Bulk ferromagnetism and large changes in photoluminescence intensity by magnetic field in $\beta$-Ga$_2$O$_3$.

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In this letter we report observation of room temperature ferromagnetism in bulk Ga$_2$O$_3$. We also observe large (10-60%) increase/decrease in photoluminescence. In the red (700 nm wavelength)/blue (500 nm) with the application of small magnetic field (0.4 Tesla). We argue, that ferromagnetism occurs entirely due to chains of oxygen (O(3) sites, Fig. 5) vacancies. We propose a simple model to explain, origin and location of moment, formation of ferromagnetic dislocation needles, and strong increase/decrease of red/blue photoluminescence intensity with magnetic field.

Ever since the discovery of ferromagnetism in graphite$^1$, CaB$_6^2$, HfO$_2$ $^3$, a new paradigm of ferromagnetism has opened up, which Coey$^4$ aptly calls d$^0$ ferromagnetism. Unlike traditional ferromagnets where moments come from unpaired d or f electrons, these materials have no obvious source of magnetic moment. Recently ferromagnetism was also reported in TiO$_2$ and In$_2$O$_3$ thin films$^5$. Ferromagnetism in nanoparticles of Al$_2$O$_3$, ZnO, SnO$_2$, CeO$_2$ is observed by Sundaresan et al$^6$ and conjectured to be a universal property of metal oxides with either empty or filled d or f energy levels, in nanoparticle form. There are strong phenomenological reasons to believe that the common origin of ferromagnetism in all these materials might be due to defects and vacancies in the solid$^7$. Theoretically Monnier et al$^{14}$ have predicted moment formation near missing $B_6$ octahedra (anion vacancy) in CaB$_6$. Elfmov et. al$^{13}$ had predicted small moment formation near cation vacancy in Rocksalt structure binary metal oxides (CaO). The basic idea is to have atomic vacancies that have large local symmetry, so that electrons/holes residing in the vacant sites have degenerate orbitals available. Local Hund’s exchange forces parallel alignment of the defect site electrons and give rise to non zero moment. Experimentally we dont know much about the spin structure in these materials and the role of different kind of defects are also not known. Neither do we have a chemical intuition about the requisite kind of defects that might hold moments. In this paper, we report bulk (grain size larger than 30 micron) ferromagnetism in Ga$_2$O$_3$. To our knowledge nobody has found this before. We also find a large (15-20%) increase in photoluminescence intensity with application of small magnetic field (0.4 Tesla). Starting from the structure of Ga$_2$O$_3$ we present a simple intuitive model, that identifies O(3) type anion vacancies (see Fig. 1) as the one that shows moment. Our model helps in understanding, ferromagnetism as well as increase in Photoluminescence with magnetic field in a unified way.

Ga$_2$O$_3$ powder of 99.999% pure was obtained from Alfa Aesar, UK. Powder was calcined at 950°C in static air for 24 hours and furnace cooled. Powder was compacted into pellets of 10 mm diameter under a pressure of 70 MPa. The pellets were annealed for 24 hours at 1200 and 1300°C in a closed environment of low oxygen fugacity. Room temperature X-ray powder diffraction (XRD) pattern was recorded in 2q range 15 to 120 degrees with a step interval of 0.05 degrees using STOE diffractometer operated in Bragg-Brentano geometry. Magnetization (M) as a function of temperature and field (H) measurements were carried out in a MPMS-7 Tesla Quantum Design system from 2 K to 340 K. Optical photoluminescence (PL) was studied using 324 nm line of He-Gd continuous wave laser as excitation and dispersion with three set of holographic blazed 1800 grooves/mm gratings in a double subtractive triple monochromator (Juvin-Yvon T64000 spectrograph) in a back scattering configuration. A liquid N2 cooled back-thinned CCD detector is used for the detection of scattered intensity. The room temperature (RT) powder X-ray diffraction of $\beta$-Ga2O3 is shown in Figure 1 and the inset of Fig. 1 shows the Raman spectra recorded at RT. The diffraction pattern could be indexed to monoclinic structure (Space group: C 2/m). The zero field cooled (ZFC) and field cooled (FC) thermomagnetisation curves for H=100 and 2000e are shown in Fig. 2. It is seen that the magnetization for H= 200 Oe larger that for H=1000e and that they exhibit a temperature of irreversibility ($T_{irr}$) at about 300K, clearly indicating the presence of ferromagnetic ordering. In all the measurements, a dominant paramagnetic contribution emerges for T < 20K. The DM (MFC-MZFC) vs T plot (inset of Fig 2) demonstrates the presence of a robust ferromagnetic state with a Curie transition temperature $T_C = 303K$. The hysteresis loops recorded at T= 150, 55 and 2K are shown in Fig. 3. The loops exhibit vanishingly small remanent magnetization ($12 \times 10^{-3}$ emu/g) and coercive field (136 Oe) (Fig. 3(a)), much similar to that of diluted magnetic semiconductors. Though the loops exhibit a closure, they are progressively sloppy with decrease of temperature signifying the presence of paramagnetic contribution, consistent with thermomagnetisation results (Fig. 2).

