Influence of electronic structure parameters on the electrical transport and magnetic properties of $Y_{2-x}Bi_xIr_2O_7$ pyrochlore iridates

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We report the systematic study of structural, magnetic and electrical transport properties of $Y_{2-x}Bi_xIr_2O_7$ (x = 0.0, 0.1, 0.2, 0.3) pyrochlore iridates. The chemical doping enhances electrical conductivity and antiferromagnetic correlation substantially. The replacement of non-magnetic Y^{3+} ion with non-magnetic Bi^{3+} in $Y_2Ir_2O_7$ tends to reduce the octahedral distortion thus enhancing the antiferromagnetic correlation. Raman spectroscopy shows that the Ir - O bond contract slightly and the R - O' bond turn longer as disorder and phononic oscillation are reduced with Bi doping, leading to wider t_{2g} bands, which enhances the electrical conductivity. Additionally, the enhancement in electrical conductivity and antiferromagnetic correlation with Bi^{3+} doping is attributed to the hybridization between the $Y^{3+}(4p)/Bi^{3+}(6s/6p)$ orbital with $Ir^{4+}(5d)$ orbital as a result of enhancement in Ir - O - Ir bond angle and contraction in Ir - O bond length.

I. INTRODUCTION

In recent years, 5d iridates have proved to be a fertile ground for new physics driven by the interplay between the onsite Coulomb repulsion (U = 0.5 - 3eV), strong crystal field effect (CF = 1 - 5eV) and spin-orbit coupling $(\lambda_{SOC} = 0.1 - 1eV)^1$, potentially leading to novel quantum phases such as a topological Mott insulator², Weyl semimetal³, axion insulator^{1,3}, superconductor⁴, continuous metal insulator transition (MIT)⁵ etc. The interplay of competing interactions are controlled⁶ *inter-alia* by the Ir - O - Ir bond angle and Ir - O bond length, which can be tuned by chemical⁷⁻¹¹, physical¹²⁻¹⁴ or surface¹⁵⁻¹⁸ strain pressure. A small perturbation in R-site¹⁹⁻²³ or Ir-site^{7-9,11} in $R_2Ir_2O_7$ (R = Y, Bi or rare earth elements) pyrochlore iridates may easily destabilize the ground state.

Experimental studies show that the Ir - O - Ir bond angle increases as the R-site ionic radius increases resulting in a wider t_{2q} bandwidth and MIT⁶. Depending on the substituted element, the SOC and U can be tuned using chemical doping at Ir-site. For example, lighter d element compared to $Ir^{4+}(5d^5)$ would reduce the SOC and enhance U simultaneously. For $Y_2 Ir_2 O_7$, the magnetic properties are determined by the contribution from Ir^{4+} ion. $Y_2 Ir_2 O_7$ shows a spin-glass like behaviour or canted ferromagnetic transition at temperature T ~ $160 K^{22-25}$. Chemical doping of isovalent non-magnetic $Ti^{4+}(3d^0)^{-8}$ and magnetic $Ru^{4+}(4d^4)$ ⁷ ions [both have smaller SOC and larger U than Ir individually at magnetic $Ir^{4+}(5d^5)$ site in $Y_2 Ir_2 O_7$ compounds would lead to enhancement in Ir - O - Ir bond angle and reduction in Ir - O bond length. This produces marginal enhancement of electrical conductivity with large increase in antiferromagnetic correlation. Strikingly, chemical doping of magnetic $Cr^{3+}(3d^3)$ ⁹ ion at magnetic Ir^{4+} site reduces Ir - O - Ir

bond angle and enhances Ir - O bond distance subtantially, giving rise to orders of magnitude enhancement of electrical conductivity and ferromagnetism.

So far as doping at *R*-site is concerned, previous reports on chemical doping of $Ca^{2+} - 3p^6$ at $Y^{3+} - 4p^6$ site in $Y_2 Ir_2 O_7$ system alter the electron band width of $Ir - t_{2q}^{22,23}$ and show enhancement of electrical conductivity along with weakening of antiferromagnetic correlation. On the other hand, introduction of isovalent nonmagnetic $Bi^{3+} - 6s/6p$ ion at non-magnetic Y^{3+} site in $Y_2 Ir_2 O_7$ does not alter the t_{2g} band width and yet show $MIT^{26,27}$. While studying the magnetization and Hall resistivity below magnetic transition temperature for the $Y_{2-x}Bi_x Ir_2 O_7$ series with small doping concentration x, Aito et al.²⁶ and Soda et al.²⁷ observed hysteretic behaviours, suggesting that the glass-like feature could also be a magnetic state at low temperatures. Additionally, based on μ SR measurements Fernandez et al.²⁸ observed weakening of this behaviour with introduction of Bi content i.e., magnetically ordered state in un-doped compound reduced as Bi doping content increased. It was proposed that in $Y_{2-x}Bi_xIr_2O_7$, the magnetically ordered state associated to Ir^{4+} magnetic ions remained same but the paramagnetic volume fraction got larger and larger. Very recently, a gapped out Weyl-semimetal phase has also been reported in the Bi doped $Y_2 Ir_2 O_7$ nanoscale system^{29,30}. These observations underline the fact that there is requirement for deeper understanding of magnetic state as it is possibly connected to the topological Weyl semimetal³ state in $Y_2 Ir_2 O_7$. Despite several reports on chemical doping at non-magnetic R = Ysite, detailed analysis of the experimental results as well as finding a correlation between electronic structural parameters and magnetic and electrical transport properties, is presently lacking. Moreover, given the MIT in $Y_{2-x}Bi_xIr_2O_7$ series, the electronic transport behaviour requires to be explored more thoroughly including in the presence of magnetic field.

