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Synthesis and characterization of cerium substituted hematite by sol–gel method

Nimai Chand Pramanik [a,*], Tarequl Islam Bhuiyan [b], Makoto Nakanishi [b], Tatsuo Fujii [b], Jun Takada [b], Sang Il Seok [a]

[a] *Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon 305-600, Korea*

[b] *Department of Applied Chemistry, Faculty of Engineering, Okayama University, Okayama 700-8530, Japan*

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Abstract

Fine particles of cerium substituted hematite with different compositions were prepared by the sol–gel method from the aqueous solution of their corresponding metal salts. Mixed hydroxides of Fe^{3+} and Ce^{4+} were obtained by reacting aqueous NH_3 with the aqueous solution of $FeCl_3$ and $Ce(NH_3)_2(NO_3)_6$ at pH 2.5–3.0) and they were heat treated at different temperatures between 400 and 1200 °C in air for 2 h to get the mixed oxide product. Thermal analysis and X-ray diffraction studies revealed the coexistence of Fe_2O_3 and CeO_2 phase separately up to 900 °C, and covalent interaction between them above 1000 °C, which was evidenced by the shifting of the XRD peaks. Unit cell parameters and the cell volumes (V) of the samples derived between 1000 and 1200 °C were found to be in the range $a = 5.045 - 5.048 \pm 0.007$ Å, $c = 13.774 - 13.815 \pm 0.041$ Å and $V = 303.608 - 304.874$ Å^3 respectively. It was observed that both the lattice parameters and the cell volumes were higher than that of the pure α-Fe_2O_3 ($a = 5.036$ Å, $c = 13.749$ Å, $V = 301.976$ Å^3) system. The expansion of lattice parameters further supported the incorporation of the large Ce^{4+} ion into the α-Fe_2O_3 matrix. The lattice parameter increased with increasing Ce^{4+} ion loading. FESEM studies showed the growth of the particles with increasing temperature though it was suppressed due to the presence of Ce^{4+} ions as compared to the pure system.

Keywords: Cerium substituted Fe_2O_3; Sol–gel method; XRD; Crystal growth

1. Introduction

Oxides of iron are common compounds which are widespread in nature and also readily synthesized in the laboratory. Hematite (α-Fe_2O_3, called ‘bengara’ in Japanese), a well-known compound of iron, which is chemically stable, self-preservative in character and most abundant in nature. It is one of the most primitive pigments which exhibited various shades of colors ranging from yellow → red dark brown → purple → black [1]. In 1000 BC, the paintings of Ajanta and Ellora caves in India were drawn by utilizing the red–yellow–black color of the hematite. The existence of wide range of colors of the hematite appears mainly due to the variation in crystallinity [2], particle size [3], shape and extent of aggregation [4], and also cation substitution [2,5]. Out of the various factors affecting the color of hematite, cation substitution has received current interest [6–9] due to the fact that the properties of the substituted hematite, such as the position of the visible and infrared absorption bands, magnetic and electrical properties, crystal size, etc. change regularly with increasing the substitution. For example, substitution of Al and Si changes the color tones of the hematite [2,5], while the substitution of trace of Zr, Nd, Hf, Ta and Ge improves its semiconductivity [10,11] and other fascinating properties. Our earlier work described the influence of Al and Si substitution on the color of hematite [12,13]. The effects of cation substitution on crystal sizes, the magnetic properties and color with the atoms of relatively lower ionic radii have already been

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[*] Corresponding author. Tel.: +82 42 860 7326; fax: +82 42 861 4245. *E-mail address:* ncpramanik@rediffmail.com (N.C. Pramanik).

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reported by several workers [2,3]. But the preparation of lanthanide substituted hematite, especially with higher ionic radii (like La, Ce, Nd, etc.) was not explored so much [10,11]. Furthermore, the reports on the preparation of Ce^{4+} substituted hematite (α-Fe_2O_3) are scanty. Therefore, our interest is to prepare various M^{n+}-substituted α-Fe_2O_3 (M^{n+}=various metal ions of lanthanide series having higher ionic radii as compared to that of Fe^{3+}) by sol–gel method, and study their structures and other physical properties, like magnetic, crystal growth, etc. The point to be noted here that out of the conventional preparative techniques, sol–gel processing has been identified as one of the versatile methods for the preparation of homogeneous and high purity products at relatively lower temperature. The main advantage of this method is not only to reduce the annealing temperature but also to control the size and shape of the particles. In this context, our present work describes the preparation and structural characterization of the Ce^{4+} ion substituted hematite by sol–gel method, and also the effect of Ce^{4+} ion on the crystal growth of the substituted product.

