Direct evidence of the existence of Mn$^{3+}$ ions in MnTiO$_3$

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Abstract – We investigate the room temperature electronic properties of MnTiO$_3$ synthesised by different preparation conditions. For this purpose, we prepared MnTiO$_3$ under two different cooling rates, one is naturally cooled while the other is quenched in liquid nitrogen. The samples were studied using optical absorbance, photoemission spectroscopy and band structure calculations. We observe significant changes in the structural parameters as a result of quenching. Interestingly, in the parent compound, our combined core level, valence band and optical absorbance studies give evidence of the Mn existence in both $2^+$ and $3^+$ states. The fraction of Mn$^{3+}$ ions has been found to increase on quenching MnTiO$_3$ suggests an increase in oxygen non-stoichiometry. The increase in the fraction of the Mn$^{3+}$ ions has been manifested a) as slight enhancement in the intensity of the optical absorbance in the visible region. There occurs persistent photo-resistance when the incident light is terminated after shining; b) in the behaviour of the features (close to Fermi level) in the valence band spectra. Hence, the combined analysis of the core level, valence band and optical absorbance spectra suggests that the charge carriers are hole like which further leads to the increase in the electrical conductivity of the quenched sample. The present results provide a recipe to tune the optical absorption in the visible range for its applications in optical sensors, solar cell, etc.

Multiferroic materials find its application for various fields like high density data storage, solar cell, optical, humidity and magnetic sensor applications, etc. [1–5]. These properties arise because of the intricate coupling between charge, spin, orbital and lattice degrees of freedom. MnTiO$_3$ is one such system which has shown to exhibit multiferroic properties along a particular crystallographic axis [6]. The system under study belongs to the ilmenite family and stabilises in an hexagonal (layered) structure with $R3$ space group down to low temperatures [7]. At room temperature, this material is paramagnetic.

The compounds under study also find their application in the field of solar cells [8] owing to their strong absorption of light in the visible region. In MnTiO$_3$, it has been predicted [9] that the conductivity mechanism is of $p$-type. Based on the high temperature (from 300 to 500K) conductivity, Seebeck coefficient experiments, it was attributed that the mechanism could be due to the presence of a higher oxidation state of Mn like Mn$^{3+}$. Apart from this, based on the value of the effective magnetic moment (4.55 μB) obtained for the Mn ion in MnTiO$_3$, the value is smaller than that of the spin only value of Mn$^{2+}$. It was predicted that there could be incomplete ordering of Mn and Ti ions or the presence of Mn$^{3+}$ ions in this compound [10].

Apart from this, if Mn$^{3+}$ exists in this compound, it is expected to be reflected in the core level spectra through the behaviour of the satellite peaks. The signature of such states is also expected to be manifested in the optical absorption spectrum of the MnTiO$_3$. The peak observed in the visible region has been attributed to the intra-shell 3d transition of the transition metal ion and the one in the ultra violet (UV) region is linked with inter-band transition [11]. To understand its implications on the optical, transport and electronic structure, we have synthesised MnTiO$_3$ under different conditions and studied the above properties using x-ray diffraction, optical absorbance spectroscopy, photoemission spectroscopy and band structure calculations. Two compounds of MnTiO$_3$ were prepared by the usual solid state route only with...

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the difference that in one of the sample, the cooling was natural (MTO\textsubscript{uq}) while in the other it was quenched (MTO\textsubscript{q}) in liquid nitrogen.

Our results show that on quenching the sample, there occur, changes in the structural parameters, optical absorbance, core level and valence band spectra and the electrical resistivity. All the experiments were carried out at room temperature. We have observed the signature of Mn\textsuperscript{3+} ions in addition to Mn\textsuperscript{2+} ions even in the MTO\textsubscript{uq}. The fraction of the Mn\textsuperscript{3+} ions has been found to increase on quenching the sample. This further leads to an increase in the optical absorbance in the visible region, a persistent photo-resistance when the incident light is terminated after illuminating it and a decrease in the electrical resistivity. The features of the optical absorbance and valence band spectra were identified based on band structure calculations.

The samples were prepared by the conventional solid state route. The starting materials, MnCO\textsubscript{3} and TiO\textsubscript{2}, were ground using mortar and pestle and sintered at 1200°C for 24 hours in air. After this, we observed unreacted TiO\textsubscript{2} peaks in the x-ray diffraction pattern. A suitable amount of extra MnCO\textsubscript{3} was added and sintered until the single phase compound was formed. After the sintering process, the sample was allowed to cool naturally. This constitutes the MTO\textsubscript{uq} sample. To prepare the MTO\textsubscript{q} sample, the pellets of MTO\textsubscript{uq} were sintered at 1200°C for 1 hour and quenched in liquid nitrogen.