In the present work, we have studied the interrelation

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between electronic structural parameters and magnetic and electrical transport properties of $Y_{2-x}Bi_xIr_2O_7$ (x = 0.0, 0.1, 0.2, 0.3) compounds using XRD, FE-SEM, XPS, Raman spectroscopy, dc magnetization and magnetotransport measurements. We show that isovalent doping of non-magnetic Bi^{3+} ion at non-magnetic Y^{3+} site in $Y_2Ir_2O_7$ system alters the electronic structural parameters such as lattice constant, bond angle, bond length and charge states of Ir leading to orders of magnitude enhancement of electrical conductivity and enhanced antiferromagnetic correlations compared to the undoped $Y_2Ir_2O_7$ compound.

II. EXPERIMENTAL METHODS

The samples $Y_{2-x}Bi_x Ir_2 O_7$, x = 0.0, 0.1, 0.2, 0.3 were synthesized by solid state reaction route following the protocol reported by same authors $^{9,10,15-18,31,32}$ and elsewhere^{26,27}. High purity stoichiometric mixtures of IrO_2 [Alfa-Aesar, Permion (r)], Bi_2O_3 [SIGMA-ALDRICH] and Y_2O_3 [SIGMA-ALDRICH] with purities of 99.99% were ground, pressed into pellets and sintered at 1000° C for 24h. The process of grinding, pelletization and sintering (at 1050° C for 24h) were repeated once more for doped compound, i.e. x = 0.1, 0.2, 0.3. For the parent compound i.e. x = 0.0, stoichiometric mixtures of IrO_2 and Y_2O_3 were ground, pelletized and then sintered between 950° C and 1050° C for 10 days with several intermediate grindings. The quality of compound and crystal structure were analyzed by powder X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1.54$ Å) at room temperature. The chemical compositions and micro structural morphology of the samples were measured by energy dispersive x-ray spectrometry (EDX) using field emission scanning electron microscope (FE-SEM) [JSM-7100F, JEOL]. The temperature dependence electrical transport properties were measured by conventional four probe technique. The magnetic measurements were carried out using a Quantum design physical property measurement system (PPMS). The X-ray photoelectron spectroscopy (XPS) were measured using a PHI 5000 Versa Probe II scanning XPS system. A micro-Raman measurements were performed using a JY-Horiba micro Raman system having a grating with 1200 grooves/mm (resolution ~ 0.6cm^{-1} /pixel). The excitation source was 514.5nm laser line of Ar^+ laser with laser power on the sample is 5.86mW. The laser was focused to a spot size of $\sim 2-5 \ \mu m$ on the sample.

III. RESULTS AND DISCUSSION

Figure 1 shows powder X-ray diffraction (XRD) pattern for $Y_{2-x}Bi_xIr_2O_7$ series with x = 0.0, 0.1, 0.2 and 0.3. The XRD spectra with diffraction peaks for the undoped compound (x = 0.0) consistent with the reported study⁹. With substitution of Bi at Y-site, major change



FIG. 1. Powder XRD profile along with Rietveld refinement taking pyrochlore cubic structure have been shown for $Y_{2-x}Bi_xIr_2O_7$ series. Arrows represent impurity phases. Inset shows the Bi doping concentration dependent goodness of fit value obtained from Rietveld fitting.



FIG. 2. Field emission scanning electron microscope (FE-SEM) micrograph for polycrystalline (a) undoped (x = 0.0), and (b) x = 0.3 sample: inset shows formation of faceted single crystals. Energy dispersive x-ray spectrometry (EDX) spectra of (c) x = 0.0, and (d) x = 0.3 samples.

in XRD peak position is not observed. It is expected because their matching ionic radii $[Bi^{3+} = 1.17\mathring{A}$ and $Y^{3+} = 1.01\mathring{A}]^{33}$. Indeed, XRD spectra does not change notably with doping concentration x except some impurities such as Bi_2O_3 , IrO_2 , Y_2O_3 and Ir, which is present minimally ($\leq 3\%$) in the series. The XRD spectra have

