Structure, Morphology and Color Tone Properties of the Neodymium Substituted Hematite

Tarequl Islam BHUIYAN

Dept. of Applied Chemistry

Okayama University

3-1-1 Tsushima-naka, Okayama, Japan

Makoto NAKANISHI

Dept. of Applied Chemistry

Okayama University

3-1-1 Tsushima-naka, Okayama, Japan

Tatsuo FUJII

Dept. of Applied Chemistry

Okayama University

3-1-1 Tsushima-naka, Okayama, Japan

Jun TAKADA*

Dept. of Applied Chemistry

Okayama University

3-1-1 Tsushima-naka, Okayama, Japan

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Co-precipitation method has been employed to fabricate neodymium substituted hematite with different compositions from the aqueous solution of their corresponding metal salts. Thermal analysis and X-ray diffraction studies revealed the coexistence of Fe_2O_3 and Nd_2O_3 phases up to 1050°C and formation of solid solution phase among them at 1100°C and above temperatures, which was evidenced by shifting of the XRD peaks. Unit cell parameters and the cell volumes of the samples were found to increase by adding Nd^{3+} ions in the reaction process. FESEM studies showed the suppression of particle growth due to the presence of Nd^{3+} ions. Spectroscopic measurement evidenced that neodymium substituted hematite exhibited brighter yellowish red color tone than that of pure α-Fe_2O_3.

1. INTRODUCTION

Iron is the fourth most abundant element (5.1%mass) in the lithosphere. Iron oxides are widespread in nature and ubiquitous in soils, rocks and sea floor. The name Hematite originates from the Greek word for blood, haima. Hematite called "Bangla" i.e. Bengala in Japanese, is the well-known compound of iron

*E-mail: jtakada@cc.okayama-u.ac.jp

oxide. Its chemical composition contains a high percentage of iron (70%) and it is the primary ore used to create iron. It is believed that ancient people grinded the ore into powder, diluted it with water, animal fat or natural resin, and created a starchy substance use for paintings. The ancient Egyptians used Hematite in the creation of their magical amulets. These precious treasures of human culture could not have been preserved till today without the benefit of iron oxide.

The development of the various properties of hematite has received considerable attention due to their promising characteristics and wide range of applications as ceramic pigments [1], sensor for the detection of dangerous gases [2] and raw material for the synthesis of magnetic oxide powders [3]. Due to the variation in crystallinity [2], particle size [3], shape and extent of aggregation [4] and cation substitution [5] hematite exhibits wide range of colors. Cation substitution has received current interest due to the fact that the properties of the substituted hematite change with increasing the substitution [6, 7]. Influence of Al and Si substitution on the color tone of hematite [8, 9] already has been discussed. The effects of cation substitution on crystal sizes, the magnetic properties and color tone with the atoms of smaller ionic radii have already been reported [2]. But the preparation of lanthanide substituted hematite, especially with larger ionic radii is scanty. Our previous study have been described the structural characterizations of cerium substituted hematite by sol gel method [10]. Furthermore, the reports on the preparation of Nd^{3+} substituted hematite are not explored so much. Out of the conventional preparative techniques, co-precipitation has been identified as one of the promising process for the preparation of homogeneous and high purity products. Lanthanide element is being popular as raw materials for the fabrication of substituted hematite because of their known low-toxicity [11]. The main advantage of this method is not only to fabricate low toxic substituted hematite, but also to control the size and shape of the particles by controlling over the amount of Nd^{3+} ion in the reaction process.

