Evolution of physical properties in hole doped Sr$_2$IrO$_4$: a J$_{\text{eff}} = 1/2$ magnetic insulator

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Abstract. Recently 5$d$ transition metal oxides (TMOs) particularly iridates have received extensive attention of researchers due to potential for exotic physics. Sr$_2$IrO$_4$ is extensively studied iridate over the past several years. Sr$_2$IrO$_4$ received great attention of researchers due to structural similarities with parent high T$_C$ cupric superconductor La$_2$CuO$_4$. The layered perovskite Sr$_2$IrO$_4$ believed to stabilize in J$_{\text{eff}} = 1/2$ ground state and it is a magnetic insulator. The Sr$_2$IrO$_4$ shows weak ferromagnetic ordering below ~225 K, originating from the canted anti-ferromagnetic arrangement of the J$_{\text{eff}} = 1/2$ moments. Sr$_2$IrO$_4$ become interest compound for experimental research since it has been theoretically predicted to be superconductor upon electrons/hole doping. In this paper, we endeavour to tune SOI, U and introduce hole in electronic band by substituting Ru$^{4+}$ (4$d^4$ S = 1) for Ir$^{4+}$ (5$d^5$ J$_{\text{eff}} = 1/2$) in Sr$_2$IrO$_4$. We investigated the effect of Ru doping on structural and magnetic properties of Sr$_2$IrO$_4$. We observe evolution of both a and c lattice parameters in the meantime the octahedral distortion ($\theta_{\text{oct}}$) also decreases with doping. Further, our magnetization study shows suppression in transition (T$_C$), hysteresis with Ru doping. We found introduction of hole in Sr$_2$IrO$_4$ prominently effect the structural and magnetic properties.

1. Introduction

In 5$d$ iridates active interactions such as: crystal field effect (CFE), on site coulomb interaction (U) and spin orbital coupling (SOC), compete among each other create new balance of interacting energies which promote novel electronic and magnetic phases in these materials. The most studied iridate layered perovskite Sr$_2$IrO$_4$ believed to stabilize in novel J$_{\text{eff}} = 1/2$ ground state it is a magnetic insulator driven by strong SOC. It is recently found that the electronic ground state is influenced by strong SOC of Ir ion in an octahedral environment which splits the t$_{2g}$ band into lower J$_{\text{eff}} = 3/2$ quartet and upper J$_{\text{eff}} = 1/2$ doublet. The J$_{\text{eff}} = 1/2$ band is so narrow that modest U opens a Mott gap by splitting it into upper and lower Hubbard bands, thus driving it to unconventional Mott insulator.[1] The establishment of novel J$_{\text{eff}} = 1/2$ ground state has induced exotic properties in iridates. Sr$_2$IrO$_4$ crystallize in reduced tetragonal structure with space group I4$_1$/acd. The reduced symmetry is due to tiling of IrO$_6$ octahedral around c-axis. [1-7] Further, the structural organization of Sr$_2$IrO$_4$ is quite interesting and play crucial role in deciding physical properties of this material. The magnetic ground state in Sr$_2$IrO$_4$ is canted type antiferromagnetic (AFM) which gives rise to ferromagnetic component with Transition temperature (T$_C$) around 225 K. The spin canting nature is give rise to anti symmetric Dzialoshinskii-Moriyam interaction driven by SOI and IrO$_6$ octahedra distortion. [3-8]. The ground state in this material is result of delicate balance of interacting energies viz. SOC, CFE and U, since tuning the strength of these energies can tune the physical properties. Motivated by this fact we adopt chemical doping of Ru$^{4+}$ (4$d^4$) for Ir$^{4+}$ (5$d^5$) this will tune both SOC and U, moreover introduce a hole...
into the band. Tuning of this crucial perimeter will perturb the ground state and hence evolve physical properties of this compound. [5-10]

In this paper we investigate the evolution of structural and magnetic properties of Sr$_2$IrO$_4$ with Ru doping. The structural characterization is done with X-ray diffraction. We observe evolution of lattice parameter with Ru doping. The octahedral distortion which is crucial in deciding physical properties reduces with doping and $<\text{Ir-O-Ir}>$ bond angle increases. Both temperature and field dependent magnetization is studied to understand the magnetic properties. We observe sample undergo paramagnetic (PM) to ferromagnetic (FM) phase transition and suppression of $T_C$ with reduce magnetic moment. However, the effective paramagnetic moment increases and Curie temperature decreases. The isothermal magnetization $M(H)$ shows decrease in coercivity and remnant magnetization.

