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XPS evidence for Fe^{2+}/Ti^{4+} and Fe^{3+}/Ti^{3+} mixed-valence nature of ilmenite found in Sri Lanka

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Oxidation states of Fe and Ti atoms in ilmenite ($FeTiO_3$) is a subject of great interest as the two possible configurations, i.e. Fe^{2+}/Ti^{4+} and Fe^{3+}/Ti^{3+} play an important role in the electronic structure and properties of the material. In this paper, we report the use of high resolution XPS data to understand the mixed valence nature of ilmenite deposits found in Sri Lanka. $FeTiO_3$ is a naturally occurring mineral found in many places in the east coast of Sri Lanka. Beach sand containing high concentrations of ilmenite is commonly referred to as "black sand". The main source of TiO_2 in the global market originates from the naturally occurring ilmenite. Pyrometallurgical methods and hydrometallurgical methods are the two widely used industrial methods to extract titanium dioxide (TiO_2) from ilmenite minerals. Purified ilmenite samples were obtained from Lanka Mineral and Sands Ltd in Sri Lanka and used as it is. X-ray diffraction (XRD) analyses were performed using a Stoe STADI/P powder diffractometer. XPS data were accumulated using a Kratos Axis Ultra X-ray photoelectron spectroscopy. Curve fitting and data analysis were carried out using CasaXPS software. Ilmenite shows absorption peaks at energies of about 1, 2.5, and 4 eV. The 1 eV transition can be attributed to a t_{2g} - e_g transition of octahedral Fe^{2+}, the 2.5 eV transition to a Fe^{2+}–Ti^{4+} charge transfer transition and the 4 eV transition to an O –Ti charge transfer. XPS scans of $FeTiO_3$ for the regions Ti($2p_{1/2}$, $2p_{3/2}$), Fe($2p_{1/2}$, $2p_{3/2}$) and O(1s) were compared with TiO_2 and Ar^+ sputtered TiO_2 surfaces. In the latter, oxidation states of Ti show mixed valence character, i.e. Ti^{3+}/Ti^{4+}. Appearance of a well defined peak at 455.2 eV, similar to the peak observed for the reduced TiO_2 clearly indicates the existence of Ti^{3+} atoms in the ilmenite lattice. Preliminary data indicate the existence of both Fe^{2+}/Ti^{4+} and Fe^{3+}/Ti^{3+} mixed-valence states in natural ilmenite found in Sri Lanka in contrast to the synthetic $MTiO_3$ type materials. Therefore, the electronic, chemical and physical properties would expect to be different to the synthetic $FeTiO_3$.

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