2. EXPERIMENTAL

2.1 Powder Preparation

A series of experiments has been conducted by maintaining different compositions of Fe:Nd atomic ratio ranging from 100:0 to 90:10 by co-precipitation method. $FeCl_3 \cdot 6H_2O$ and $NdCl_3 \cdot 6H_2O$ were dissolved in distilled water to make 0.2 M aqueous solution of the corresponding metal salts. The solution was stirred magnetically at room temperature for 3h. Then aqueous NaOH solution of 0.4 M was prepared and stirred magnetically under ambient condition. The mixture of 0.2 M of $FeCl_3 \cdot 6H_2O$ and $NdCl_3 \cdot 6H_2O$ solution was slowly added to the 0.4 M NaOH solution following magnetically stirred until the pH of the solution lies in the range of 9.30. Dark brown colored metal hydroxides were formed and aged under an ambient condition for 12h. Then the resultant product was filtered and washed by distilled water until the conductivity of solution being 0.55 S/cm in order to remove all chlorides from the product. The wet powder was then dried at 120°C for 12h in air and then heated at different temperatures between 300 and 1200°C for 2h in air.

2.2 Physical measurements

Characterizations procedure has been performed using Thermogravimetric and Differential Thermal Analysis (TG-DTA), X-ray diffractometer (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Spectrophotometer Analysis system. TG-DTA measurements were carried out with a heating rate of 10 K/min in air comparing with standard α-Al_2O_3 by using Rigaku Thermo Plus TG 8120 instrument. Structural characterizations of samples were performed on RIGAKU RINT 2500 X-ray powder diffractometer using CuKα radiation (λ= 1.5418 Å). Silicon powder (a = 5.4308 Å) was used as an internal standard and the diffraction patterns were calibrated with respect to Si (220) reflection. Hitachi S-4300 FESEM with 15 kV EHT (electrical high tension) was employed to study SEM measurements. The wavelength-dependant reflection of a surface relative to a white standard was measured using a Spectrophotometer Minolta C-2600D.

3. RESULTS AND DISCUSSION
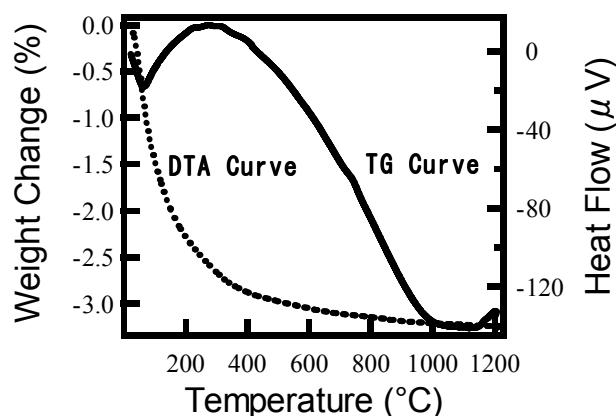
3.1 Study of Thermal analyses

Fig.1 Thermogravimetric and differential thermal analysis curves for the sample prepared by co-precipitation method (Fe:Nd = 90:10 at%).

It was observed by TG-DTA that gel powders obtained after drying at 95°C displayed a broad endothermic weight loss centered at 180°C, which is due to the presence of entrapped water in the gel powder. Consequently the step wise weight loss at TG curve from 180°C to 400°C associated with exothermic peak might be due to the decomposition of hydroxide to oxide materials respectively (Fig.1).

3.2 X-ray diffraction studies

Characteristic reflections of the diffraction patterns of the samples were heat treated up to 1200°C identified to their corresponding phases as α-Fe_2O_3 and Nd_2O_3 (Fig.2). When the samples
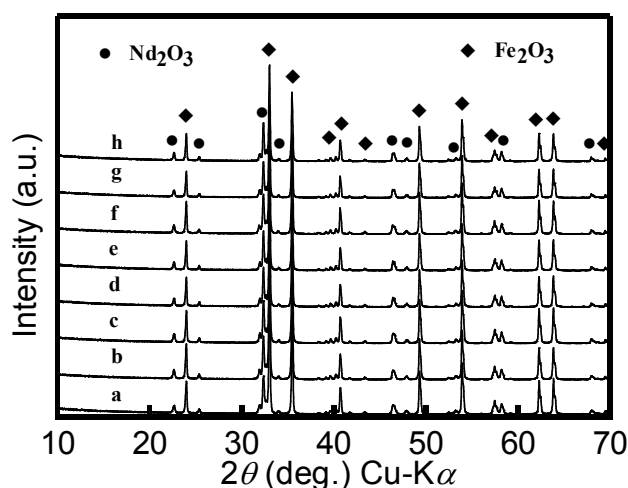
Fig.2 XRD pattern of the samples obtained at Fe:Nd = 95:5 at% at a) 500°C, b) 600°C, c) 700°C, d) 800°C, e) 900°C, f) 1000°C, g) 1100°C and h) 1200°C