2. Experimental Details
The polycrystalline samples of Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$ (x = 0.0 and 0.1) were prepared using standard solid state method using ingredients SrCO$_3$ and IrO$_2$ and RuO$_2$ from Sigma Aldrich. The high purity ingredients were thoroughly mixed and grinded well. The fine ground powder then calcinated at 900 °C for 24 hour with heating and cooling rate set to 3°C/min. The calcinated powder is further grounded for half an hour and pressed into pallet and sintered at 1000 °C and 1100 °C for 24 hours each with intermediate grindings to achieve sample homogeneity. The sample preparation procedure described in detail elsewhere.[8-12] The phase purity of the samples has been checked using powder x-ray diffraction (XRD) with a Rigaku MiniFlex diffractomer with CuKα radiation. The XRD data is used for structural analysis with the help of Full Proof software. Both temperature and field dependent DC magnetization (M) data have been collected using a vibrating sample magnetometer (PPMS, Quantum Design).

3. Result and Discussion
3.1. Structural study
XRD patterns of Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$ sample series are shown in Fig. 1, the comparison of XRD patterns shows no extra peak evolves with doping. Inset Fig. 1 shows Rietveld refinement analysis of parent compound. The structural analysis shows that all samples are in single phase and chemically pure. All
samples crystallize in tetragonal phase with I4_1/acd space group. The refined lattice parameters are \(a = b = 5.4980(2) \, \text{Å}\) and \(c = 25.779(1) \, \text{Å}\) for \(x = 0.0\) sample, both \(a\) and \(c\) lattice parameters decreases with Ru doping. We also find a rotation of IrO_6 octahedra decreases from \(~11.3^\circ\) around \(c\) axis for parent compound to \(9^\circ\) for \(x = 0.1\) sample.

![Figure 2](image_url)

**Figure 2.** (a) ZFC and FC magnetization data measured in 10 kOe are plotted as a function of temperature for \(\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4\). (b) Inverse susceptibility (\(\chi^{-1}\)) shows Curie-Weiss behaviour.

### 3.2 Magnetization Study

Fig. 2(a) shows the temperature dependant magnetization \(M(T)\) data collected in ZFC and FCW protocol in the temperature range of 5 K – 300 K in an applied field of 10 kOe. The \(M(T)\) data show a phase transition from paramagnetic (PM) to weak ferromagnetic (FM) state with \(T_C \approx 225\) K for parent compound. However, with Ti doping \(T_C\) decreases. Fig. 2(b) shows the inverse susceptibility as a function of temperature. In PM regime the magnetic susceptibility is fitted with Curie-Weiss law expressed as:

\[
\chi = \frac{C}{T - \theta_P}
\]

Where \(\chi\) is magnetic susceptibility, \(C\) is the Curie constant and \(\theta_P\) is the Curie temperature. We calculated effective paramagnetic moment for all samples using fitting parameters. We found the \(\mu_{\text{eff}} = 0.56 \mu_B/\text{f.u}\) for parent compound and \(\mu_{\text{eff}}\) increases with Ru doping.

To further understand the magnetic properties we measured isothermal magnetization \(M(H)\) at \(T = 5\) K shown in Fig. 3(a). The hysteresis in \(M(H)\) is suggestive of FM ordering in this material. At 5 K, the magnetic moment \(\mu_S = 0.05 \mu_B/\text{f.u}\) at \(H = 70\) kOe is observed, which decreases with Ti doping. It is quite evident from the Fig. 3(a) that corecivity and reminance decreases with doping. Fig. 3(b) shows the Arrott plot (\(M^2\) vs \(H/M\)), the extrapolation of Arrott plot at high field intercept the positive \(M^2\) axis which realize the presence of spontaneous moment in these samples.

The suppression of transition temperature \(T_C\) and moment can be explain by considering the effect of Ru substitution. Since Ru\(^{4+}\) is \(S = 1\) and Ir\(^{4+}\) is Jeff =1/2 thus Ir-O-Ru-O-Ir interaction is weaker then Ir-O-Ir-O-Ir, due to with \(T_C\) decreases and system become less ferromagnetic.
4. Conclusions
In conclusion, we successfully prepared the single phase high purity polycrystalline samples of Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$. Structural analysis reveals that samples crystalize in tetragonal structure with reduced symmetry. With Ru doping lattice parameters evolve and octahedral distortion reduces. The magnetization study shows samples undergo magnetic phase transition from PM to FM. Ru doping result in enhancing effective magnetic moment and decreases curie temperature. The M(H) data shows hysteresis which decreases with Ru doping. To further understand the magnetism in Ru doped Sr$_2$IrO$_4$ samples with even higher Ru doping need to be prepared and studied.

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