The photoluminescence measured at RT (see Fig 4) exhibits a predominant red (725 nm) and weaker UV (395 nm) and blue (525 nm) emission. UV, blue PL were found
FIG. 1: X-Ray power diffraction pattern. Inset shows the Raman spectra.

FIG. 2: Field cooled and zero field cooled magnetization versus temperature at fields of 100 and 200 Oe. Inset shows DM (MFC-MZFC) vs T plot.

FIG. 3: Hysteretic M-H loops at T=150, 55, 2 K. Inset Fig 3(a) expands the low field region, and Fig 3(b) shows M vs $H^2$ plot showing that what we see is ferromagnetism and not superparamagnetism.

FIG. 4: Photoluminescence (emission) spectra without (green line) and with (red line) external magnetic field (0.4 Tesla) for $\beta$-Ga$_2$O$_3$ vacuum annealed at 1000 K for 24 Hours. Blue line is for Prestine sample. Inset shows the percentage change in intensity with magnetic field.

to be dominant emissions in single crystals, they are substantially suppressed in the ceramic samples. Striation riding over the red emission (700 to 900 nm) is artifact of the back thinned CCD camera and is known to arise from the Ettalong effect.

Room temperature electron spin resonance (ESR) studies carried out in X-band mode using Bruker instrument could not detect any paramagnetic species. From the particle induced X-ray emission (PIXE) studies under the bombardment of proton, no impurity species could be detected except for Ni, whose concentration is determined to be less than 200ppm. From the ESR and PIXE measurements it is clear that, ferromagnetism in Ga$_2$O$_3$ does not arise from the paramagnetic impurity species. Though, non saturation of hysteresis loops at 55 and 2K (Fig. 3) could imply superparamagnetism, it is to be noted that the same measured at higher temperature (100K) exhibits a saturation and no blocking temperature, as seen in the thermomagnetisation curves (Fig. 2). Additionally, the nonscaling of M vs H/T curves (Fig. 3(a)) rules out superparamagnetism. Strong deviation of the loops from saturation with decrease of temperature signifying the presence of paramagnetic contribution, whose origin will be discussed below and is consistent with thermomagnetisation results (Fig.2). From the foregone discussion, we conclude that a long range ferromagnetic ordering is present. In the following a plausible explanation is provided for presence of ferromagnetic interaction, intimately related to defect structures.

Substantial difference exists, atleast in a quantitative way, in the defect structures between poly and sin-
FIG. 5: Structure of β-Ga$_2$O$_3$ showing three different types of Oxygen sites O(1),O(2) and O(3). The local symmetry around these sites are shown at the bottom.

Ga$_2$O$_3$ is an ionic insulating dielectric with band gap of 4.7 eV\[^7\]. Electrical conductivity is entirely due to defect electronic States with n type conductivity and arises due to oxygen vacancies. Concentration of charge carrier estimated by Hall measurement\[^2\] is about 10$^{18}$/cm$^3$ to 3.0×10$^{17}$ cm$^3$ for single crystal and polycrystalline materials. Several experiments point out partial delocalisation of electrons in Ga$_2$O$_3$, even though conductivity is always activated type with small gap(20-30 meV). There are dynamic nuclear magnetic polarisation by Overhauser effect\[^10\] and narrow EPR lines(coming from motional narrowing)\[^11\] which points to presence of mobile electrons. PL measurements\[^12\] on the other hands shows large Stoke shift, characteristics of localised electrons with large electron-phonon coupling. Conductivity is highly anisotropic in single crystals. Conductivity along b axis is in order of magnitude larger than in other directions\[^13\].

Oxygen O(1) sites are not in plane of 3 near neighbour Ga atoms. O(2) sites has tetrahedral coordination with 4 Ga atoms. O(3) sites are at the center of the plane made by 3 near neighbour Ga atoms, and forms a chain along the b axis(perpendicular to the plane of 3 Ga atoms). Local site symmetry of O(3) sites are much more than O(1)/O(2) sites. The lowest energy wavefunc-

FIG. 6: Schematic drawing of doubly degenerate donor electron wavefunctions $P_{±}$ around a O(3) vacancy.