were heat-treated between 1100 and 1200°C, the reflections due to α-Fe_2O_3 were found to be slightly shifted towards the lower angles than that of the pure α-Fe_2O_3 system (Fig.3). The shifting of XRD peaks might be due to the incorporation of larger Nd^{3+} ion (ionic radius of Nd^{3+} = 0.995 Å [12]) into the α-Fe_2O_3 matrix (ionic

radius of Fe^{3+} = 0.49 Å [12]) causing expansion of the crystal lattice. Calculation of cell volume (302.80 ± 0.5 Å³) also showed lattice expansion as compared to that of the pure α-Fe_2O_3 (301.40 ± 0.2 Å³) suggesting the Nd^{3+} ion incorporation into the hematite lattice (Fig.4).
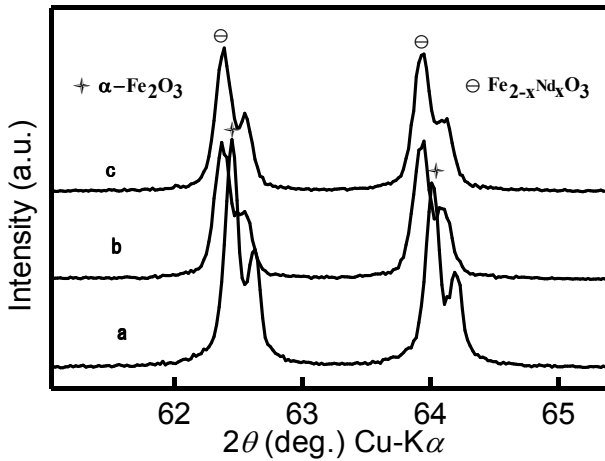

Fig.3 XRD pattern of the samples obtained at 1150°C when Fe:Nd initial compositions were a) 100:0, b) 95:5 and c) 90:10 at%
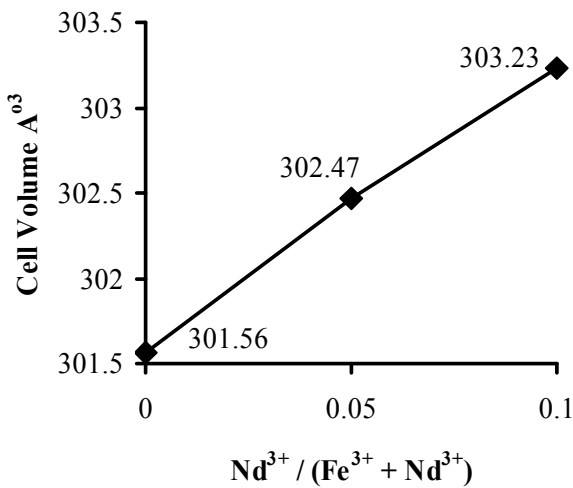

Fig.4 Cell volume of the samples obtained at 1150°C at different initial compositions

