Structural, compositional and magnetic characterization of bulk \( V_2O_5 \) doped \( ZnO \) system

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1. Introduction

Zinc oxide a direct band gap II–VI compound semiconductor having large excitonic binding energy (60 meV) at room temperature is now being the object of intense investigation owing to its attractive applications. Metal oxide doped ZnO has the potential to be a multifunctional material with coexisting magnetic, semiconducting, electromechanical and optical properties which provides an ideal avenue for interdisciplinary scientific explorations \([1,2]\). It is well known that doping often leads to dramatic changes in the electrical and optical properties of wide band gap semiconductors. Vanadium oxide doped \( ZnO \) system exhibits multifunctional properties which makes it an interesting material for technological applications. Single phase \( ZnO–V_2O_5 \) system has been considered as a diluted magnetic semiconductor (DMS) material, as ferromagnetism in DMS is one of the interesting problems of this century in condensed matter physics \([3]\). Ferromagnetism in vanadium doped \( ZnO \) was predicted theoretically by Sato and Yoshida \([4]\) and very few experimental research on \( V:ZnO \) powders was reported \([5]\). In the previous study, controversial explanations of the origin of magnetism have been proposed, but those did not clarify why doping of \( V \) ions in \( ZnO \) cause ferromagnetic ordering. \( ZnO–V_2O_5 \) system is interesting not only in terms of its room temperature ferromagnetism but also as a transparent ferromagnetic material \([6]\). On the other hand, multi-phase \( ZnO–V_2O_5 \) exhibits varistor behavior which is also quiet interesting because in all metal oxide doped \( ZnO \) systems, varistor behavior appear due to greater metal ion but in \( ZnO–V_2O_5 \) smaller vanadium ion is responsible \([7–11]\).

For proper understanding of different features of \( ZnO–V_2O_5 \) system like the formation of different phases, arise of ferromagnetic behavior, change in structure due to vanadium doping, optical band gap tuning, the appearance of vibrational modes induced by vanadium doping, etc., a detailed study is required to cover these aspects. Raman spectroscopy is a powerful tool for fast and non-destructive study of dopant incorporation, particularly when impurity-induced modes can be traced back to individual constituents and their concentration \([12]\). Although magnetic properties of a vanadium doped \( ZnO \) system are recently of interest but structural, compositional and vibrational characterization of this material has rarely been reported. With \( 3d^4s^2 \) electron configuration, \( V \) doping is expected to modify the defective structure and optical properties of \( ZnO \). This motivated us to investigate \( V_2O_5 \) (a layered crystal structure having no 3d electrons with band gap of 2 eV) doped \( ZnO \) properties in bulk form.

In this work, we studied \((ZnO)_{1-x}(V_2O_5)_x(0.05)\) system prepared by solid state reaction techniques. Our efforts were focused on the
structural, compositional and magnetic characterizations to see the changes appear in ZnO due to V₂O₅ doping as well as the competency of this material in DMS field.

2. Experiments

In the present study, (ZnO)₁₋ₓ(V₂O₅)ₓ (x = 0.01, 0.02, 0.03 and 0.05) bulk samples were prepared by standard solid state reaction technique. Appropriate amount of precursors ZnO and V₂O₅ powders were mixed and ground properly. The mixture was then calcined at 700 °C for 8 h in air. The calcined powder thus obtained was pressed to form dense pellets and sintered for 14 h at low temperature at 900 °C in air. The structural study of the pellets has been performed by using Shimadzu X-ray diffractometer equipped with a Cu Kα (λ = 1.544 Å) source. Information about vanadium and Zn bonding is obtained by Kratos-axis Ultra X-ray photoelectron spectrometer. Vibrational modes were analyzed by Renishaw Raman spectrometer and for magnetic measurements Lakeshore 7400 series vibrating sample magnetometer was employed.

