Superconductivity in V-doped Mg$_{1-x}$Ti$_2$O$_4$

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Around fifty years ago, LiTi$_2$O$_4$ was reported to be first spinel oxide to exhibit a superconducting transition $\sim 12$ K. Recently, MgTi$_2$O$_4$ has been found to be the only other spinel oxide to reveal a superconducting transition with a $T_c$ around 3 K, however, its superconducting state is realized only in thin film superlattices involving SrTiO$_3$. We find that a V-doped Mg$_{1-x}$Ti$_2$O$_4$ phase, which is reproducibly stabilized as a thin surface layer on top of stoichiometric and insulating V-doped Mg$_2$Ti$_2$O$_4$ bulk sample, exhibits high-temperature superconductivity below $\sim 16$ K. The superconducting transition is also confirmed through a concomitant sharp diamagnetic transition immediately below $T_c$. The spinel phase of the superconducting surface layer is confirmed through grazing-incidence X-ray diffraction and Micro-Raman spectroscopy. A small shift of the sharp superconducting transition temperature ($\sim 4$ K) with application of a high magnetic field (upto 9 Tesla) suggests a very high critical field for the system, $\sim 25$ Tesla. Thus, V-doped Mg$_{1-x}$Ti$_2$O$_4$ exhibits highest $T_c$, among spinel superconductors and also possesses a very high critical field.

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Identification of new superconducting materials is an extremely fascinating and challenging task in the field of condensed matter physics. In this regards, spinel compounds, which are well known for exhibiting a plethora of functional properties due to a strong coupling between its charge, spin, orbital and lattice degrees of freedom, are rarely found to be superconductors. Around five decades ago (1967), some of the sulpho and seleno spinels were successfully synthesized with superconducting transition temperatures $\sim 4$ K [1,3]. In the family of spinel oxides, superconductivity was first realized in the mixed valent titanate spinel, LiTi$_2$O$_4$, with much higher transition temperature ($T_c$) $\sim 12$ K [4]. While the mechanism driving the superconducting transition in LiTi$_2$O$_4$ still remains to be settled, the role of orbital degrees of freedom and spin-orbital fluctuations seem important [5-8]. Several investigations were performed to increase the superconducting $T_c$ of LiTi$_2$O$_4$ by doping at the Ti site with Mg, Mn, Li, Al, Cr ions, however, the $T_c$ was found to decrease rapidly with increase in doping percentage [9-12].

Superconductivity in the family of mixed titanate spinel oxide Mg$_2$TiO$_4$-MgTi$_2$O$_4$ remain controversial; in one group of studies, the Mg$_2$TiO$_4$-MgTi$_2$O$_4$ compounds were found to exhibit a zero resistive transition, albeit with the onset of diamagnetic signal at much lower temperatures (almost at 40 K smaller temperatures than the onset of zero resistance state) [13,16], other group of studies suggested these compounds to be instead semiconducting [17,18]. Recently, superconductivity has been reported in a superlattice consisting of Mg$_2$TiO$_4$ and SrTiO$_3$ with a $T_c$ $\sim 3$ K (where substrate induced strain was found to play a critical role) [19] and in Mg: Ti$_5$O$_{10}$ (possessing orthorhombic Ti$_5$O$_{10}$ structure) film on the (011)-oriented substrate (MgAl$_2$O$_4$) with a $T_c$ $\sim 5$ K [20]. Bulk Mg$_2$Ti$_2$O$_4$, containing Ti$^{3+}$ ions, remains insulating (reported to be a Mott insulator [21,22]) down to the lowest temperature and undergoes an insulator to high-temperature metal (or semiconducting [13]) transition around 260 K. This phase transition is also accompanied with a Ti$^{3+}$-ion related Jahn-Teller distortion driven tetragonal to cubic structural and a Ti spin-singlet transition [23,24]. The low-temperature tetragonal phase hosts a unique tetramer orbital ordering involving the Ti$_{12g}$ orbitals along $<111>$ direction and is chiral ($P4_12_2$) [21,22,25]. V doped MgTi$_2$O$_4$ still remains a Mott insulator down to the lowest temperature [26,27], however, V doping leads to a unique mixed valence state for both Ti (both Ti$^{3+}$ and Ti$^{4+}$) and V ions (both V$^{3+}$ and V$^{2+}$), as it is energetically favourable for some of the Ti$^{3+}$ ($3d^1$) ions to donate their single electron (and thereby become Jahn-Teller inactive $3d^0$) to the doped V$^{3+}$ ($3d^2$) ions (which also then becomes Jahn-Teller inactive $3d^3$) [27]. This mixed valence state of the transition metal ions in V-doped MgTi$_2$O$_4$ accompanied with a unique band structure leads to exotic functional properties, like a dc current-induced insulator to metal switching at ultra-low electric field [27]. The present results on the emergence of superconductivity on the surface layer of V-doped MgTi$_2$O$_4$ (associated with a Mg$_{1-x}$Ti$_1.4$V$_{0.6}$O$_4$ spinel phase), further charge-doped due to Mg deficiency, with a much higher $T_c$ ($\sim 16$ K) (the highest $T_c$ among spinels) and a very high upper critical magnetic field value is, thus, extremely promising. To prepare the polycrystalline Mg$_{11-x}$V$_{0.6}$O$_4$ sample, MgO (10% excess Mg taken following [18]), V$_2$O$_5$, Ti$_2$O$_3$ and metallic Ti powders were thoroughly mixed, ground and casted into a pellet. The resultant pellet was subsequently annealed at 1080°C under vacuum condition in a sealed quartz tube. While the bulk of the sample was found to be black in colour (corresponding to the MgTi$_{1.4}$V$_{0.6}$O$_4$ phase), a combination of two phases could be detected as a thin-surface layer, one of them being the black-coloured bulk phase and another an emergent grayish coloured phase. To investigate
the structural phase of the surface layer, we have carried out the grazing-incidence X-ray diffraction (GIXRD) with very low incident angle using Cu-Kα source. The powder X-ray diffraction (XRD) of the bulk sample was obtained after scraping off the thin grayish surface layer to investigate the structural phase. Micro-Raman experiments were carried out using a 532 nm laser source to further investigate the structural phases of the grayish and dark regions of the thin surface layer. Temperature-dependent four-probe resistivity and magnetization measurements were carried out using a Physical Property Measurement System (PPMS). The resistivity measurements were carried out by painting electrical contacts on the MgTi$_{1.4}$V$_{0.6}$O$_4$ sample, with and without (obtained by scraping with a sand paper) the thin grayish surface layer, as shown in the insets of Fig.1(a).