The absorbance spectra were collected using the powder x-ray diffraction (xrd) technique with Smart lab 9 kW rotating anode x-ray diffractometer. Within the detection limit of XRD, no traces of secondary phases were found in the xrd patterns. Temperature-dependent DC susceptibility measurements were carried out using the MPMS set-up in the temperature range from 300 K to 4 K at an applied field of 0.1 T. The Neel temperature (T\textsubscript{N}) for both the samples is around 60 K.

The absorbance spectra were collected using the UV-Vis spectrophotometer (Shimadzu-2450) with a deuterium lamp in the wavelength range from 200 nm to 800 nm. The spectrophotometer was calibrated using barium sulphate powder. The photocurrent measurements were performed by depositing aluminium electrode patterns through a shadow mask by thermal evaporation deposition technique. The thickness and the electrode separation was about 150 nm and 100 \mu m, respectively. Ni contacts were made on the electrodes. A three watt white LED light was used as a source of irradiation.

The room temperature photoemission experiments were performed using a monochromatic AlK\alpha (1486.6 eV) source, with an energy resolution of 400 meV and Scienta Analyser (R3000). The sample surface was cleaned in situ by scraping with a diamond file. The binding energy was calibrated by measuring the Fermi energy of Ag in electrical contact with the sample. The base pressure during the measurement was 5 × 10\textsuperscript{−10} mbar. All the core levels except for C 1s spectra were collected after surface cleaning.

The spin polarised calculations for MnTiO\textsubscript{3} were carried out by using the state-of-the-art full potential linearized augmented plane wave (FP-LAPW) method within local density approximation using the elk code [12]. The calculations were carried out in the hexagonal phase using the room temperature lattice parameters [7]. The muffin-tin radii used were 2.4, 1.95 and 1.46 a.u. for Mn, Ti and O, respectively. The convergence was achieved by considering 512 \textit{k} points within the first Brillouin zone. The error bar for the energy convergence was set to be smaller than 10\textsuperscript{−4} Hartree/cell.

The crystal structure of MnTiO\textsubscript{3} is shown in fig. 1. In fig. 2(a), we show room temperature x-ray diffraction patterns of MTO\textsubscript{q} and MTO\textsubscript{uq}. As compared to the unquenched sample, the quenched one exhibits a shift in the position of the xrd peaks, inset to fig. 2(a) and also a variation in its relative intensities. This suggests changes in the lattice parameters and also in the atomic positions. These changes can be attributed to the freezing of the high temperature phase as a result of quenching. Both the xrd patterns were indexed using the R3 space group. The structural parameters were obtained using the Rietveld profile refinement software [13,14]. The goodness of fit thus obtained is \sim 1.4. The lattice parameters thus obtained for MTO\textsubscript{uq} and MTO\textsubscript{q} are \textit{a} = 5.1363 and 5.135 Å; \textit{c} = 14.2791 and 14.2810 Å, respectively. It is interesting to note that the volume of the Mn\textsubscript{6} octahedra has increased but the Ti\textsubscript{6} octahedra has decreased with quenching, figs. 1(b) and (c). The behaviour of the volume of the octahedra was obtained based on the behaviour of the average Mn/Ti-O bond lengths. Keeping this in mind, one may expect significant changes in their electronic structure and hence their magnetism, multiferroic properties and optical properties etc. To observe the effect of such structural changes in the optical properties, optical absorbance experiments were carried out.

Figure 2(b) shows the normalised optical absorbance spectra collected for both the samples. The optical absorbance was normalised by the area under the curve.
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Fig. 2: (Colour online) Comparison of the xrd patterns of MTO$_q$ (solid circle) and MTO$_uq$ (solid line) samples. The inset shows the absorption spectra in the visible region. The resistance change after switching ON and OFF the white light (c) MTO$_q$ and (d) MTO$_{uq}$ samples. The inset shows the set-up. (e) Comparison of the DC susceptibility of MTO$_{uq}$ (red open circles) and MTO$_q$ (blue open circles) carried out at an applied field of 0.1 T.

The absorbance spectra show significant contribution to the wide energy range covering UV and visible regions. Two broad peaks A and B centered around 695 nm (1.8 eV) and 365 nm (3.4 eV), respectively, are observed. The quenched sample shows a slight increase in the absorbance in the visible region while in the UV region it remains almost the same as the unquenched one.

