Structural, Optical, and Magnetic Properties Of FeVO$_3$

Pooja Singh[1,2, a)],Anurag Gupta[1,2]and Anjana Dogra[1,2, a)]

[1] *Academy of Scientific and Innovative Research (AcSIR), CSIR-NPL Campus, Dr. K.S. Krishnan Marg, New Delhi 110012, India*
[2] *National Physical Laboratory, Council of Scientific and Industrial Research, Dr. K.S. Krishnan Marg, New Delhi 110012, India*

[a)] Corresponding author:pooja7503@gmail.com;anjanad@nplindia.org

Abstract. We report the structural, optical, and magneticproperties ofpolycrystalline FeVO$_3$synthesized by solid state reaction technique.While FeVO$_3$ has rhombohedral crystal structure with space group *R-3c (167)*identical to the parentα-Fe$_2$O$_3$, the lattice volume reduces due to the replacement of Fe^{3+}with V^{3+} having smaller ionic radii. The most remarkable outcome of doping is reduction in band gap from 2.1 (α-Fe$_2$O$_3$) to 1.5 eV (FeVO$_3$), which is favorable for photo-electrochemical applications. Although the canted ferromagnetism persists in FeVO$_3$, an enhancement in magnetic moment is observed as compared to the parent compound.

INTRODUCTION

Hematite (α-Fe$_2$O$_3$)has gatheredconsiderable attention due to its applications inphotovoltaic,photo-electrochemical (PEC) devices,catalysis, magnetism, gas sensors, and Li ion batteries[1-3].Its remarkable properties include band gap of $\approx$ 2 eV (covering40% of the solar spectrum), chemical stability under most oxidizing condition, earth abundance, low cost, non-toxicity, and ease in materialsynthesis.However, α-Fe$_2$O$_3$ in its native structure and composition inherently adds few disadvantages as a technologically important energy material. These include low electrical conductivity due tosmall electron mobility, hole diffusion length, and short carrier lifetime. These factors result in low experimental PEC efficiency of $\approx$2 % in comparison to the predicted theoretical efficiency of $\approx$ 13 % [4]. More efficientlight harvesting can be achieved byband structure engineering via chemical dopant [5, 6]. Moreover, the negative formation energy of dopedα-Fe$_2$O$_3$with transition metal oxidesalso confirms the thermodynamic stabilityof the resultant material [6]. In particular,theoretical calculations have predictedthat V doping leads to significantly enhanced absorption intensity and dispersed conduction band minima, therebyincreasingthe carrier mobility and enhancingthe PEC efficiency [6].

In this work, we report the successful synthesis of polycrystalline FeVO$_3$(50 % Vanadium doped α-Fe$_2$O$_3$) sample synthesized bysolid state reaction method. This study reveals that the dopinghas significantly improved the optical and magnetic properties of Hematite.

EXPERIMENTAL TECHNIQUE AND MEASUREMENTS

We have prepared FeVO$_3$from α-Fe$_2$O$_3$ and V$_2$O$_5$ (99.999% pure) as the starting materialstaken in 1:1 molar ratio. The mixture was ground thoroughly in mortar pestle to homogenize it. The pre-sintering followed by final sintering at 1200°C for 12hours is performed with intermediate grinding, which produces yellowish brown powder at the end. The chemical analysis was performed by energy-dispersive X-ray measurement (EDX) with scanning electron microscope. Thestructural phase was identified usingpowder X-ray diffraction (XRD).While Cary 5000 UV-VIS-NIR spectrophotometer was employed to recordUV-VIS spectra,the magnetic measurements of the samples were carriedout in SQUID.