FIG. 7: Schematic drawing of defect site electron energy levels and the electronic transions responsible for UV, Blue and Red emission in β-Ga$_2$O$_3$.

tions of the O(3) vacancy site electrons will presumably be like, $P_{±} = \frac{1}{\sqrt{2}}(S ± P_{z})$, where $z$ is along the chain b axis. This symmetry related degeneracy , forces the two electrons on the neutral O(3) vacancy sites to occupy singly two degenerate $P_{±}$ orbitals in a spin triplet $S = 1$ state. $P_{±}$ wavefunctions(Fig 6) have considerable overlap(large hopping matrix element) along the chain direction. To have double exchange operating between the O(3) vacancy sites we propose the existence of some fraction of O(3) vacancy sites with one electron with the other electron promoted to a nearby Ga atom which moves to an interstitial position. This is a O(3) Vacancy-Ga interstitial pair(PR from now on). This pair has a vacancy in either $P_{±}$ orbital around the O vacancy site. This vacancy is a carrier. So if the O(3) vacancies are bunched along chain segments, each having some number of PR’s ( charge carriers) then, local ferromagnetism follows naturally. The double exchange and electronic delocalisation is happening only on the O(3) vacancy chains . The original Ga$_2$O$_3$ lattice sites acts as just a template. Isolated O(3) vacancies will give paramagnetic signals. O(3) vacancy chains without sufficient number of $P^+$ centers are likely to be antiferromagnetic(superexchange) and not contribute to total moment. Assuming 0.2% of O(3) vacancies (each holding about 1 $µ_B$ moment) and assuming about half of them taking part on double exchange along fragmented chains, we estimate a moment of 5×10$^{-3}$ emu/gm , which is close to the observed moment(8×10$^{-3}$ emu/gm) at H=7 Tesla and T=2 K.

Large $T_c$, low value of the net moment, the persistence
of some paramagnetic component to the total moment at the lowest temperatures, all makes the bulk ferromagnetism problem very challenging.

Photoluminescence comes from transition of electrons between different kinds of defect related (centered) states. Their energies all fall within the band gap. Hajnal et al has estimated by semiempirical quantum chemical calculations, the energy levels of donor electrons coming from O(1), O(2) and O(3) sites at 4.2,4.3(shallow donor) and 2.8(deep donor) eV. In Fig. 7 we schematically draw different levels and show the photoluminescent transitions. We believe the red emission at 700 nm(1.3 to 1.7 eV) is predominantly due to electronic transitions when, a donor electron from O(1) or O(2) vacancy site jumps to the unoccupied (P+ or P−) level of a PR. The electron that jumps down to the O(3) sites must come with right spin direction(parallel to the spin of the already existing electron . This local Hunds rule constrain affects the spin direction(parallel to the spin of the already existing electron). This local Hunds rule constrain affects the transition in the red region. The net spectral weight under the red emission line, W is given by,

\[ W \propto N_1 \cdot N_2 \cdot N_p \cdot \cos\left(\frac{\theta_{1,2} - \theta_3}{2}\right) \]

where \( N_1 \) and \( N_2 \) are the number of electrons in O(1) and O(2) vacancies, \( N_p \) is the number of O(3) vacancy-Ga intertial pair. The cos factor depends on the relative spin orientations of the electron in the initial state at O(1) or O(2) site and the lone occupied electron present in the final state O(3) vacancy site. The incoming electron must come with correct spin. This is the origin of the strong increase of the Red emission net spectral weight with the application of very small magnetic field. For Blue emission on the other hand, the final state is an acceptor state which is nondegerenate. So if it already contain an electron, it can only accept an electron of opposite spin. This becomes difficult with application of magnetic field. That is why Blue/UV emission intensity gets supressed with magnetic field.

To summarise, we found Bulk ferromagnetism in \( \beta \)-Ga2O3. We also find large increase/decrease in photoluminescence in the red/blue region, with application of small magnetic field(0.2 Tesla). We propose, the magnetic moments arise from O(3) vacancy chains(dislocation lines). Recent works on Fe doped \( \text{HfO}_2\) and Co doped \( \text{TiO}_2\) points out that magnetism in these dilute magnetic semiconductors could be due entirely to the anion vacancies. Ubiquitous presence of charged dislocations in ZnO and GaN improving conductivity(magnetism ?) all suggests that magnetism in these materials may be improved by controlling density of dislocations. Light induced magnetism and large chage in photoluminescence intensity with magnetism in all these materials should be looked for.

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