been analyzed by Rietveld refinement program. The refinement results show all the compounds exihibt a nearly pure pyrochlore phase of cubic $Fd\bar{3}m$ (227) except for few impurity phases shown in Fig. 1 consistent with what others have been reported 22,24 . These impuries are either diamagnetic or paramagnetic in nature, hence have negligible contribution to the physical properties. Statistical goodness of fit is defined as $F^2 = [R_{wp}/R_{exp}]^2$, where, R_{exp} is the observed weighed profile factor and R_{wp} the expected weighed profile factor in Rietveld refinement³⁴. The goodness of fit as a function of *Bi* doping concentration (x) shown in inset of Fig. 1 suggest the quality of fitting. Interestingly, Fig. 3a shows that the lattice parameters increases with increasing Bi doping concentration (x). It is expected that smaller $Y^{3+}(1.01\text{\AA})$ are replaced by larger $Bi^{3+}(1.17\text{\AA})$ ion in $Y_2Ir_2O_7$. The enhancement of lattice constant may be associated to the increase in Y-site ionic size. The representative field emission scanning electron microscope (FE-SEM) micrograph for two members of this present series i.e. x = 0.0 and 0.3 are shown in Fig. 2a,b. The SEM micrograph of parent sample [Fig. 2a] reveals nearly uniform distribution of closely packed grains of different shapes of particles with average particle size $1\mu m$. On the other hand, Fig. 2b shows faceted formation of particles. Inset of Fig. 2b displays the faceted single crystal wires with typical length ranging between 1-50 μm , loosely attached to the surface of polycrystalline sample of x = 0.3. Such formation of faceted single crystal possibly due to self-flux growth involving Bi_2O_3 as a flux³⁵. The chemical composition of desired element in polycrystalline $Y_{2-x}Bi_xIr_2O_7$ series was recorded by energy dispersive x-ray spectrometry (EDX) taken over a large area of the sample shown in inset of Fig. 2c,d], show the average expected presence of Ir, Bi, Y and O in nearly stoichiometric ratio as shown in Fig. 2c,d. It can be noticed that the Ir/Y ratio is \sim 0.84 in the x = 0.0 sample and the Ir/(Y+Bi) is ~ 0.95 in the x = 0.3 sample, suggest that those samples are Ir-deficient. The low Ir/Y ratio for undoped compound is not surprising due to volatile nature of $IrO_3^{19,36}$. The higher value of Ir/(Y+Bi) ratio for x = 0.3 sample as compared to x = 0.0 might by associated to the volatile nature of Bi and stability of Ir in $Y_{2-x}Bi_xIr_2O_7$ series.

In ideal pyrochlore iridates with formula $R_2Ir_2O_6O'$, the four non-equivalent ions reside at following coordinates: R at 16d site (0.5, 0.5, 0.5), Ir at 16c (0, 0, 0) site, two types of oxygen, O and O' ions coordinated tetrahedrally reside at the 48f(r, 0.125, 0.125, where r termed as positional parameter) and 8b(0.375, 0.375, 0.375) sites, respectively. The Pyrochlore crystal structure show perfect octahedron about (0, 0, 0) for the value of x = 0.3125give rise to perfect cubic field for Ir cation in this $Ir - O_6$ octahedra³⁷. Figure 3b reveals the adjustable positional parameter as a function of Bi doping concentration x. The estimated value of the positional parameter for the parent compound turns out to be 0.355, greater than the ideal value, suggesting disordered and compressed $Ir - O_6$ octahedra. For the $Y_{2-x}Bi_xIr_2O_7$ series, positional pa-



FIG. 3. Bi doping content dependent (a) Lattice parameter, (b) positional parameters r of O atom, (c) Ir - O bond length (d) Ir - O - Ir bond angle for the $Y_{2-x}Bi_xIr_2O_7$ series.



FIG. 4. Oxygen coordination environment showing the effect of R cation size on the local structure of (a) small Y cation in $R_2Ir_2O_7$ system, (b) larger Y cation in $Y_{2-x}Bi_xIr_2O_7$.

rameter decreases with increase of the Bi content, leading towards ideal IrO_6 octahedra with reduced crystal field. The doping dependence of Ir - O bond distance and Ir - O - Ir bond angle are shown in Fig. 3c,d, respectively. The bond length decreases while bond angle increases with increasing concentration of Bi in $Y_{2-x}Bi_xIr_2O_7$ series. This is due to the introduction of heavy Bi^{3+} atom with greater ionic size than $Y^{3+6,38}$. This implies reduction of distortion in the $Ir - O_6$ octahedra and enhancement in the hybridization of Y(4p)/Bi(6s and 6p) with O(2p) and Ir(5d) states. This is also consistent with the non-monotonous variation of F^2 against Bi doping [inset of Fig. 1], giving rise to increased A-site ionic radius. The enhancement in Ir - O - Ir bond angle and reduction in Ir - O bond length can be understood by Fig. 4a,b. Cartoon shows the arrangement of atoms in the un-doped compound where the coordination environments of each oxygen atom is associated with two Ir and two Y cations to make a distorted octahedra along c-axis in the unit cell [Fig. 4a]. When Bi^{3+} is introduced, it pushes the oxygen atom further away from the R-site along the perpendicular bisector of the Ir - O - Ir triangle, thus increasing the Ir - O - Ir bond angle [Fig. 4b].