RESULTS AND DISCUSSION

STRUCTURAL CHARACTERIZATION

α- Fe_2O_3 and V_2O_3 constitute same corundumstructure with similar electronic structural properties. Being transition metals with comparable ionic radii, the doping Fe site of Fe_2O_3 with V is expected to lend little steric hindrance towards the formation of $FeVO_3$.Thus, the doping is expected to yield a perfect miscible solid solution.Furthermore, we have confirmed the Vanadium incorporation into α-Fe_2O_3 lattice from the chemical composition analysis using EDX.The quantitative analysis of Fe and V peaks indicates 1:1 atomic ratio between Fe and V. This result confirms that 50% V was successfully doped in α-Fe_2O_3. To check the structural properties of the samples, we have performed Rietveld refinements of powder XRD pattern forundoped and doped α-Fe_2O_3 samples as shown in Fig. 1.$FeVO_3$ has a rhombohedral crystal structure with space group R-$3c$ (167)identical to the parentα-Fe_2O_3. Moreover, it is clear from Fig. 1 that the peaks of doped sample ($FeVO_3$) are shifted with respect to the peaks of undoped samples. This can be explained with the consideration of smaller ionic radii of V^{3+}in contrast to Fe^{3+}resulting into smaller lattice spacing.We observe reduction in the lattice constantsof the doped samples as expected. The in-plane lattice parameter decreases from 5.031 Å (α-Fe_2O_3) to 4.99 Å ($FeVO_3$) whereas out-of-plane lattice parameter reduces from 13.744 Å (α-Fe_2O_3)to 13.612 Å ($FeVO_3$).
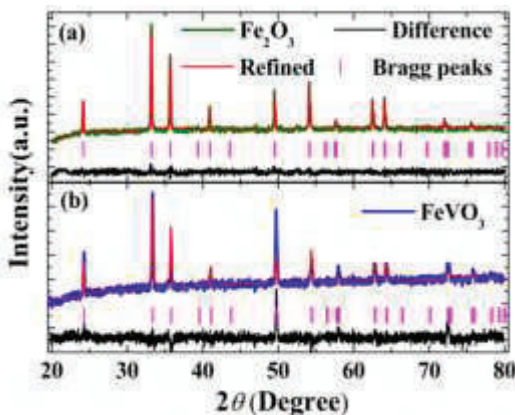

FIGURE 1. Powder XRD pattern with Rietveld refinement of(a)α-Fe_2O_3, and(b) $FeVO_3$.

OPTICAL CHARACTERIZATION

In order to determinethe effect of doping on band gap, the absorption spectra of both the samples were recorded usingUV-VIS spectrophotometer. Subsequently, the band gap was estimated using Tauc relation given as:

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(1)$$

where, α is absorption coefficient, $h\nu$ is photon energy, A is constant, and E_g is the band gap. While the exponent n corresponds to 2 for indirectband gap, it is 1/2 for direct band gap.The Tauc plotswith the fits for direct band gap are shown in Fig. 2. The intercepts of the extrapolated fits on energy axisyield direct band gap as 2.07eV for α-Fe_2O_3 and 1.5eV for $FeVO_3$. Clearly,the doping reduces the band gap significantly. This is favorable forits application as photo-electrode for water photo-oxidationas the band gap of1.3-1.4 eV is referred as ideal for maximum absorbance of sunlight[5].Now, we discuss the possible reason for such outcome. Theoretical calculations of α-Fe_2O_3 reveal that thevalence band maxima (VBM) mainly consist of O2$p$bands while the conduction band minima (CBM) mainly consist of unoccupied Fe3d states. The optical transition occurs fromO2$p$to Fe t_{2g}*sub band(ligand to metal transfer) which falls in UV range.Butwhen all spin up $Fe^{3+}(3d^5)$ ions in α-Fe_2O_3get replaced by V^{3+} ($3d^2$)after dopingV. The 3d^2 states of V hybridize with O 2p states near VBMwith the unoccupied stateson the

