/atom, Max. Force, 0.3 eV/nm, the Max. stress, 0.05 GPa, Max. displacement, 0.0001 nm, through the convergence test, the plane energy cutoff is 380 eV, and the Monkhorst-Pack special K point is $4 \times 4 \times 4$.

The parent LaCuSO belongs to a tetragonal layered structure of the ZrCuSiAs-type with a space group P4/nmm, No.129, Z=2. $a$=b=3.99250 Å, $c=8.55250$ Å, $\alpha=\beta=\gamma=90^{\circ}$. The atomic positions are La: 2c (1/4,1/4,0.14219); Cu: 2b (3/4,1/4,1/2); S: 2c (1/4,1/4,0.3117)and O: 2a(3/4,1/4,0).The optimized lattice constants are $a=b=3.97118$ Å and $c=8.49978$ Å. In order to calculate the electronic structure and study the optical property of $(\text{La}_{0.75}\text{Ca}_{0.25})(\text{Cu}_{0.75}\text{Mn}_{0.25})$SO, we fix the Mn atom and find out the lowest energy relates with the Sr position.

![Fig.1 Crystal structure of (La,Ca)(Cu,Mn)SO which belongs to tetragonal ZrCuSiAs type.](image)

III. Electronic structure

![Fig.2 (a)Band structure and (b) DOS of parent LaCuSO.](image)

We first focus on the electronic structure of its parent compound LaCuSO according to the structure of fig. 1. As Cu is a diamagnetic metal, we calculate the electronic structure without considering its spin. The DOS and band structure were depicted in fig. 2(a) and (b). In this paper, all the DOS and band
figures are plotted with the Fermi level being zero. Obviously, LaCuSO is a direct semiconductor with the band gap 2.123eV at high symmetry G point in Brillouin zone.

The states range from -6.0 eV to 0 eV are mainly contributed by S3p, O2p and Cu3d orbital, which consist of valence bands. The top of valence bands contains primarily S3p state and Cu 3d, forming covalent Cu-S bonds around fermi surface. However, the conduction band is mainly composed of La 5d states with a gap 2eV above $E_f$.

Then we move on the band structure of (La$_{0.75}$Ca$_{0.25}$) (Cu$_{0.75}$Mn$_{0.25}$)SO with spin up and down for comparison in fig.3(a). Whether the spin is up or down, the bottom of conduct band and upper of valence band locate at high-symmetry point G in Brillouin zone, which indicates (La$_{0.75}$Ca$_{0.25}$) (Cu$_{0.75}$Mn$_{0.25}$)SO is still a direct semiconductor with a band gap 0.962eV in the spin up state while only 0.88eV in the spin down state. Compared with pure LaCuSO, the band gap apparently reduces a lot after doping, particularly in the latter state.

The DOS of (La$_{0.75}$Ca$_{0.25}$)(Cu$_{0.75}$Mn$_{0.25}$)SO are plotted in fig. 3(b). Overall, after Mn and Ca atoms are doped into the lattice, there is a polarization and hybridization between 3d states of the transition metal and the 3p of sulfur atom. The conduction bands are mainly composed of La 5d and Mn 3d band. Mn dopant plays an important role in the DOS around the fermi level. Below $E_f$ from -4eV to 0eV, the asymmetry of PDOS of Mn iron dominates in the up state, compared with that at 0.5-3eV above $E_f$, it dominates in the down state.

Fig.3  (a)Band structure and (b)DOS of (La$_{0.75}$Ca$_{0.25}$) (Cu$_{0.75}$Mn$_{0.25}$)SO with spin up and down.

In order to understand the influence of Ca and Cu co-dopants, we compare the band gap among the parents and co-doped materials with the same copants according to our previous results (see Table 1).

| Parents | Band gap(eV) | Co-doped materials | Band gap(eV) |
|---------|-------------|-------------------|-------------|
| LaCuSO  | 2.123       | La$_{0.75}$Ca$_{0.25}$Cu$_{0.75}$Mn$_{0.25}$SO | Up 0.962 |
|         |             | La$_{0.75}$Ca$_{0.25}$Cu$_{0.75}$Mn$_{0.25}$SO | Down 0.88 |
| YCuSO   | 1.250       | Y$_{0.75}$Sr$_{0.25}$Cu$_{0.75}$Mn$_{0.25}$SO | Up 1.20  |
|         |             | Y$_{0.75}$Sr$_{0.25}$Cu$_{0.75}$Mn$_{0.25}$SO | Down 1   |
| LaAgSO  | 1.40        | La$_{0.75}$Ba$_{0.25}$Ag$_{0.75}$Mn$_{0.25}$SO | Up 1.25  |
|         |             | La$_{0.75}$Ba$_{0.25}$Ag$_{0.75}$Mn$_{0.25}$SO | Down 1.12|

From the table, it is clear that after co-doping, the band gap of La$_{0.75}$Ca$_{0.25}$Cu$_{0.75}$Mn$_{0.25}$SO decrease very quickly in both up and down states.

IV. Optical properties
First-principle calculation in investigating optical property, such as loss function, reflectivity coefficient, absorption coefficient and complex dielectric constant. These optical parameters are
connected with one another and can be deduced directly from the radiative-transition-rate theory and Kramers-Kroning dispersion relation. From Fig. 4(a), (b), (c), (d) and (e), it is also clear that the position of all the peaks for \((La_{0.75}Ca_{0.25})\) \((Cu_{0.75}Mn_{0.25})SO\) have the biggest “red shift” and the intensity of them decreases mostly. It indicates that co-doped Ca and Mn reduce the energy strongly, which is consistent with the change of band gap.

![Graphs showing energy transitions](image)

**Fig. 4** Comparison of (a) loss function, (b) reflectivity, (c) absorption, (d) the real part of dielectric function and (e) the imaginary part of dielectric function among parent \(LaCuSO\), \((La_{0.75}Ca_{0.25})\) \((Cu_{0.75}Mn_{0.25})SO\), \((La_{0.75}Ba_{0.25})\) \((Ag_{0.75}Mn_{0.25})SO\) and \((Y_{0.75}Sr_{0.25})\) \((Cu_{0.75}Mn_{0.25})SO\), respectively.

Most importantly, the relative intensity of all the peaks decreases and the position of all the peaks shows “red shift” when doped. The peak intensity decreases when doping attributes to the scattering from the Ca and Mn dopant. The red shift originates from the impurity band generated by the holes to compensate the charge imbalance due to Ca doping, which agrees with the decreasing band gap when doped.

**V. Conclusions**

In conclusion, we found the band gap decrease after co-doping. \(La_{0.75}Ca_{0.25}Cu_{0.75}Mn_{0.25}SO\) decreases most quickly result from the severe scattering from the Ca and Mn dopant. On the other hand, the position of all the peaks for \(La_{0.75}Ca_{0.25}Cu_{0.75}Mn_{0.25}SO\) have the biggest “red shift” and the intensity of them decreases mostly. Thus, the difference in optical properties result from the difference in band structure (band gap).

**Acknowledgments**

This work was financially supported by the National Science Foundation of China (No.61376094) and China Scholarship Council (No. 201408330028).

**References:**

[1] K. Zhao, Z. Deng, X. C. Wang et al. 2013 Nature Communications, 4, 1442.

[2] X. J. Yang, Y. K. Li, C. Y. Shen et al. 2013 APL, 103, 022410.

[3] K. Ueda, S. Imoue and H. Hosono et al. 2001 APL, 78, 2333