The temperature dependence of the magnetic suscep-



FIG. 5. (a) Field cooled (solid continuous line) and zero field cooled (dashed line) magnetic susceptibilities as a function of temperature for $Y_{2-x}Bi_xIr_2O_7$ (x = 0.0, 0.1, 0.2. 0.3) series; inset shows Bi doping concentration dependent magnetic irriversible temperature T_{irr} . (b) The inverse of magnetic susceptibility $\chi^{-1} = H/M$ as a function of temperature. Red solid line associated to the the fit using the Curie-Weiss (CW) law. The variation of (c) Curie-Weiss temperature θ_{CW} , and (d) effective magnetic moment μ_{eff} with Bi doping content x.

tibility $\chi = M/H$ for $Y_{2-x}Bi_x Ir_2 O_7$ (x = 0.0, 0.1, 0.2, 0.3) series measured at applied magnetic field 1kOe following the zero field cooled (ZFC) and field cooled (FC) protocol. For un-doped compound, it can be noticed that χ_{ZFC} and χ_{FC} branches contain a clear magnetic irreversibility around $T_{irr} \sim 160$ K shown in Fig. 5a. Below T_{irr} a large bifurcation between χ_{ZFC} and χ_{FC} branches is obtained. It can be noticed that χ_{ZFC} curve does not show any cusp at T_{irr} . The enhancement of susceptibility below the bifurcation temperature T_{irr} suggest a bulk phase transition to an ordered state. Interestingly, the susceptibility enhances very sharply below $T \sim 25 K$, possibly due to emergence of very weak ferromagnetic components. This behaviour might be attributed to spin-glass like transition^{7,9}. As shown in the Fig. 5a, as Bi doping content increases: (I) the bifurcation temperature T_{irr} shifts toward lower temperature, and (II) the difference between χ_{ZFC} and χ_{FC} branches decreases. Inset of Fig. 5a shows almost linear reduction in T_{irr} with Bi doping content. χ_{ZFC} and χ_{FC} branches entirely merges for fully Bi doped sample i.e. $Bi_2Ir_2O_7^{38-40}$, imply paramagnetic-like behaviour. Figure 5b shows the inverse of dc magnetic susceptibility χ^{-1} vs T curve. Above the magnetic transition at high temperatures (140-300K), the linear part of the $\chi^{-1}(T)$ data for all the samples are analysed by fitting with the Curie-Weiss law, $\chi = \frac{N_A \mu_{eff}^2}{3k_B(T - \theta_{CW})}$, where C and θ_{CW} are the Curie constant, Curie-Weiss temperature, N_A is the Avogadro number and k_B is the Boltzmann constant, respec-



FIG. 6. Isothermal magnetic hysteresis loops (M-H) curves measured at temperature 2K for two representative samples x = 0.0 and 0.3 of $Y_{2-x}Bi_xIr_2O_7$ series. The solid red line is the Brillouin function fit according to Eq. 1. Bottom inset shows the enlarged view of the low magnetic field and top inset displays conventional Arrott plot.

tively. We find negative value of θ_{CW} for $Y_{2-x}Bi_xIr_2O_7$ series suggests prodominantly antiferromagnetic (AFM) correlation. The absolute value of θ_{CW} is monotonically enhancing as more Bi^{3+} ions are substituted into the $Y_2 Ir_2 O_7$ lattice shown in Fig. 5c, suggest enhancement in antiferromagnetic (AFM) correlation. Due to the extended nature of electronic wave function of Ir - 5d orbital, the hybridization of Ir - 5d and O - 2p orbitals are strong enough supporting interatomic exchange interaction as discussed earlier [Fig. 3b,c,d]. For parent compound (x = 0.0), the Ir - O - Ir bond angle is 121^{0} [very close to ideal value^{3,41}], much larger than 90⁰ promoting the super exchange interaction. With Bi doping Ir - O - Ir bond angle is enhancing and approaching towards 180° . Therefore, Ir - O - Ir AFM super exchange correlation is dominant in $Y_{2-x}Bi_xIr_2O_7$ series, lead to enhanced AFM correlation. It can be noticed that $-\theta_{CW}$ increases but the actual ordering temperature decreases. This suggests enhancement of frustration parameter $[f = \theta_{CW}/T_{irr}]$ with Bi doping. The effective magnetic moment μ_{eff} for the all samples plotted as a function of Bi doping concentration shown in Fig. 5(d). The estimated value of μ_{eff} for undoped compound is 2.2 μ_B /f.u. which is larger than the expected Hund's rule value of 1.73 $\mu_B/f.u.$ for S = 1/2. Similar inconsistency [i.e. obtained experimental value of μ_{eff} being larger than expected theoretical value of a spin 1/2 has also been reported⁷. Such disagreement with Hund's rule value is not unusual in presence of crystal field effect and strong spin-orbit coupling. It can be noticed that μ_{eff} decreases as non-magnetic Bi content increases shown in Fig. 5d.

