



Thermal properties of nanocrystalline goethite, magnetite, and maghemite

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ABSTRACT

This study investigated the high-temperature properties of nano-goethite, nano-magnetite, and nano-maghemite. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of these nano-minerals revealed that phase-transition temperatures increased with increasing particle sizes. This was due to the high surface energy of the nano-minerals with small particle sizes, which caused them to require lower energies to change their structures, and thereby, resulted in lower phase-transition temperatures. Further, the transition temperatures measured by ex situ and in situ high-temperature X-ray diffraction (XRD) were lower than those observed by TGA–DTA. This may be due to the difference in the atmosphere and heating time in the high-temperature processes. In this study, we found that the particle size of nano-minerals, atmosphere (oxygen pressure), and heating time were the key factors influencing the transition temperature, phase, and path. TGA–DTA measurements gave the initial clue to understand the phase transition, and in situ high-temperature XRD measurements helped elucidate the exact phase-transition behavior of the nano-minerals.

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1. Introduction

Nanoscale phase-transition studies of goethite (α -FeOOH), maghemite (γ -Fe₂O₃), and magnetite (Fe₃O₄) have attracted much attention because these minerals have technological applications in many fields. Nano-goethite is commonly used for magnetic records and adsorbents [1–4]; nano-maghemite is used for adsorbents, photocatalysts, magnetic media, and magnetic records [5–7]; nano-magnetite can be applied as contrast agents, drug delivery, adsorbents [8–10].

Macro-minerals (bulk minerals) and nano-minerals display different behavior in response to changes in temperature. For example, maghemite transforms into hematite at temperatures of 200–700 °C [11], and nano-maghemite transforms into nano-hematite at 450 °C [12]. Studies have also shown that the phase-transition temperature for nano-maghemite ranges from 400 °C to 700 °C [13–16]. Smith and Kidd have reported that goethite transforms into hematite at approximately 423 °C in a slightly alkaline solution [17]; Mitov et al. have shown that goethite thermally decomposes into hematite at temperatures in the region of 280–400 °C [18]. Christensen et al. using in situ synchrotron X-ray diffraction (XRD) technique, have found that nano-goethite with a particle size larger than 13 nm has a phase transition to nano-hematite in the temperature range of 177–317 °C [19].

When magnetite phase transition occurred under oxidative conditions, a two-step process, involving dehydration followed

by oxidative decomposition, resulted in hematite as the final product. The phase transition of magnetite in an inert medium (composed of N₂, Ar, and H₂) took place in two steps that were more distinct than those occurring under oxidative conditions [20,21]. Sun et al. have demonstrated that as-synthesized 16 nm magnetite annealed at 250 °C for 2 h can be transformed into maghemite under an O₂ atmosphere; however, nano-magnetite annealed at 400 °C formed Fe nanoparticles under a mixed Ar and 5% H₂ atmosphere [22].

The studies described above demonstrate that bulk minerals have different phase-transition temperatures than their corresponding nano-minerals; furthermore, the phase transition is influenced by the particle size of the minerals and the atmosphere during the transition [20–25]. Therefore, it is interesting to investigate the temperature effect on the behavior of the nano-minerals. The present study would consider three kinds of nano-minerals, including nano-maghemite, nano-magnetite, and nano-goethite. We will investigate the thermal stability of these nanocrystalline minerals using thermogravimetric analysis (TGA) and differential thermal analysis (DTA), and compare the results with the phase analyses obtained using in situ and ex situ high-temperature XRD methods.

2. Material and method

2.1. Preparation of nano-minerals

Nano-goethite, nano-magnetite, and nano-maghemite were synthesized using an inexpensive and simple co-precipitation method. The procedure for the synthesis of nano-goethite was as follows: Fe₂(SO₄)₃ was added to 1 M NaOH solution over

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a period of 4 h and then heated in an oven at 60 °C for 3 days. The resultant products were separated from the mother liquor by centrifugation. The precipitates were dried in an oven at 100 °C for 24 h, and thus goethite nanoparticles were obtained. For the synthesis of nano-magnetite, N₂ gas was bubbled into deionized water for 30 min to remove O₂. Next, NH₄Cl was added to the prepared solution, with stirring for a period of 10 min, and then, FeCl₂ and FeCl₃ were added to the NH₄Cl solution. The precipitates were separated from the mother liquor using a magnet and washed using deionized water to obtain nano-magnetite. Nano-magnetite powders were calcined at 300 °C for 3 h and then cooled to room temperature to obtain nano-maghemite.

2.2. Characterization of nano-minerals

After preparation of these nano-minerals, their morphology and grain size were observed using the transmission electron microscopy (TEM, 200 kV, Tecnai G2, Philips, The Netherlands). Their crystal structures were characterized by powder XRD (30 kV, CuK α , D8 Advance, Bruker, Germany). In order to determine specific surface area, N₂ gas adsorption–desorption isotherms were measured at –196 °C using autosorbing N₂-adsorption devices (ASAP 2020, Micromeritics, USA).

