# Dynamic Shock Wave Driven Simultaneous Crystallographic and Molecular Switching between α-Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles- A new finding

A.Sivakumar<sup>1</sup>, A.Rita<sup>1</sup>, S.Sahaya Jude Dhas<sup>2</sup>, K.P.J.Reddy<sup>3</sup>, Raju Suresh Kumar<sup>4</sup> Abdulrahman
I. Almansour<sup>4</sup>, Shubhadip Chakraborty<sup>5</sup>, K. Moovendaran<sup>6</sup>, Jayavel Sridhar<sup>7</sup>,
S.A.Martin Britto Dhas<sup>1\*</sup>

<sup>1</sup>Shock Wave Research Laboratory, Department of Physics, Abdul Kalam Research Center, Sacred Heart College, Tirupattur, Vellore, Tamil Nadu, India – 635 601

<sup>2</sup>Department of Physics, Kings Engineering College, Sriperumbudur, Chennai, Tamilnadu, India - 602 117

<sup>3</sup>Department of Aerospace Engineering, Indian Institute of Science, Bangalore, Karnataka, India - 560 012

<sup>4</sup>Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh, Saudi Arabia- 11451

<sup>5</sup>Institut de Physique de Rennes, UMR CNRS 6251, Université de Rennes 1, 35042 Rennes

Cedex, France

<sup>6</sup>Institute of Physics, Academia Sinica, Taipei-11529, Taiwan

<sup>7</sup>Department of Biotechnology (DDE), Madurai Kamaraj University, Madurai 625 021, Tamil Nadu, India

Corresponding Author: <u>martinbritto@shctpt.edu</u>

### **Experimental Section**

The synthesis of the hematite NPs and shock wave loading procedure were followed as per the previous publication.<sup>53</sup> Briefly, 0.1 M of iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) was dissolved in 200 ml double-distilled water. 0.2 M mono hydrated citric acid of 70 ml solution was added drop-wise to the iron nitrate solution under vigorous stirring. After that, the obtained orange solution was heated to 70 °C until gel was formed and the dried gel was annealed at 700 °C for 3 h. The final product was obtained as the red hematite powder sample.

The shock wave loadings were carried out for the prepared hematite nanoparticles using a semi automatic Reddy tube. The details of the shock loading procedure are given as a supporting document. In the present experiment, three identical samples have been chosen, and among the samples, one sample has been kept as the control while the other two samples have been used for shock wave loading with 200 and 400 shock pulses, respectively. Shock waves of Mach number 2.2 have been used for this experiment wherein one shock pulse has the transient pressure and temperature as 2.0 MPa and 864 K, respectively. After finishing the shock wave loadings, all the three samples have been analytically characterized.

#### **Details of shock loading experiment**

The required shock waves are generated by an in-house semiautomatic Reddy Tube which is capable of producing shock waves up to Mach number 4.5. It has three sections such as driver, driven and diaphragm sections. The driver and driven sections are made of seamless steel tubes of 48 cm and 33 cm length, respectively and both have the same inner diameter of 1.5 cm. Atmospheric air is used as the working substance for the required shock wave generation which is supplied by a tabletop mini 1 HP air compressor that has the capacity of 8 bars pressure storage. The diaphragm section separates the driver section and the driven section. Carbonless paper diaphragms are fed into the diaphragm section with the help of a motor. While the atmospheric air is being compressed into the driver section, at the critical pressure, the diaphragm is ruptured such that the shock wave is generated and moves along the driven section. The schematic diagram of the shock tube is presented in Fig.S1.



Fig.S1 Schematic diagram of the shock wave loading setup

One end of the driver section is connected to the diaphragm section which has two pneumatic cylinders and the other end is connected to the compressor. The pressurized air is also utilized for the operation of pneumatic cylinders. Using the pressure controller of the driver section, we can control the input pressure range of the driver section.