The magnetic field (H) dependence isothermal magne-

tization (M) for two representative samples x = 0.0, 0.3of the $Y_{2-x}Bi_xIr_2O_7$ series measured at temperature 2K is shown in Fig. 6. The M-H data show non-linear trends with no sign of saturation up to 10T. The coercive field H_C , saturation magnetization M_S and remanent magnetization M_R show considerable reduction compared to the un-doped sample. It is obvious that $Y_{2-x}Bi_xIr_2O_7$ series have tendency towards an increased AFM correlation, supports the enhanced negative θ_{CW} with increased Bi doping content. A narrower magnetic hysteresis loops for x = 0.3 compared to x = 0.0 sample can be seen at low magnetic field [bottom inset of Fig. 6], suggesting very weak FM component. This result is possibly due to the canted antiferromagnetic spin coupling instead of ferromagnetic correlation. The coexistence of very weak ferromagnetic component on the large AFM background suggests that only a partial fraction of short-range ordered spins freeze at low temperature into random direction. This behaviour might be attributed to spin-glasslike transition, possibly arising due to local structural disorder and magnetic frustration. Further, we studied the M-H data using Brillouin function fit⁴². For $R_2 I r_2 O_7$, the low temperature magnetic state can be explored including an effective spin J = 1/2, where

$$\frac{M}{M_S} = B_{1/2}(y) \tag{1}$$

where $B_J(y) = \left[\frac{2J+1}{2J}\right] coth \left[\frac{y(2J+1)}{2J}\right] - \frac{1}{2J} coth \frac{y}{2J}$ $M_S = ng_J\mu_B J$, $y = \begin{bmatrix} g_J\mu_B J \\ k_BT \end{bmatrix} H$, μ_B is Bohr magneton, g_J is the Lande's g-factor. The value of effective magnetic moment $\mu_{eff}^{M(H)}$ is calculated using $\mu_{eff} =$ $g_{I}\mu_{B}\sqrt{J(J+1)}$, where g_{J} is obtained from the Brillouin function fit shown by solid red line in Fig. 6. The estimated value of fitting parameters of M-H data are $g_J =$ 0.6 (x = 0.0), 1.1 (x = 0.3) and $\mu_{eff}^{M(H)} = 0.6 \mu_B$ (x = 0.0), 0.95 μ_B (x = 0.3), respectively. While the estimated $\mu_{eff}^{M(H)}$ for x = 0.3 sample is very close to the effective magnetic moment $\mu_{eff}^{M(T)} = 1.1 \mu_B$ obtained from M-T data, the $\mu_{eff}^{M(H)}$ for x = 0.0 sample is smaller than $\mu_{eff}^{M(T)}$ = 2.2 μ_B . It is clear that the Brillouin function deviates from the experimental M-H data [Fig. 6], suggesting nonparamagnetic trend. Top inset of Fig. 6 shows conventional Arrott plot^{8,18} for x = 0.0 and 0.3 samples. It is clear that estimated intercept [\sim -2.1 (x = 0.0), -0.1 (x = (0.3) from straight line fitting at M^2 -axis is negative and decreasing with Bi doping content. It suggests that low temperature magnetic state is non-ferromagnetic type in un-doped compound, and Bi doping decreases the nonferromagnetic type behaviour in $Y_{2-x}Bi_xIr_2O_7$ series.

In order to further investigate the possibility of spinglass-like behaviour in Bi doped $Y_2Ir_2O_7$ pyrochlore iridates, we have measured the isothermal remanent magnetization. For this measurement, the samples are ZFC from room temperature to 5K. A dc magnetic field of



FIG. 7. (a) Time dependence of the normalized isothermal remanent magnetization measured at temperature 5K with waited time $t_w = 10^3$ s for the two representative samples x = 0.0, 0.3 of the $Y_{2-x}Bi_xIr_2O_7$ series. Solid red line show corresponding fit of data using Eq. 2. (b) Semi-log plot of normalized magnetization as a function of time. Dashed red line are due to the fit using Eq. 2. Solid green line shows linear portion.

1kOe is applied after stabilizing the temperature and waiting upto 10^3 s, and magnetization is measured as a function of elapsed time t. Figure 7(a) shows the time dependence of ZFC isothermal remanent magnetization normalized with magnetization value M(t = 0) for two representative samples x = 0.0, 0.3 of the *Bi* doped $Y_2Ir_2O_7$ series. For x = 0.0 sample, M(t)/M(0) increases with time without any sign of saturation, although x = 0.3 sample is trying to achieve saturation at higher time scale. We have analysed the normalized magnetic relaxation data with fitting of stretched exponential function⁴³

