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Structural characterization of titania by X-ray diffraction, photoacoustic, Raman spectroscopy and electron paramagnetic resonance spectroscopy

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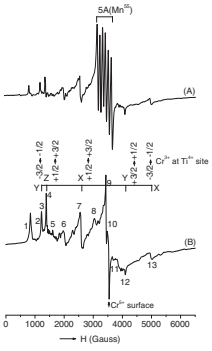
HIGHLIGHTS

- XRD, PAS, Raman and EPR studies to characterize titania.
- Presence of both rutile (91%) and anatase (9%) phases.
- PAS spectrum showed the presence of V^{4+}, Cr^{3+}, Mn^{4+} and Fe^{3+} species.
- EPR studies revealed the presence of $V^{4+}(d^1)$, $Cr^{3+}(d^3)$, $Mn^{4+}(d^3)$ and $Fe^{3+}(d^5)$ at Ti^{4+} sites.

GRAPHICAL ABSTRACT

EPR spectra of titania mineral at room temperature (A) as it is (containing microcrystals) and (B) recorded after grinding it for 30 min (polycrystalline samples).



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ABSTRACT

A titania mineral (obtained from East coast, Orissa, India) was investigated by X-ray diffraction (XRD), photoacoustic spectroscopy (PAS), Raman and Electron Paramagnetic Resonance (EPR) studies. XRD studies indicated the presence of rutile (91%) and anatase (9%) phases in the mineral. Raman investigation supported this information. Both rutile and anatase phases have tetragonal structure (rutile: space group $P4_2/mnm$, $a = 4.5946(1)$ Å, $c = 2.9597(1)$ Å, $V = 62.48(1)$ (Å)^3, $Z = 2$; anatase: space group $I4_1/amd$, 3.7848(2) Å, 9.5098(11) Å, $V = 136.22(2)$ (Å)^3, $Z = 4$). The deconvoluted PAS spectrum showed nine peaks around 335, 370, 415,485, 555, 605, 659, 690,730 and 785 nm and according to the ligand field theory, these peaks were attributed to the presence of V^{4+}, Cr^{3+}, Mn^{4+} and Fe^{3+} species. EPR studies revealed the presence of transition metal ions $V^{4+}(d^1)$, $Cr^{3+}(d^3)$, $Mn^{4+}(d^3)$ and $Fe^{3+}(d^5)$ at Ti^{4+} sites. The EPR spectra are characterized by very large crystal filed splitting (D term) and orthorhombic distortion term (E term) for multiple electron system ($s > 1$) suggesting that the transition metal ions substitute the Ti^{4+} in the lattice which is situated in distorted octahedral coordination of oxygen. The possible reasons for observation of unusually large D and E term in the EPR spectra of transition metal ions ($S = 3/2$ and $5/2$) are discussed.

Introduction

Titania, titanium dioxide (TiO_2) exists in three crystallographic polymorphs namely anatase, brookite and rutile. All the three crys-

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tal structures are made up of distorted TiO_6 octahedra connected to each other in different fashion. Rutile adopts a tetragonal structure (space group; $P4_2/mnm$, D_{4h}^{14}) in which two opposing edges of each octahedron are shared to form linear chain along the [0 0 1] direction and the TiO_6 chains are linked together via corner connections [1] whereas anatase exists as tetragonal structure (space group; $I4_1/amd$, D_{4h}^{19}) has no corner sharing but has four edges shared per octahedron. The crystal structure of anatase is made up of zigzag chains of the octahedral linked together through edge sharing (Fig. 1). Whereas, Brookite has orthorhombic modification (space group; Pbca, D_{2h}^{15}) in which the octahedral share three edges and corners and the dominant structural feature is a chain of edge sharing. The distorted TiO_6 octahedra are arranged parallel to the *c*-axis and are cross linked by shared edges [2]. TiO_2 currently finds application in pigments [3], cosmetics ultrathin capacitors [4], photovoltaic cells [5,6] and catalysis[7,8] whose properties can be changed significantly by the presence of transition element such as iron, chromium, manganese and vanadium. The applications for TiO_2 strongly depend upon the crystal structure, morphology and size of the particles. Each crystalline modification has different physicochemical properties such as density, refractive index and photochemical reactivity. Rutile has the highest density and refractive index among the three phases and therefore has been widely employed in pigments and cosmetic industries. Chemical purity and the crystal size are the main factors which determine the color of the pigment and photocatalytic degradation of paint resin [3]. Since TiO_2 is now the most widely used commercial opacifier, it is known that just a few parts per million (1 ppm = 1 μg/g) of the transition metal ion in titanium dioxide pigment profoundly affect the pigment color and photocatalytic degradation of paint resin [9]. In addition to these, TiO_2 also possess the photocatalytic activity and hence is used for the destruction of organic pollutants [10] and for disinfection of water [11]. The presence of metal ions in this matrix can move the absorption edge of TiO_2 from UV into blue region of the visible spectrum and hence offer potential improvement in the light harvesting ability of TiO_2 photocatalyst [12,13] Recent reports describe the use of Colloidal TiO_2 particles of both structures loaded with suitable catalyst in light induced water cleavage schemes where the semi-conductor nature of TiO_2 plays an important role [14]. Different structural modifications of TiO_2 show different physicochemical properties and therefore are used for different applications. Anatase generally shows better performance than its rutile counterpart in photocatalytic applications [15]. The brookite phase is the least studied mainly owing to the difficulties encountered in obtaining its pure form, though it seems to have marked photocatalytic activity (compared to anatase) in the dehydrogenation of 2-propanol [16].