2.3. Thermal analysis of nano-minerals

The high-temperature properties of these nano-minerals were investigated by TGA and DTA performed at a heating rate of 10 °C/min and temperature range of 25–900 °C (STA449 F3, Netzsch, Germany). Structural changes were measured using ex situ and in situ high-temperature XRD. The ex situ high-temperature XRD procedure was as follows. The sample was heated to the temperature required for analysis and then kept for 1 h in the high-temperature furnace. After cooling to room temperature, the crystal phase of the sample was examined by XRD (D8 Advance, Bruker, Germany). For the in situ high-temperature XRD analysis (HT-XRD 6000, Shimadzu, Japan), the sample was loaded into the sample chamber under a vacuum of $\sim 1 \times 10^{-2}$ Torr. The sample was heated to the required temperature and kept for 5 min, and then, real-time XRD measurement was performed after each required temperature adjustment.

3. Results

3.1. Characterization of nano-minerals

Fig. 1 shows the XRD pattern of the nano-minerals. It is apparent that nano-goethite has an orthorhombic structure with a polycrystalline phase, and both nano-magnetite and nano-maghemite exhibit a polycrystalline cubic structure. The morphology and particle size of these nano-minerals were investigated by TEM, as shown in Fig. 2. The crystal shape of nano-goethite is virgulate (acicular), and the crystals are aggregated. Nano-goethite can be classified as nanorods with an average particle size of 55–70 nm in width and 200–300 nm in length. Nano-magnetite and nano-maghemite both have a cubic crystal shape, with crystal sizes of around 50–70 nm and 30–46 nm, respectively. Both can be classified as nanoparticles. Moreover, the surface areas are 33.5, 29.3, and 30.7 m²/g for nano-goethite, nano-magnetite, and nano-maghemite, respectively. These results suggest that the surface areas of these nano-minerals are approximately the same.

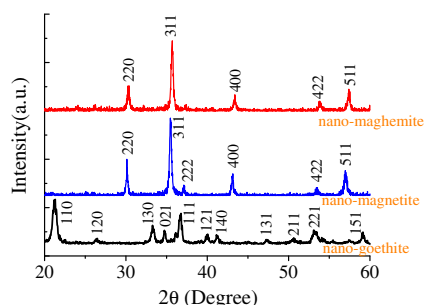


Fig. 1. The XRD pattern of nano-goethite, nano-magnetite, and nano-maghemite.

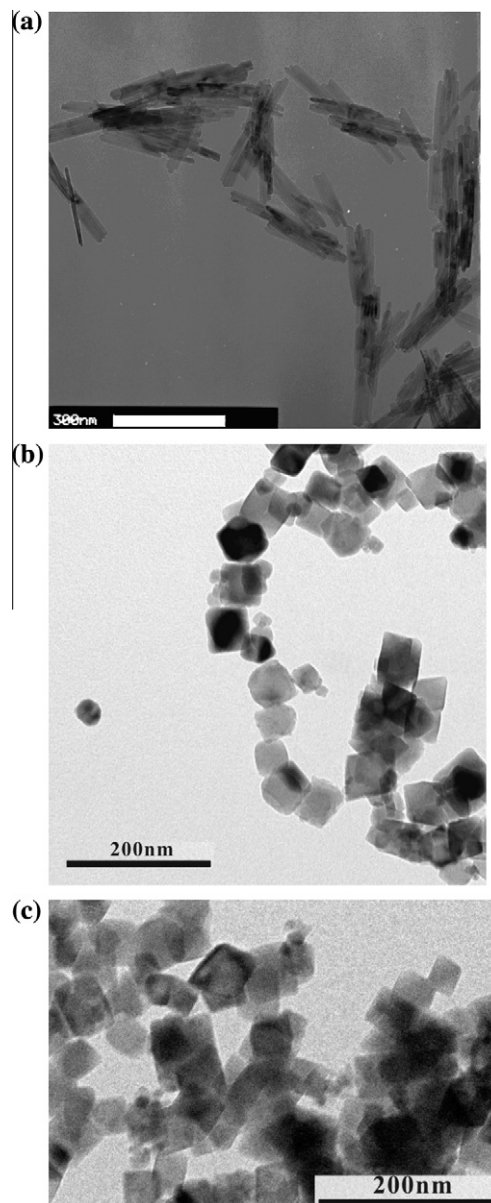


Fig. 2. TEM images of (a) nano-goethite, (b) nano-magnetite, and (c) nano-maghemite.

3.2. TGA–DTA

Fig. 3(a)–(c) shows the TGA–DTA curves of these nano-minerals at the heating rate of 10 °C/min, over the temperature range 25–900 °C. The TGA curve (Fig. 3(a)) suggests a mass loss of 2.5 wt.% at temperatures from 25 °C to 200 °C and 12.0 wt.% at temperatures from 200 °C to 300 °C, thought to be caused by the desorption of physically and chemically adsorbed water, respectively. One apparent endothermic peak (at 265.8 °C) is observed in the heating process. This peak corresponds to the nano-goethite dehydration hindered by the formation of nano-hematite.

The TGA curves in Fig. 3(b) and (c) show an apparent mass loss for nano-magnetite and nano-maghemite. A weak endothermic peak is observed at approximately 100 °C for nano-magnetite and nano-maghemite, indicating the removal of physically adsorbed water. Exothermic peaks occur at 554.1 °C and 576.1 °C for the nano-magnetite and nano-maghemite, respectively. These are attributed to phase transitions as nano-magnetite and nano-maghemite are transformed into hematite phase. The phase-transition

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