#### **Operation of the shock tube**

Pressure of the air in the driver section is gradually increased by the air compressor until the diaphragm ruptures which leads to the generation of shock wave traveling along the axis of the driven section. The required numbers of test samples are to be placed one by one in the sample holder which is typically placed 1cm away from the open end of the driven section. Subsequently, required numbers of shock pulses are loaded on the respective test sample with an interval of 5 sec between each shock pulse. 50 number of shock pulse means that the sample is exposed for 50 times by shock wave of a particular Mach number. After the completion of the shock wave loading experiment, the control and shock wave loaded samples are sent for analytical studies.

It is worth noting that the loading of static high-pressure is different from that of loading with dynamic shock transient pressure which has the pulse duration of only a few microseconds. In the case of static compression, pressure is increased gradually so that very high energy is required to induce structural changes in solids.

### **Characterization Techniques:**

Powder XRD analysis (Rigaku - SmartLab X-Ray Diffractometer, Japan) was utilized to analyze the crystallographic structural features of the control and shocked samples over 2 $\theta$  ranging 10–80° using Cu K $\alpha$  (0.154 nm) radiation. Micro Raman spectrometry (LabRAM HR Evolution, France) was employed to assess the phase formation details of the samples over the wavenumber region 100–1000 cm<sup>-1</sup> and with the 532 nm wavelength laser source. Ultra-violet Diffused Reflectance spectrometry was utilized to record the optical properties of the samples between 200 and 1200 nm. A scanning electron microscope (Tescan Vega 3), operating at the acceleration voltage of 10 kV, was used to understand the morphology of the title material. A vibrating sample magnetometer (Lake Shore, Cryotronics) was employed to monitor the magnetic properties of the test specimens.

# **Rietveld refinements**



Fig.S2 Rietveld refinements of the control  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and 200 shocked  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples (Fe<sub>3</sub>O<sub>4</sub>)

Structural	control a-Fe <sub>2</sub> O <sub>3</sub>	200 shocked $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>
Parameters		sample (Fe <sub>3</sub> O <sub>4</sub> )
a (Å)	5.030 (4)	8.421 (6)
b (Å)	5.030 (4)	8.421 (6)
c (Å)	13.762(4)	78.421 (6)
$\alpha(^{\circ})$	90	90
β(°)	90	90
γ (°)	90	90
V (Å) <sup>3</sup>	301.542	597.16
R (%)	1.929	2.397
Space Group	<i>R</i> -3c	Fd-3m

Table.S1 Structural parameters of the pristine and shock wave exposed L-Tartaric acid crystals

#### **Electrochemical Analysis and Impedance spectral analysis**

Furthermore, we have recorded the Electrochemical Analysis and Impedance spectral analysis for the supporting evidence for the understanding of the presence of the oxidations states of the sample and found clear difference for the in the potential energy and electrical resistance values and the observed values are presented in Fig.S3. Figure 1a clearly showed that the Fe<sub>3</sub>O<sub>4</sub> NPs have the higer potential energy than that of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NPs and it is due to the occurrence of the mixed oxidation state in the Fe<sub>3</sub>O<sub>4</sub> phase such as Fe<sup>2+</sup>/Fe<sup>3+</sup> and electrical resistance values are well agreed with the electrochemical analysis. Fe<sub>3</sub>O<sub>4</sub> has higher electrical conductivity than that of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> due to the mixed oxidation states. Based on the electrochemical results, it is clear that the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> at 200 shocked conditions and furthermore we strongly confirmed that there is no signature for the formation of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. If,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is formed, we may not observe any changes in the potential energy difference. Because  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> state has only Fe<sup>3+</sup> ions in the crystal lattice.



Fig.S3 Comparison of CV curves at 100 mVs<sup>-1</sup> (b) Cole – Cole plots of the control and 200 shocked  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NPs

## **TEM Images**



Fig.S4 TEM Images of the control and shocked  $Fe_2O_3$  samples (a) Lattice fringe pattern of the control  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (b) SAED pattern of the control  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NPs (c) Lattice fringe pattern of 200 shocked  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Fe<sub>3</sub>O<sub>4</sub>) (d) SAED pattern of 200 shocked  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NPs.