$$\frac{M(t)}{M(t=0)} = exp\left[\frac{t}{\tau}\right]^{\gamma} \tag{2}$$

where γ is stretching exponent and τ is the characteris-

tic relaxation time. The value of γ give the information about the nature of energy barriers involved in magnetic relaxation. System exhibiting a single energy barrier should give an exponential magnetic relaxation for the value of $\gamma \geq 1$. In real system, several energy barriers involved in magnetic relaxation, lead to a distribution of relaxation times. The solid red lines shown in Fig. 7 are due to fitting of stretched exponential Eq. 2, giving the value of $\gamma = 0.37$ (x = 0.0) and 0.4 (x = 0.3), respectively. Simultaneously, It can be noticed that Bi doping decreases the relaxation time τ [x = 0.3, $\tau \sim 2.4 \times 10^7$] almost by two order as compared to un-doped compound [x $= 0.0, \tau \sim 8.5 \times 10^9$]. The estimated values of γ and τ are in good agreement with the values observed for spin-glass system⁴⁴. This clearly suggest that Bi doping relaxes the system at a faster rate. Figure 7(b) displays time dependent semi-logarithmic plot of normalized magnetic relaxation data. Parent compound shows continuous increase of magnetization with time. On the other hand, sample x = 0.3 enters in a regime of saturation at higher time scale (after τ_2). In this regime, the magnetization change tends to zero for $t \gg \tau_2$ and for $t \ll \tau_1$, the magnetization varies linearly with time 43,45 , consistent with a distribution function of finite width. Therefore, it can be concluded that $Y_{2-x}Bi_xIr_2O_7$ series looks like glassy mixed phase.

Electrical resistivity as a function of temperature for $Y_{2-x}Bi_xIr_2O_7$ series is shown in inset of Fig. 8a. The value of resistivities at room temperature for all the samples are as follows: 0.18 $\Omega - cm$ (x = 0.0), 0.03 $\Omega - cm$ $(x = 0.1), 0.02 \ \Omega - cm \ (x = 0.2), and 0.005 \ \Omega - cm \ (x = 0.2)$ = 0.3). The x = 0.0 sample is known to show insulating like behaviour in the whole temperature $range^{9,15}$, which diminishes with Bi doping. For doping level x =0.1, insulator like temperature dependence is observed, while for x = 0.2 and 0.3, we find much lower resistivity with minima at temperatures ~ 140 K, 130 K, respectively. As the conduction mechanism in parent sample follows the power law model, $\rho = \rho_0 T^{-n}$, where n is the power law exponent & ρ_0 is the prefactor, respectively, the $\rho(T)$ data are analyzed by fitting to the power law in the temperature range 14-90K (x = 0.0), 14-70K (x= 0.1), 14-50K (x = 0.2), 14-35K (x = 0.3) shown in inset of Fig. 8a. The fitting parameters are estimated to be n, & $\rho_0 \sim 3.1$ & $9 \times 10^5 \ \Omega - cm$ (x = 0.0), 1.4 & 42 $\Omega - cm$ (x = 0.1), 0.6 & 0.3 $\Omega - cm$ (x = 0.2), $0.1 \& 0.005 \ \Omega - cm \ (x = 0.3)$, samples. The MIT state in $Y_{2-x}Bi_x Ir_2 O_7$ series is of general interest. While replacement of Y^{3+} with Ca^{2+} leads to hole doping, which in turn, gives rise to a finite density of states near the Fermi level^{22,23}, the introduction of Bi in $Y_2 Ir_2 O_7$ system does not create holes but fills up the 5d orbital. The greater ionic radius of Bi^{3+} (1.17 Å) compared to Y^{3+} (1.01 Å) introduces disorder into the compound by spatially deforming the cell volume. Substitution of Bi^{3+} ions enhances the hybridization between the $Bi \ 6s/6p$ orbital with the Ir 5d orbital^{6,38}. The energy of this hybridization is much larger than the SOC and coulomb



FIG. 8. (a) Magnetoresistance as function of applied magnetic field for $Y_{2-x}Bi_xIr_2O_7$ series measured at temperature 2K. Inset shows log-log plot of resistivity (ρ) as a function of temperature (T); ρ (T) of x = 0.0 sample is shown on right y-axis. The solid black line represents the theoretical fit due to power law. (b) Quadratic field dependence of MR.

correlation, which makes the Ir 5d bandwidth wider and drives the system into a metallic state. However, another fact that may push $Y_{2-x}Bi_xIr_2O_7$ to MIT state is an enhancement in the Ir - O - Ir bond angle as Bidoping content increases. It is known that for strong hybridization of p orbital of oxygen with t_{2q} - $Ir^{4+}(5d^5)$ orbital, Ir - O - Ir angle should be 180° in a Π type interaction. Because of the enlarged nature of Ir - 5dorbitals, the mixing of O(2p) - Ir(5d) is sufficient, thus favouring the interatomic exchange interaction. The reported Ir - O - Ir bond angle is 116^0 in $Y_2 Ir_2 O_7$ system, much greater than 90^0 supports the Ir - O - Ir antiferromagnetic superexchange interaction, leading towards a noncollinear and strong magnetic frustration⁷. On the other hand, the Ir - O - Ir angle is 131.4° in metallic $Bi_2Ir_2O_7^{46}$. Thus, it could be argued that the reason for improved conduction in Bi doped $Y_2 Ir_2 O_7$ compounds,

possibly due to enhancement in Ir - O - Ir bond angle as shown in Fig. 3d. Strikingly, such dependency of electrical transport behaviour on electronic structure parameters is almost similar to the behaviour under the applied hydrostatic pressure for the compound $A_2Ir_2O_7$ (A = Gd, Eu, Sm and Bi)^{13,14}.