We first discuss the structural phases for the bulk and the grayish surface layer, as investigated through powder XRD and GIXRD measurements. As seen through a comparison with XRD diffraction pattern of standard MgTi$_2$O$_4$ in Fig.1(a), the bulk of the synthesized MgTi$_{1.4}$V$_{0.6}$O$_4$ is found to stabilize into a cubic spinel phase. Along with the main spinel phase, a small fraction of a secondary phase of Ti$_2$O$_3$ (corundum) (the corresponding XRD peaks are indicated by asterisks) can also be detected. Since the Ti$_2$O$_3$ is not superconducting [29, 30] (also the bulk sample, without the surface layer, is found to be insulating), its presence does not affect the present results. To probe the structural phase of the surface layer, GIXRD with a very low incident grazing angle of 1.5° was performed, so that the X-ray beam mostly get diffracted from the surface layer. Clear, though weak (due to low sample volume), characteristic XRD peaks corresponding to two spinel phases, which vary in their lattice parameters (thereby leading to a splitting in the XRD peak positions), can be detected through GIXRD (as seen in Fig.1(b)). Notably, the GIXRD peaks of the thin grayish surface layer do not match with the XRD pattern corresponding to the Ti$_6$O$_{10}$ orthorhombic structure of the superconducting Mg-Ti-O superconducting films [29]. Representative splitting of the (440) (Fig.1(b)), (311), (511) (not shown here) XRD peaks, which arise from the presence of two spinel phases in the surface layer, are clearly seen. The observation of two spinel phases (as seen through GIXRD), is in consistence with an inspection of the top grayish surface layer under a microscope (as seen in image of inset of Fig.2), which clearly exhibit two distinct sample regions, i.e. overlapping grayish islands interspersed on relatively blackish sample regions, with the relative content of the later increasing with depth in the sample. The decrease in intensity of the second (higher 2θ) peak (∼ 62.1°) in GIXRD (as seen in Fig.1(b)), collected with a larger incidence angle of 4.5° (which, thereby, probes the structure deeper into the sample) suggests that the higher 2θ peaks, associated with a smaller lattice parameter, correspond to the grayish regions of the surface layer. Further, a systematic decrease in the bulk lattice parameter (leading to a tuning of the corresponding XRD peak positions to higher angles [28]) on reducing the Mg content in a control Mg$_{x}$Ti$_2$O$_4$ series, synthesized with lower sintering temperature (to reduce further Mg loss), is clearly observed. The spinel phase corresponding to the higher 2θ XRD peaks (seen in Fig.1(b)) is, thus, likely off-stoichiometric (most likely Mg deficient due to its increase volatility at higher sintering temperature), while the spinel phase corresponding to the lower 2θ XRD peaks is near stoichiometric (comparable to the bulk, as seen in Fig.1(a), which is black in colour).