site of unoccupied Fe $3d$ states and upper energy levels. Thus, the hybridization leads to additional optical transition from V t_{2g} to Fe $t_{2g}*$ (metal to metal transfer) which falls in near infrared range [1,6]. The schematic of the band diagram and optical transitions are shown in the inset of Fig. 2.
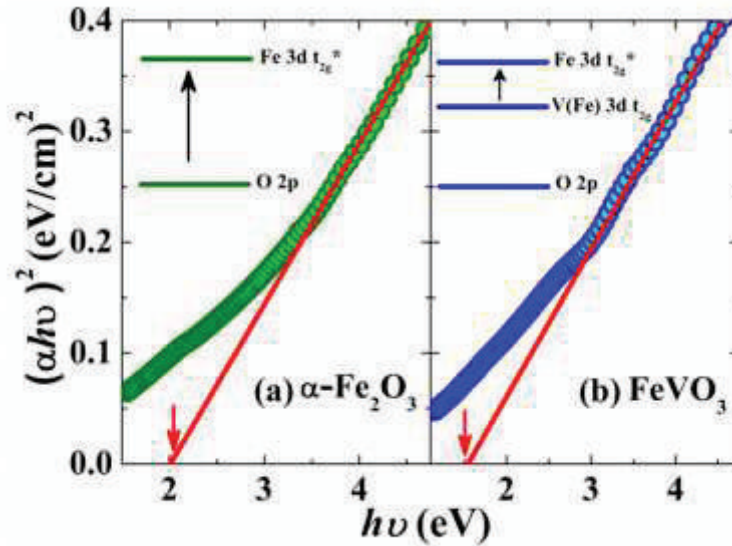

FIGURE 2. Tauc plot of (a) α-Fe$_2$O$_3$ and (b) FeVO$_3$. The arrows indicate the direct band gap (E$_g$). The inset shows the band diagram in each compound.

MAGNETIC CHARACTERIZATION

Figure 3 displays the magnetic field dependent magnetization (M-H) of α-Fe$_2$O$_3$ and FeVO$_3$ at 300 K. The hematite behaves as a canted ferromagnet with weak ferromagnetism in the temperature range of 260–950 K. We clearly see that the magnetic hysteresis is present up to 10 kOe even though the moment does not saturate in FeVO$_3$. Such behavior is a representative of typical canted ferromagnetas observed in the parent compound [7]. It is noteworthy that the magnetization is significantly enhanced with doping, which has been ascribed to the hybridization of O $2p$ with Fe $3d$ and V $3d$ orbitals by theoretical calculations [6]. Also, with doping, we observe 30% increase in remnant magnetization and the coercive field decreases from 3.01 kOe to 2.51 kOe.
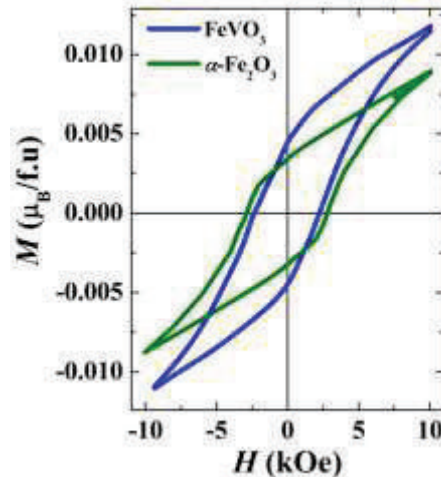

FIGURE 3. Magnetization as a function of magnetic field for α-Fe$_2$O$_3$ and FeVO$_3$ at 300 K.

CONCLUSION

We have investigated the structural, optical, and magnetic properties of solid state synthesized polycrystalline $FeVO_3$ samples. Although the doping does not change the rhombohedral crystal structure, the lattice volume reduces due to the doping of smaller V^{3+} ions in place of Fe^{3+}. We observe a huge reduction in band gap from 2.07 eV to 1.5 eV, which signals it as a potential candidate for photo-electrode. Furthermore, the magnetic characterization reveals the ferromagnetic contribution gets enhanced with doping. Here, we have shown that the chemical doping is an effectiveway of improving optical and magnetic properties of hematite.

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