Figure 8a shows the magnetoresistance (MR) as a function of magnetic field measured at temperature 2K. MR is defined as $\left[MR = \frac{\rho(H) - \rho(0)}{\rho(0)} \times 100\right]$. The undoped compound (x = 0.0) is known to show positive MR at low magnetic field accompanied by negative MR with quadratic field dependence at higher magnetic field 15 . The negative MR is progressively suppressed with Bi doping shown in Fig. 8a, although, quadratic field dependence is still observed shown in Fig. 8b. The MR behaviour produced by quantum interference in presence of strong SOC is described by two time scales⁴⁸. (I) spin-flip time τ_{so} , and (II) the dephasing time τ_{ϕ} . When $\tau_{\phi} \gg \tau_{so}$, i.e. non-magnetic impurity scattering is dominant, destructive quantum interference between time reversed trajectories is obtained, leading to weak antilocalization and a positive MR. In $\tau_{\phi} < \tau_{so}$ regime, i.e. when SOC is weak, the quantum interference is always in-phase and constructive giving rise to negative MR with increasing magnetic field (Weak localization). The weakening of negative MR with Bi doping imply enhancement of spinorbit coupling due to the replacement of lighter Y^{3+} with non-magnetic heavier Bi^{3+} .

Figure 9a shows de-convoluted spectra of Ir 4f corelevel XPS of two representative sample x = 0.0, 0.3of $Y_{2-x}Bi_x Ir_2 O_7$ series using asymmetric Gauss-Lorentz sum function. XPS peaks are labeled following the proto-col reported elsewhere^{9,10,36,49}. For Ir^{4+} , $4f_{7/2}$ and $4f_{5/2}$ electronic states arise at binding energy around 62eV and 65eV due to spin-orbit coupling, respectively, which are represented by blue solid line and blue dashed line in Fig 9a. Similarly, higher oxidation state Ir^{5+} centered at 63.7eV and 67eV shown by green solid line and green dashed line, respectively in Fig 9a for $4f_{7/2}$ and $4f_{5/2}$. Fitted result show very small contribution from the Ir^{5+} oxidation state along with major contribution from the Ir^{4+} charge state for x = 0.0 sample, consistent with previous reports^{9,15,17,22}. For Bi doped compounds, the contribution from Ir^{5+} is minimally increased. It suggest the marginal increase in Ir oxidation state, i.e. Ir^{4+} and $Ir^{4.2+}$, as Bi doping content increases shown in Fig. 9d. Therefore, it seems that replacement of Y^{3+} by Bi^{3+} does not support the formation of higher oxidation states. However, it can create anion vacancies at O' sites which is favorable due to presence of polarizable Bi^{3+} cation at Y^{3+} site⁴⁶. Figure 9c shows Y3d XPS for x = 0.0, 0.1, 0.2, 0.3 samples. Variation in the Bi - 4f and Y - 3dXPS spectra with different doping concentration of Bican also be seen. The Y - 3d shows a single feature at 156.4eV and 158.3eV, suggest that only $\tilde{Y^{3+}}$ is present in the x = 0.0 sample. On the other hand, we observe a superposition of the Y - 3d and Bi - 4f XPS peaks.



FIG. 9. (a) deconvoluted Ir 4f peaks for x = 0.0, 0.3 samples, (b) deconvoluted O 1s peaks of the x = 0.0, 0.3 compounds. (c) Y 3d and Bi 4f XPS for x = 0.0, 0.1, 0.2, 0.3 compounds, (d) Intensity ratio I^{5+}/I^{4+} Ir^{5+} and asymmetry factor (shown in inset) as a function of Bi doping content (x), where I = Ir.



FIG. 10. Deconvoluted XPS valence band spectrum of Ir-5d (a) x = 0.0, (b) x = 0.3 samples. (c) Density of states estimated according to the protocol reported elsewhere⁴⁷.

It is clear that Y - 3d peaks exhibit the Bi - 4f peak due to overlapping of energy ranges. The details about XPS of Bi doped Y_2O_3 is given eleswhere⁵⁰. In further support of mixed oxidation state, the O 1s XPS spectra for x = 0.0, 0.3 compounds are shown in Fig. 9b. The peaks located at binding energies 529eV and 531.4eV are attributed as lower O(L) and higher O(H) binding energy peaks, respectively. The O(L) is assigned to oxygen lattice of $Y_{2-x}Bi_xIr_2O_7$ series while O(H) is related to oxygen vacancies or $defects^{51}$. The enhancement in the peak area ratio of $\frac{O(H)}{O(L)}$ against Bi doping content suggests the enhancement in oxygen vacancies in the compounds with increased Bi doping. We have estimated asymmetry factor in Ir 4f XPS following the protocol reported eleswhere^{46,49} and plotted as a function of Bidoping content (x) shown in inset of Fig. 9. It is obvious



FIG. 11. Intensity normalized Raman spectra of two representative samples x = 0.0, 0.3 of $Y_{2-x}Bi_x Ir_2 O_7$ series measured at room temperature in the spectral range 200-800cm⁻¹.

