Structure and interface of samarium/anatase nanocomposites lead to visible light absorption and superparamagnetism

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Abstract

In this study, we have synthesized $Ti_{(1-x)}Sm_xO_2$ ($x = 0, 5, 10, 15$ & 20%) nanocomposites using a sol – gel route. Titanium (Ti) isopropoxide and samarium (Sm) nitrate hexahydrate were used as precursors. Nanocomposites so obtained were calcined between 400 and 700 °C. A two phase mixture of titania and samarium oxide (Sm_2O_3) could be expected as such a high level of Sm addition. While X–Ray Diffraction (XRD) showed a predominantly single phase anatase-like structure of $Ti_{(1-x)}Sm_xO_2$ lattice parameters significantly deviate from what should be expected from a solid solution of Sm in analatse if Vegard's law had been followed. Energy dispersive X ray spectroscopy (EDS), however, showed a homogeneous distribution of Sm. Transmission electron microscopy (TEM) along with selected area electron diffraction (SAED) did not show any crystalline phase of either metallic Sm or samarium oxide (Sm_2O_3). The presence of Sm_2O_3 has also confirmed by X-ray Photoelectron Spectroscopy (XPS), which did not see any metallic Sm in the composite. Inter-planar distances obtained from Fast Fourier Transform (FFT) of high resolution TEM lattice images in both pristine and 5% Sm added TiO_2 corresponded to the crystalline structure of anatase but with significantly different morphology, which was somewhat devoid of any second phase inclusions. This leads us to suspect that samarium added at 5% level is already greater than its solubility limit in anatase. The excess Sm is most likely present around anatase in an oxidized but very thin and amorphous state which was not discernible in conventional TEM lattice imaging. Nevertheless, a concomitant reduction in particle size was observed due to Sm addition. For example, anatase calcined at 600 °C had an average particle size of 53 nm (±10 nm), while 5% Sm added titania calcined at 700 °C showed a significant reduction in average size (16 ±7 nm). The reduction in particle size was persistent when added Sm was increased to 10%, 15% and 20%. In addition to such crystal growth inhibition Sm addition also introduced visible light absorption states (between 400 and 500 nm) commensurate with optical states arising from Sm^{3+} in an amorphous environment. Preliminary vibrating sample magnetometry (VSM) data shows that weak ferromagnetism of pristine anatase can transform into superparamagnetic behavior as the amount of Sm added increases. This observation, while curious and intriguing, needs further investigations, however.