3. Results and discussion

XRD patterns of (ZnO)₁₋ₓ(V₂O₅)ₓ₀.05 samples in Fig. 1 show diffraction peaks that can be indexed to the peaks of ZnO wurtzite structure (ICSD-26170) and some impurity phases. The impurity phases are marked as ‘▲’ and ‘★’ in the magnified spectrum of 5% vanadium doped ZnO sample, shown in inset of Fig. 1. The peaks corresponding to impurity phases are that of zinc divanadium oxide (ZnV₂O₆) as secondary phase, marked as ‘★’, along with the small traces of V₂O₅, marked as ‘▲’, which are quite easily observed with increasing V₂O₅ doping percentages. All the unpronounced peaks, in inset of Fig. 1, appearing at 2θ = 31.7°, 34.4°, 36.2°, 47.6°, 56.6°, 62.8°, 67.8°, 72.5° and 76.9° can be attributed to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), (0 0 4) and (2 0 2) planes of ZnO, respectively. For the quantitative analysis of the XRD patterns, Rietveld method was used for (ZnO)₁₋ₓ(V₂O₅)ₓ₀.05 series.

The change in ZnO lattice parameters due to different vanadium doping concentrations, obtained from Rietveld refinements, is shown in Table 1. One typical XRD refinement for (ZnO)₀.95(V₂O₅)₀.05 is shown in Fig. 2. In vanadium doped ZnO system, marginal increase in the lattice parameters, particularly in c parameter for 3 and 5% doping, is observed as compared to that of the lattice constants of ZnO in the standard data (ICSD-26170). The change in lattice parameters depends on the ionic radius of the doping atom, which can substitute the Zn ion in the lattice. It is desirable in DMS that the doping atom must substitute the ions of the host lattice. In ZnO system, dopants of 2+ oxidation state mostly substitute the Zn²⁺ ions in the lattice due to charge matching. In case of vanadium doping, the ionic radius of V²⁺ (0.93 Å) ion is quite bigger than the Zn²⁺ (0.60 Å) ion. If V²⁺ ion substitutes Zn²⁺ ion in the lattice then the change in the lattice parameters is expected due to ionic radii mismatch which has also been reported by others [13]. The small increase in c parameter, for

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**Table 1**

Refinement parameters for (ZnO)₁₋ₓ(V₂O₅)ₓ pellets.

<table>
<thead>
<tr>
<th>Material</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ZnO)₀.95(V₂O₅)₀.01</td>
<td>3.2501</td>
<td>5.2032</td>
<td>47.60</td>
</tr>
<tr>
<td>(ZnO)₀.96(V₂O₅)₀.02</td>
<td>3.2506</td>
<td>5.2033</td>
<td>47.61</td>
</tr>
<tr>
<td>(ZnO)₀.97(V₂O₅)₀.03</td>
<td>3.2535</td>
<td>5.2091</td>
<td>47.75</td>
</tr>
<tr>
<td>(ZnO)₀.98(V₂O₅)₀.05</td>
<td>3.2505</td>
<td>5.2042</td>
<td>47.62</td>
</tr>
</tbody>
</table>
higher doping concentration of 3 and 5%, leads us to believe that some V\textsuperscript{2+} ions have indeed substituted the Zn\textsuperscript{2+} ions in ZnO lattice. In order to get clearer information about the oxidation states of vanadium, the XPS studies were conducted and are discussed in detail in the later section.

The Raman spectroscopy was performed on doped samples to obtain more information on their structural composition. The wurtzite ZnO structure belongs to the space group \textit{C\textsubscript{6h}}\textsuperscript{2}, with two formula units per primitive cell. The Raman-active zone-center optical phonons predicted by the group theory are \( A_1 + 2B_1 + E_1 + 2E_2 \). The phonons of \( A_1 \) and \( E_1 \) symmetry are polar phonons and exhibit different wave numbers for the transverse optical (TO) and longitudinal optical (LO) phonons. Non-polar phonon modes with symmetry \( E_2 \) have two wave numbers: \( E_2(\text{high}) \) is associated with oxygen atoms and \( E_2(\text{low}) \) is associated with Zn sublattice. The \( B_1 \) modes are infrared and Raman inactive (silent modes). All described phonon modes have been reported in the Raman scattering spectra of bulk ZnO [14,15].