TABLE I. Indexed Raman peaks with their respective wavenumbers

Modes	T_{2g}^{1}	T_{2g}^{2}	T_{2g}^{3}	T_{2g}^{4}	E_g	A_{1g}	T1
Wavenumber	305	350	550	630	391	523	665

that less conducting parent sample exhibit less asymmetry compared to high conducting x = 0.1, 0.2, 0.3 samples. Asymmetry in *Ir* 4f line shapes can be attributed to the 5*d* conduction electron screening, which could also explain the enhanced conductivity of the doped samples.

Furthere, we measured XPS valence-band spectra (VBS) to determine the unoccupied and occupied density of states (DOS) for x = 0.0 and 0.3 samples. We have deconvoluted the XPS valence-band spectra using a sum of Lorentzians and Gaussian to determine the contributions of $O-2p^{47}$. The two peaks, centered at binding energy 1.2eV and 4.7eV shown in Fig. 10a,b are assigned as Ir-5d (t_{2q}) state and O-2p state, respectively. The contribution of Ir-5d band is estimated by subtracting the O-2p contributions shown in Fig. 10c. We obtain enhancement in DOS attributed with Ir-5d band in x =0.3 sample as compared to un-doped compound, which is consistent with lower resistivity and MIT behaviour of the x = 0.3 sample. The enhancement of Ir-5d peak close to Fermi energy level (E_F) regime in x = 0.3 sample might be due to the marginally enhanced oxidation state of Ir compared to x = 0.0 compound. This makes the $Y_{2-x}Bi_x Ir_2 O_7$ system more conducting.

To further explore structural change and the possible cause behind the huge reduction in electrical resistivity in Bi doped samples as compared to parent compound, Raman spectroscopy has been carried out. Figure 11 shows Raman spectra recorded at room temperature for x =0.0, 0.3 samples. An ideal cubic pyrochlore iridate with formula $R_2 Ir_2 O_6 O'$, space group $F d\bar{3}m$ should have six Raman active fundamental modes⁵² distributed among

 $A_{1g} + E_g + 4T_{2g}$ modes, involving only vibrations of oxygens at both 48f and 8b sites. Table I show indexed modes with their respective wave numbers. The four peaks named as T_{2g}^1 , \tilde{T}_{2g}^2 , T_{2g}^3 and T_{2g}^4 are Raman active while the peak named as T1 has been reported as second order scattering for pyrochlore oxides. The most characteristic features of Ir-pyrochlore spectra are a sharp mode at ~ 391cm^{-1} , and ~ 523cm^{-1} which includes contributions from the E_q mode and A_{1q} mode, respectively. It have been shown that intermediate vibrational modes $E_g T_{2g}^3$ and $A_{1g} T_{2g}^2$ arise due to vibrations of Ir - O and R - O' bond. Here, A_{1g} mode is related to the positional parameter, directly affecting the R - O' bond environment. For x = 0.3 sample, $E_g - T_{2g}^3$ vibrational mode shift towards lower wave number, while A_{1g} - T_{2g}^2 modes towards higher wave number as compared to parent compound. This feature are arising due to enhancement in hybridization between Y(4p)/Bi(6s), O-2p and Ir-5dorbitals suggest reduction in Ir - O bonds consistent with XRD shown in Fig. 3c and enhancement in R - O' bonds. In this process t_{2q} bandwidth increases as the *R*-site ionic radius increases lead to enhanced electrical conductivity.

The plausible scenario for the MIT in the $Y_{2-x}Bi_xIr_2O_7$ series compounds is related to the modification in structural parameters, arising due to the isovalent Bi substitution at the Y-site as distinct from the previous studies which rarely focus on the relation between structural parameters and the magnetic and the electrical transport properties^{22,23,26,27}.

IV. CONCLUSION

We have investigated the structural, magnetic, and electrical transport properties of the pyrochlore iridates $Y_{2-x}Bi_xIr_2O_7$. The replacement of Y^{3+} with Bi^{3+} stabilizes the antiferromagnetic correlation and enhances electronic conductivity. The XRD analysis shows Ir – O - Ir bond angle increases and Ir - O bond length decreases as distortion in $Ir - O_6$ octahedra is reduced against increasing Bi^{3+} doping content. The X-ray photoemission spectroscopy measurements suggest marginal enhancement in Ir oxidation states ranging from Ir^{4+} to $Ir^{4.2+}$ with Bi doping, promoting the anion vacancies at O' site. The enhancement in electrical conductivity with Bi^{3+} is likely a consequence of hybridization between the Y(4p)/Bi(6s), O - 2p and Ir - 5d orbitals. Raman spectroscopy shows contraction in Ir - O bonds [consistent with XRD results] and elongation in R - O'bonds as disorder and phononic oscillation are reduces by Bi doping, leading to orders of magnitude enhancement of electrical conductivity along with MIT. On the other hand, enhancement in antiferromagnetic correlation can be explained in term of increased Ir - O - Ir bond angle against Bi doping. Bifurcation between χ_{ZFC} and χ_{FC} at higher temperature with hysteretic isothermal magnetization at low magnetic field might be associated to spin-glass-like transition rather than long-range ordering,

as confirmed by magnetic relaxation measurements.

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