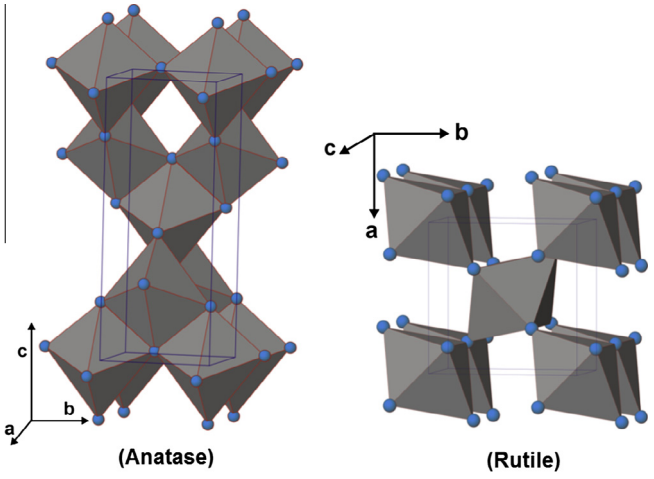

Fig. 1. Structures of titania (rutile left side and anatase right side).

Most of the other experimental methods that have been quite useful, for example, the characterization of transition metal ions present in TiO_2 cannot be applied at these low levels (ultra trace levels). EPR spectroscopy is a non-destructive technique used for identification, characterization and quantification of paramagnetic transition metal ions associated with minerals as in the present case, because this technique is highly sensitive and used for detection of paramagnetic impurities to the extent of less than 5 ppm [17–25]. Apart from these, studies using EPR and PAS spectroscopy [26–29] provide information about the chemical environment and bonding properties of the paramagnetic species in minerals, which in turn, influence the physico-chemical properties of the mineral suitable for specific applications. However, the assignments of an EPR signal recorded from a multi mineral system such as soil and clay, to a specific mineral phase or its chemical form is often difficult because of the spectral overlap of different paramagnetic species. An experimental approach based on the changes in EPR signals upon thermal and chemical stability is reported in literature [19] to characterize the chemical environment of the paramagnetic ions with the complex mineral system.

In the present study, the XRD and Raman studies were performed to identify the phase purity of the mineral while EPR and PAS studies were used for the identification and characterization of paramagnetic transition metals associated with titania mineral.

Experimental

X-ray diffraction measurements

The phase purity and crystal structure of the mineral was analyzed by powder XRD studies. The XRD data was recorded in the two theta range of 10–90° on a PANalytical Powder X-ray diffractometer (X'Pert-Pro) using monochromatized Cu Kα radiation, Ni-filter, 45 kV voltage, 40 mA. The quantitative phase analyses and refinement of the structural parameters were carried out by Rietveld refinement method using the Fullprof-2000 program (Rodriguez-Carvajal, J., Fullprof: a program for Rietveld Refinement and Profile matching analysis of complex powder diffraction patterns ILL) [30].

Photoacoustic spectroscopy measurements

The PAS experiments were performed using an indigenously designed spectrometer consisting of a 250 W tungsten-halogen lamp used as an excitation source, the radiation of which was modulated by variable speed chopper (33 Hz). A monochromator in combination with the appropriate absorption filters was used for wavelength selection and to eliminate higher order effects. The beam leaving the monochromator was directed into a PA cell. The signal was pre-amplified and fed to a lock-in amplifier connected to a computer. The PA signal was normalized by taking the ratio of signal due to sample to that of carbon black, to eliminate the spectral variation of the illumination source [31].

Infra-red and Raman spectroscopy measurements

The IR absorption spectra was obtained in mid infrared (MIR) (4000–400 cm^{-1}) region at 4 cm^{-1} resolution using Bruker Vertex 80V FTIR spectrometer. Globar source, KBr beam splitter and DLaTGS (MIR) detector was used for recording the spectra of mineral samples of 1% in KBr pellets. Raman spectrum was recorded on a homemade Raman spectrometer equipped with peltier cooled Charge Coupled Devices (CCD) and 488 nm argon ion laser, with resolution of ~1 cm^{-1}.