Inset in Fig. 3 shows room temperature Raman spectrum of ZnO bulk in wave number range of 50–800 cm\textsuperscript{-1}. This figure shows a typical Raman peak of ZnO bulk at 438 cm\textsuperscript{-1} which corresponds to the \( E_2(\text{high}) \) vibrational mode. Mostly, the \( E_2(\text{high}) \) mode is representative of the band characteristic of wurtzite phase [16]. A very small peak for \( E_2(\text{low}) \) mode also appears at 98 cm\textsuperscript{-1}. Also, the additional low intensity peaks were observed at 332.1, 379.0, 583.3 cm\textsuperscript{-1} with one broader peak at 656.0 cm\textsuperscript{-1}. The band at 656 cm\textsuperscript{-1} is known to be the vibrational mode which appears due to the second-order Raman processes (multiple-phonon processes). The peak at 583.3 cm\textsuperscript{-1} corresponds to the longitudinal optical (LO) phonons of \( A_1 \) mode and the peak at 332 cm\textsuperscript{-1} corresponds to transverse optical (TO) phonons of \( A_1 \) mode [17]. The \( A_1 \) mode arises due to some defects like oxygen vacancies, Zn interstitials and also their complexes. On the other hand, the phonons corresponding to the \( E_1 \) mode were also observed, the peak at 379.0 cm\textsuperscript{-1} corresponds to \( E_1(\text{TO}) \) mode. The appearance of \( A_1 \) or \( E_1 \) mode gives us hint that the lattice vibrations occur either parallel or perpendicular to the \textit{c}-axis, respectively, which is confirmed from the optical emission of phonons in transverse and longitudinal directions [16].

Raman spectra of \((\text{ZnO})_{1-x}(\text{V}_2\text{O}_5)_x\) \( x = 0.05 \) bulk samples are shown in Fig. 3. Raman spectra of doped bulk samples showed many peaks corresponding to additional modes along with ZnO peaks in the spectra in the range of 50–1200 cm\textsuperscript{-1}. The regions, dominated by the several peaks of vanadium oxide modes, are in the range of 130–340 cm\textsuperscript{-1} and 750–1000 cm\textsuperscript{-1} with some ZnO modes. We see a slight shifting in the position of ZnO modes in vanadium doped ZnO samples.

The peaks at 378.0 and 438.2 cm\textsuperscript{-1} corresponding to \( E_1(\text{TO}) \) and \( E_2(\text{high}) \) modes, respectively, in ZnO samples are also present in vanadium doped ZnO samples but with a significant shift in mode positions. The \( A_{1\text{g}}(\text{TO}) \) mode which appears around 332 cm\textsuperscript{-1} in Raman spectrum of undoped ZnO is not seen in doped samples. From careful analysis we observed that \( A_{1\text{g}}(\text{TO}) \) mode, which appears mostly due to second-order Raman processes (multiple-phonon processes), is overlapped by some other modes in our samples. For better understanding about this mode we de-convoluted the Raman peak at 321.4 cm\textsuperscript{-1} which is shown in Fig. 4. After de-convolution, we see that this broader mode is a combination of the Gaussian peaks mostly appears at 313.6, 322.2 and 330.6 cm\textsuperscript{-1}. The peak at 330.6 cm\textsuperscript{-1} represents \( A_1(\text{TO}) \) mode of ZnO. The peak at 313.6 cm\textsuperscript{-1} indicates the mode which might be due to the bending vibration of the triply coordinated oxygen \((V_3–O)\) bonds [18,19].

The Raman peaks of lower frequencies at 136.8 and 189.4 cm\textsuperscript{-1}, in Fig. 3, appear due to the stretching mode of \((V_2\text{O}_2)_n\) which correspond to the chain translation [18,19]. The peak at 264.6 cm\textsuperscript{-1} represents V–O–V bending mode [20]. The appearance of mode at 579.4 cm\textsuperscript{-1}, which is due to ZnO longitudinal optical (LO) phonon mode having \( E_1 \) symmetry, clearly shows the presence of defects (the defects attributed due to O vacancies and Zn interstitials). The modes towards higher wave number side, in the range of 750–1000 cm\textsuperscript{-1}, arise due to vanadium doping in ZnO as these peaks were absent in pure ZnO sample. The peaks in 900–1000 cm\textsuperscript{-1} range may correspond to the terminal oxygen (V–O) stretching mode arising due to unshared oxygen [19].