Figures 2(c) and (d) show the behaviour of the surface resistance as a function of the exposure time when the samples were irradiated with white light. In the case of MTO$_q$, in the dark condition, the surface resistance was about 150 MΩ and reduced to 50 MΩ when the white light was switched on. In the case of MTO$_{uq}$, resistance reduced from 115 MΩ to 50 MΩ. Such increased change in the resistance exhibited by MTO$_q$ is mainly because of an increased optical absorbance as compared to the MTO$_{uq}$ sample. In both the samples, when the white light illumination is withdrawn, the increase in the resistance consists of two components. In the beginning, it is fast and later on it is slow. It takes about 15 minutes to reach the dark resistance value. This shows its ability to exhibit persistent photo-resistance. This means that there occur some trap states that lead to the increase in the lifetime of the excited carriers. To understand the origin of such trap states, more experiments need to be performed.

To understand the origin of the behaviour of peak A, it is important to know a) the valence state of the elements present in the compound; b) and also the behaviour of the valence band. The above points can be captured based on the behaviour of the binding energy and the satellite features of the core levels and the valence band spectra.

At room temperature, we have collected O 1$s$, Mn 2$p$, Ti 2$p$ core level spectra and also valence band spectra. In comparison to the MTO$_{uq}$ sample, the peak position of the C 1$s$ (due to adventitious carbon) of MTO$_q$ is found to be shifted by 0.2 eV towards a lower binding energy. In figs. 3(a), (d) and 4, we show the room temperature core level spectra of O 1$s$, Mn 2$p$, and Ti 2$p$ respectively. The peak position of the Mn 2$p$$_{3/2}$ spectra of the MTO$_uq$ sample is shifted towards higher binding energy as compared to the samples that do not show charging [15]. The binding energy positions of the O 1$s$ and Ti 2$p$$_{3/2}$ peaks are in line with titanates [16]. This suggests charging effect in this sample. The effect of the photoionisation cross section is different in different core levels. Hence the above-mentioned core levels will have a different effect of charging. In the case of the MTO$_q$ sample, all the core levels are shifted towards a lower binding energy due to reduced charging. This is because the room temperature resistivity of MTO$_q$ (0.11 MΩ cm) is drastically reduced as compared to the MTO$_{uq}$ (89.48 MΩ cm) sample. In general, when there is inhomogeneous charging, the line shape of the core levels are expected to be affected. But in the current study, the line shapes appear to be the same.

We now study in detail the information obtained from the core levels keeping the above constraints in mind.

All the spectra exhibit multiple structures. The O 1$s$ spectra are fitted with 3 peaks, figs. 3(b), (c). Peaks a
and $b$ constitute the contribution from the av Mn-O and Ti-O bonds, respectively. This arises due to the different Madelung potential. The weak feature $c$ arises due to the impurities from the surface and grain boundaries. In fig. 3(d), we show the comparison of the Ti 2$p$ core levels. The peaks 1 and 2 are the spin orbit (SO) split Ti 2$p$ of MTOq (solid circles) and MTOq (solid triangles). The satellite features of the core level spectra are a good indicator for the valence state. The satellite peaks observed in the Ti 2$p$ core level are similar to those observed in SrTiO$_3$ [17]. Hence Ti in both the samples is in 4+ state.

The comparison of the Mn 2$p$ spectra of both the samples is shown in fig. 4. Peaks 1 and 2 constitute the spin orbit split ones, namely 2$p_{3/2}$ and 2$p_{1/2}$. Interestingly, 3 satellite peaks are observed and labelled as s1, s1’ and s2’. The satellites s1 and s1’ are the ones corresponding to Mn 2$p_{3/2}$ and 2$p_{1/2}$, respectively, of the Mn$^{2+}$ ions [15,18]. The feature s2’ corresponds to the satellite feature of the Mn 2$p_{3/2}$ peak while the satellite feature that corresponds to Mn 2$p_{3/2}$ is hidden within the Mn 2$p_{1/2}$ peak. In the case of MTOq s2’ is weak, while, in the case of MTOq, it is predominant. This suggests that Mn exists in higher oxidation states other than Mn$^{2+}$, see the inset of fig. 4 in both the compounds. This can be understood in the following way.

