

## Effects of Tetrahedral $\text{Fe}^{2+}$ on the Structural, Magnetic and Electronic Properties of Solution-based Titanomagnetite Thin Films

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Polycrystalline titanomagnetite ( $\text{Ti}_x\text{Fe}_{3-x}\text{O}_4$ ) thin films prepared by using a sol-gel process exhibited a phase-pure spinel ( $\text{Fd}\bar{3}\text{m}$ ) structure for Ti compositions up to  $x = 0.6$ . An X-ray photoelectron spectroscopy (XPS) investigation disclosed an increase of the  $\text{Fe}^{2+}$  concentration with increasing  $x$ , indicating a reduction in ionic valence,  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ , induced by  $\text{Ti}^{4+}$  occupation of the cationic sublattice. Analyses on XPS and X-ray diffraction spectra of the  $\text{Ti}_x\text{Fe}_{3-x}\text{O}_4$  samples suggest that the  $\text{Fe}^{2+}$  ions prefer the tetrahedral sites while the  $\text{Ti}^{4+}$  ions prefer the octahedral sites of the sublattice. Magnetic hysteresis measurements on the  $\text{Ti}_x\text{Fe}_{3-x}\text{O}_4$  films revealed significant loss of the saturation magnetization ( $M_s$ ) with increasing  $x$ :  $M_s$  is reduced to 50% that of  $\text{Fe}_3\text{O}_4$  for  $x = 0.10$  and to 10% for  $x = 0.60$ . The big loss of  $M_s$  caused by small Ti doping suggests a significant disruption of the inter-site  $\text{Fe}^{3+}-\text{Fe}^{3+}$  super-exchange interaction in thin-film titanomagnetites.

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