The surface composition of the vanadium doped zinc oxide samples were examined by X-ray photoelectron spectroscopy (XPS) (Kratos Ultra) measurements. XPS spectra were recorded using Al \( K\alpha \) radiation. According to the different characterizing binding energies of different elements on the surface of bulk samples, we can examine the elemental composition on the surface of the material. The characteristic binding energy peaks corresponding to all expected elements i.e. Zn, V and O were found in the survey scans. The XPS for Zn 2p, V 2p and O 1s core peaks are shown in Figs. 5–8.
The BE of the C 1s level of adventitious carbon is widely taken as reference peak for energy calibration. The XPS study, in the EUROCAT program [21,22], of supported vanadium oxides on TiO\textsubscript{2} showed a large spread on the V 2p binding energies when the C 1s signal was taken as reference. Mendialdua et al. [23] have shown that the O 1s signal is a better energy reference than the C 1s for the V 2p binding energies of vanadium oxides. Indeed, taking the O 1s as binding energy reference eliminates the spread on the V 2p binding energy values for V\textsubscript{2}O\textsubscript{5}. In the present study, we calibrated our XPS spectra with both C 1s and O 1s peak and found that they yield similar peak shifting of elements. So we took adventitious carbon as a reference for calibration of BE peaks in the present study.

Zn 2p core peaks for vanadium doped samples, in Fig. 5, showed quite symmetrical behavior in binding energy for all doping percentage. The binding energies of Zn 2p\textsubscript{3/2} peaks, are located around 1020.5 eV which show a difference of 0.9 eV from the BE reported in the literature data for ZnO (1021.4 eV) [24]. In the Zn 2p core peaks the shift in the binding energy to the lower energy side can be attributed to the formation of spinel ZnV\textsubscript{2}O\textsubscript{6} secondary phase and also due to some other possible complex bonding of other vanadium ions in ZnO lattice.
The O 1s peak in Fig. 6 shows asymmetric behavior, indicating the presence of multi-component species. The typical O 1s peak can be fitted by two Gaussians peaks centered at 529.4 and 530.5 eV. The peak at about 529.4 eV is due to the ZnO crystal lattice oxygen and the peak at 530.5 is considered to be the satellite peak of vanadium. Zimmermann et al. [25] have shown, theoretically and experimentally, that the V 2p core level spectra of the pure vanadium oxides, such as V$_2$O$_5$, VO$_2$ and V$_2$O$_3$, contain satellite peaks due to a strong hybridisation between V 3d and O 2p levels and found them on the higher BE side of O 1s spectrum. For V$_2$O$_5$ doped ZnO, we also find the vanadium satellite peak situated on the high binding energy side at 530.5 eV.

V 2p core peaks, shown in Fig. 7, are intense for higher doping concentrations. Several authors used the V 2p$_{3/2}$ peak for data analysis while other used the V 2p$_{1/2}$ peak. In this analysis, we used V 2p$_{3/2}$ peak for data analysis after subtracting the background by Shirley function. V 2p$_{3/2}$ binding energy peak appears around 516.8, 516.7, 516.7 and 516.8 eV for 1, 2, 3 and 5% vanadium doped ZnO samples, respectively. The appearance of V 2p$_{3/2}$ peaks around 516.7 eV is in good agreement with the previously reported binding energies for V$^{4+}$ [21,26]. The shift in the BE permits the determination of the oxidation state if the BE values for different oxidation states are known. The main peaks for 1, 2, 3 and 5% vanadium doped samples showed slight symmetrical behavior indicating thereby the existence of more than one oxidation states. In order to get more clarity about the presence of vanadium oxidation states, we de-convoluted all the vanadium peaks of doped samples. Almost similar peak fitting was observed for all the samples. The typical de-convolution results for 3% vanadium doped ZnO sample is shown in Fig. 8. The core peak spectrum is fitted by using four Gaussian peaks at binding energy of 515.9, 516.7, 518.2 and 523.8 eV with the first three peaks corresponding to V 2p$_{3/2}$ and the last peak to V 2p$_{1/2}$. The peaks at 515.9 and 516.7 eV indicate the presence of V$^{4+}$ valence state while the peak at higher BE of 518.2 eV corresponds to higher oxidation state vanadium i.e. V$^{5+}$ valence. Hence from the XPS results done on the surface of samples, it is clear that in our samples only V$^{4+}$ and V$^{5+}$ oxidation states of vanadium are present and the V$^{2+}$ ions are not present as no peak at about 513.7 eV was observed.