2. Experimental

2.1. Preparation of Ce^{4+} substituted hematite

Cerium substituted hematite materials with different initial solution compositions (Fe:Ce atomic ratio ranging from 95:5 to 85:15) were prepared by following a general experimental procedure. The detail of the experimental procedure is described below.

Calculated amount of $FeCl_3.6HO$ (Aldrich, ≥98%) and $Ce(NH_4)_2(NO_3)_6$ (Aldrich, ≥98.5%) was dissolved in deionized water to make 1.0 M aqueous solution of the corresponding metal ions. The solution was stirred magnetically for several minutes, and then aqueous NH_3 solution (10% v/v) was slowly added to it until the pH of the solution lies in the range 2.5–3.0. A dark brown colored metal hydroxides formed and were aged at an ambient condition for several days (5–7 days). Excess deionized water was added to the above suspension and stirred vigorously for 3 h. Then the product was filtered, and washed thoroughly with dilute NH_3 (1% v/v) and deionized water until all chlorides were removed from the product. The solid thus obtained was then dried at 95 °C for 48 h in air and then heated at different temperatures between 400 °C and 1200 °C for 2 h in air.

Samples of pure α-Fe_2O_3 and CeO_2 (described as Fe:Ce=100:0 and 0:100) were also prepared and heat treated in a similar manner for comparison.

2.2. Physical measurements

Thermogravimetric and differential thermal analyses (TG and DTA) of all the samples were carried out between 30 and 1200 °C using Rigaku Thermo Plus TG 8120 instruments. α-Al_2O_3 was used as the reference and the temperature was increased at a heating rate of 10.0 K/min. Structural characterization of samples was performed on Rigaku RINT 2500 X-ray powder diffractomer using Ni-filtered CuKα radiation (λ=1.5418 Å). Silicon powder (a=5.430758 Å) was used as internal standard and the reflection patterns were calibrated with respect to Si (220) reflection. Morphologies of the particles were studied by Hitachi S4300 field emission scanning electron microscope (FESEM) with 15.0 kV EHT (electrical high tension).

3. Results and discussion

3.1. Study of thermal analysis

Fig. 1 shows the representative TG-DTA curves for the sample containing Fe:Ce=95:5. Comparing the TG-DTA curves of the sample with that of the pure system (Fe:Ce=100:0, 0:100), it was

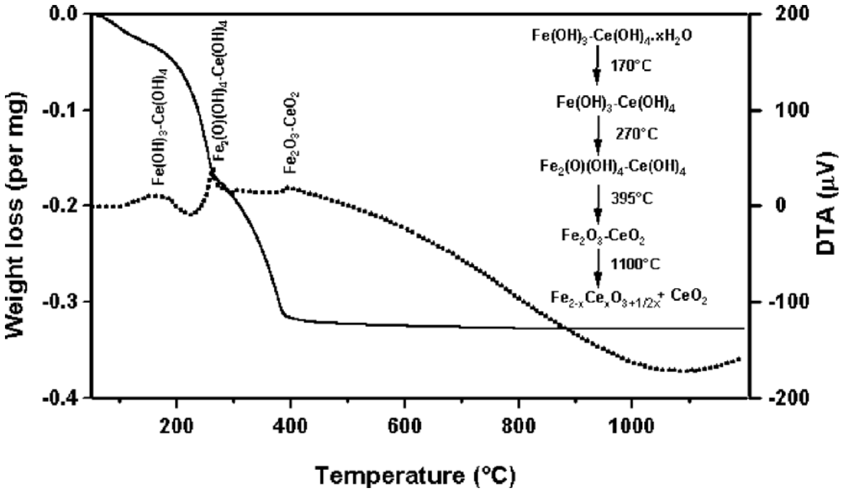

Fig. 1. Thermogravimetry (TG, — line) and differential thermal analysis (DTA,- - - - line) curves for the sample prepared by sol–gel method (Fe:Ce atomic ration=95:5).