The shape of the Mn 2$p_{3/2}$ spectra does not match with the spectra of the compounds like MnO$_2$, SrMnO$_3$ [19] that contain Mn$^{3+}$ ions. So we have ruled out the contribution of Mn$^{4+}$ to s2’. If the feature s2’ is due to the Mn$^{3+}$ ions as in the case of Mn$_2$O$_3$, Mn$_3$O$_4$, manganites compounds [18,20,21], the peak separation between the Mn 2$p_{1/2}$ and the satellite peak is expected to lie in the range 10–11.3 eV. In our case, it is ~12 eV. Keeping the above points in mind, we have attributed the satellite feature s2’ to the presence of Mn$^{3+}$ ions. The presence of Mn$^{3+}$ ions in addition to Mn$^{2+}$ and Ti being in 4+ state suggest oxygen non-stoichiometry to maintain charge neutrality. In the case of the MTOq sample as compared to MTOuq, the increase in the intensity of s2’ suggests an increase in the content of Mn$^{3+}$ ions and hence an increased oxygen non-stoichiometry. In the literature, in the case of MnTiO$_3$, the value of $T_N$ has been reported to lie in the range 60–64 K [7,22]. It is interesting to note that in the case of MTOq, we have not observed changes in the value of $T_N$ with increase in Mn$^{3+}$ content. This could be due to the fact that the content of Mn$^{3+}$ ions is not sufficient to lead to the shift in the value of $T_N$.

Figure 5, shows the valence band (VB) spectra of both the samples. We observe that the VB spectrum of MTOq is shifted towards a lower binding energy with respect to MTOuq. Here, zero binding energy marks the Fermi level ($\epsilon_F$). In the BE range 8 eV to $\epsilon_F$, the MTOuq sample shows 4 features, while MTOq shows only 3 features. The feature A1 is suppressed in the latter case. To understand the behaviour of the features of the optical absorbance spectra and the VB spectra, band structure calculations were carried out, see fig. 6. We now look into the results of band structure calculations to understand the optical and the valence band spectra.

The energy vs. momentum ($k$) curves for both the spin channels are given in fig. 6(a). We do not observe any crossing of bands across the Fermi level ($\epsilon_F$) suggesting an insulating ground state. The band gap obtained from the valence band maximum (VBmax) of spin-up channel to the conduction band minimum (CBmin) of the spin-down channel is about 1 eV. The VBmax and the CBmin occur at two different symmetry points which is suggestive of an indirect band gap semiconductor, fig. 6(a). In the VB region, close to $\epsilon_F$ (fig. 6(a)) we observe the contribution only of the spin-up channel and in the CB region, the contribution is from the spin-down channel only. In optical transitions, the main contribution comes from direct band transitions. It is interesting to note that the band occurring around 1.3 eV is nearly dispersion less. This could be the possible reason for broad peaks observed in the optical absorbance spectra.

Figures 6(b)–(d) show the total density of states (TDOS) for up- and down-spin channels and the partial DOS corresponding to Mn 3$d$, Ti 3$d$ and O 2$p$ states as a function of energy. In the VB region close to $\epsilon_F$, the contribution from Mn 3$d$ states is dominant with less contribution from O 2$p$. Around ~0.6 eV, the hybridisation of Mn 3$d$ with the O 2$p$ states is more as compared to the region around ~2.4 eV. There is also a negligibly small
in the unoccupied part of the conduction band will increase. From this one can understand that on quenching the sample, a doping of the holes occurs which could be the possible reason for the increase in the conductivity. This is manifested in the VB spectra in terms of a decrease in the intensity of the A1 feature. The valence band spectra (fig. 5) exhibit a gap at the $\epsilon_F$ suggesting the insulating nature of both the samples. Such a behaviour suggests an increase in the carrier concentration of holes in the MTO$q$ sample. As a result the conductivity of the quenched sample is expected to be more than the unquenched one. This is in line with our resistivity results. We believe that our results will be useful in designing materials for optical sensors, and solar cell applications keeping in mind the cross link between the electronic structure, optical and transport properties.

In summary, we have studied room temperature structural, optical and electronic properties of quenched and unquenched polycrystalline MnTiO$_3$. Our results show that the quenched sample exhibits a slight increase in the absorption in the visible region as compared to the unquenched one. In the UV region, the absorption of both the samples is identical. The features of the optical absorbance spectra have been identified based on the results of band structure calculations. The change in the surface resistance when illuminated with white light is more in the case of the quenched sample as compared with the unquenched one. When the irradiated light is terminated, the samples show a persistent photo-resistance. Based on the combined results of optical absorbance, core level, valence band studies, we find that Ti exists in the 4+ valence state and Mn exists in the 2+ and 3+ valence states even in the parent compound. The fraction of Mn$^{3+}$ ions increases on quenching the sample although not sufficiently enough to shift the value of $T_X$. The presence of Mn$^{3+}$ ions has been attributed to oxygen non-stoichiometry. Keeping in mind the above results and also the decrease in the room temperature electrical resistivity of the quenched sample suggest that the charge carriers that participate in the conduction process are holes. Our results show a direct link among the structural, electronic and optical properties and will help in better designing such materials for optical sensor and solar cell applications.

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