Magnetic characterizations were done for all the samples by using vibrating sample magnetometer. The shapes of hysteresis curves, shown in Fig. 9, indicate the overlapping of diamagnetic signal on ferromagnetic signal of samples. The cause of diamagnetic behavior in our samples is not known. Also, the consistency of central position of hysteresis with zero-field predicts the absence of anti-ferromagnetism. The M–H curves showed weak magnetic behavior for all samples. The observation of ferromagnetic behavior indicates that the V$^{2+}$ ions have been substituted the Zn sites without changing the wurtzite structure of ZnO and have formed ZnVO.

But these results are not in agreement with the results of XPS studies conducted on the sample surfaces, discussed before, which indicate the presence of V$^{4+}$ and V$^{5+}$ in ZnO lattice. It may be important to mention over there that XPS is essentially a surface probing tool with very small probing depth. The surface of the bulk sample may essentially show higher valance state because of the oxidation of vanadium by atmospheric oxygen Therefore to resolve inconsistency in the results of the VSM and XPS, we etched all the samples up to 100 nm and did another set of XPS scanning. After etching, we observed the overlapping of different vanadium peaks in the vanadium core peak spectra of all samples, here shown only for 3 and 5% vanadium doping.

The de-convolution of vanadium 2p$_{3/2}$ core peak of etched sample of 3% V$_2$O$_5$ doped ZnO was done by Gaussian peak fitting. The fitted peaks at BE of 513.8, 515.6 and 518.0, shown in Fig. 10, indicate V$^{2+}$, V$^{4+}$ and V$^{5+}$ valence states. For further confirmation V 2p$_{3/2}$ core peak of etched 5% V$_2$O$_5$ doped ZnO sample, shown in Fig. 11, is de-convoluted by three Gaussian peaks at BE of 513.8, 515.5 and 516.5 eV which also indicates presence of V$^{2+}$, V$^{4+}$ and V$^{5+}$ valence states, respectively.

The XPS results of etched samples clearly shows that vanadium exist in V$^{2+}$, V$^{4+}$ and V$^{5+}$ valence state which is in agreement with the VSM results and points to the fact that in addition to undesirable impurity phases, the ZnVO phase, desirable in DMS is also formed in our bulk samples.
4. Conclusions

In the present study, ferromagnetism in bulk vanadium doped ZnO system was achieved. The Rietveld refinement of XRD data showed a small change in the lattice parameters, especially for 3 and 5% doped samples. The marginal increase in the lattice parameters indicates the substitution of vanadium valance ions in the ZnO lattice. Raman spectra showed the shift in the ZnO modes which also indicates the presence of vanadium ions in the study matrix. For further confirmation, XPS analysis was done on the surface of samples which indicates only the 4+ and 5+ oxidation states of vanadium ions and no 2+ oxidation state of vanadium ions was observed on the sample surface. The ferromagnetic behavior observed in M–H curves, however, hinted towards the presence of 2+ vanadium oxidation state. This inconsistency between XPS and VSM was attributed to the oxidation of the samples surface by ambient oxygen. To exclude the surface oxidation effect, all samples were etched up to 100 nm and analyzed again. XPS survey of the etched samples clearly exhibited the presence of V2+ oxidation states confirming the formation of ZnVO phase and thus consequently explains the observation of ferromagnetism in the vanadium doped ZnO bulk samples.

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References