To further investigate the structural properties, Micro-Raman measurements were carried out by preliminary focusing the laser beam on the grayish and black regions of the surface layer, as shown in Fig.2. The corresponding Raman peaks and their positions, the reproducibility of which were checked between different regions, clearly suggest spinel phases for both these regions [31,35]. The observed main peak around 230 cm$^{-1}$ in the Raman spectra for the black region, is reported to be associated with vibrations involving mainly the AO$_4$ (in our case with MgO$_4$) units of the spinel phase [32,34]. The decrease in intensity in the Raman spectra of grayish region suggests the A-site off-stoichiometry and associated disorder for the grayish surface layer. Due to a preponderance of the grayish sample regions over the black sample portions (as seen in inset of Fig.2), in the top layer (both having typical grain sizes of ∼ 1 μm, which is also comparable to the Raman laser-beam spot-size), a small hump, at around 300 cm$^{-1}$, corresponding to the main peak of the gray sample area, becomes discernible in the Raman spectrum collected on the black sample regions, as seen in Fig.2. However, the shift in the main peak positions (shown in inset of Fig.2) of the grayish region to higher wavenumber in comparison to the corresponding spectra for the black region indicates a decrease in lattice parameters for the grayish region, in consistence with the GIXRD results.

The temperature-dependent four probe resistivity values of the polycrystalline MgTi$_{1.4}$V$_{0.6}$O$_4$ sample, measured with
and without the grayish surface layer, are shown in Fig. 3 (a) (schematic diagram of four probe electrical contacts shown on a real sample image). Surprisingly, while the measurement including the grayish surface layer exhibits a superconducting transition, with a high $T_c$ of around 16 K, the measurement on the sample without the grayish surface layer (i.e. property of the bulk of the sample) leads to an insulating behavior down to the lowest temperature. The high temperature insulating nature which show a similar temperature dependency for both the resistivity curves, appears to be driven by the resistivity of the bulk sample. At temperatures below around 120 K, the transport property of the grayish surface layer seems to dominate over the bulk transport property, suggesting a lower resistance for the surface layer in this temperature range. To further validate the emergence of a superconducting phase within the grayish surface layer, we have measured temperature dependent magnetization measurement on the pellet sample (which included the surface layer). Expectedly, the magnetization curve, as shown in Fig. 3 (b), clearly exhibits a sharp diamagnetic transition below the superconducting transition temperature of around 16 K (seen in the inset of Fig. 3 (b)). Notably, the observed $T_c$ for the superconducting transition is found to be the highest amongst the whole family of superconducting spinel compounds [11, 14, 36].

The temperature dependent resistivity curves, measured with varying applied magnetic fields, illustrate that even a high magnetic field of 9 Tesla remains nearly ineffective in changing the sharpness of the superconducting transition (as seen in Fig. 4 (a)) or the superconducting $T_c$ substantially ($T_c$ decreases by $\sim$ 4 K for 9 Tesla magnetic field), thereby, suggesting a very high upper critical magnetic field of this system. To estimate the critical magnetic field, the $T_c$ (taken to be the temperature at which the resistance drops to 90% of the normal state resistance) values corresponding to different magnetic fields have been plotted and fitted with some of the proposed models of superconductivity, such as Ginsburg-Landau [37, 38], Werthamer-Helfand-Hohenberg (WHH) [39] and Tinkham’s 2D model [40, 42], as shown in Fig. 4 (b). The WHH and Tinkham’s model, observed to fit the experimental data better in comparison to the Ginsburg-Landau model, suggests a very high upper critical magnetic field, such as $\sim$ 25 Tesla and 35 Tesla, respectively. Further investigations to ascertain the exact critical field value (i.e. to understand whether it is beyond the Pauli paramagnetic limit ($B_p = 1.84$ T$_c$)) will necessitate resistivity measurements with higher magnetic field values. Notably, both the estimated upper critical field values are much higher than those reported for either the sulpho and selenide superconductors (with upper critical magnetic field values less than 5 Tesla [11, 3]) or the spinel oxide superconductors (LiTi$_2$O$_4$ and superlattices of MgTi$_2$O$_4$, which have upper critical field values of $\sim$ 12 Tesla [19, 20, 43, 44]). Thus, the emergence of superconductivity in this system not only leads to the highest $T_c$ among spinel compounds but is also associated with a very high upper critical magnetic field, which is promising.

The realization of strained MgTi$_2$O$_4$ in thin-film superlattice with SrTiO$_3$ was reported to be crucial for the onset of superconductivity in MgTi$_2$O$_4$, albeit with a much lower $T_c$ and upper critical magnetic field values of $\sim$ 3 K and 12 Tesla,
In summary, we have reported the emergence of superconductivity should be investigated. and orbital fluctuations, and whether it helps in boosting superconductivity also seems very important. Particularly, as discussed earlier, V-doping into MgTi$_2$O$_4$ does bring in charge and orbital fluctuations, and whether it helps in boosting superconductivity should be investigated.

In summary, we have reported the emergence of superconductivity on a surface layer of a V-doped MgTi$_2$O$_4$ sample. The superconducting transition temperature and upper critical magnetic field is found to be five times and two times enhanced as compared to MgTi$_2$O$_4$ and SrTiO$_3$ superlattices. The sample off-stoichiometry (Mg deficiency for the spinel phase of the surface layer) along with doping of V ions seem critical for the observed superconductivity.

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