The XRD patterns of the samples, heat-treated at 1200°C showed that Nd_2O_3 still coexisted with the substituted hematite. This indicates that a very small amount of Nd^{3+} ion has been incorporated into the α-Fe_2O_3 matrix. The values of the unit cell parameters for the samples (heat treated below 1100°C) were very close to that of the pure α-Fe_2O_3 (a = 5.032 Å, c = 13.749 Å) prepared under identical conditions. Unit cell parameters and the cell volume for the mixed systems increase with increasing the atomic ratio of initial Nd^{3+} ion, suggesting the possibility of Nd^{3+} ion incorporation into the hematite.
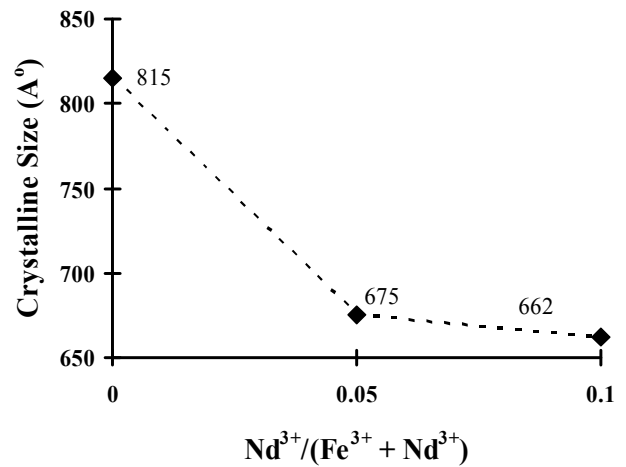

Fig.5 Crystalline size of the samples obtained at 1150°C at different initial compositions

Crystalline size calculated by Scherrer's formula was found on the decrease by increasing the amount of Nd^{3+} ion in the reaction process (Fig.5).

3.3 Morphology of the Particles

The particle size increased with increase in the heat treatment temperature due to growth of the particles as expected. But, the suppression of particle growth was observed by the presence of Nd^{3+} ion comparing with that of the pure α-Fe_2O_3 at the respective temperatures (Fig.6). The growth of the particles were gradually decreased with increasing Nd^{3+} ion in the reaction process suggesting the possibility of Nd^{3+} ion incorporation into the α-Fe_2O_3 matrix.
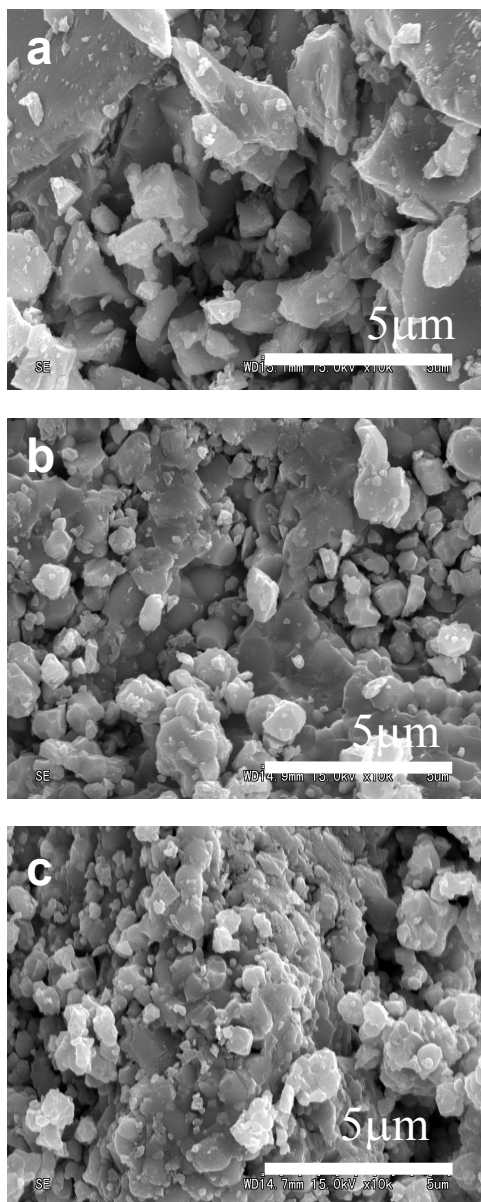
Fig.6 FESEM images of the samples prepared at 1200°C with various compositions when Fe:Nd equal to a) 100:0, b) 95:5 and c) 90:10 at%

3.5 Spectrophotometer analyses

Spectroscopic measurement showed that a brighter yellowish red color than pure hematite was fabricated by neodymium substitution into the hematite (Fig.7).
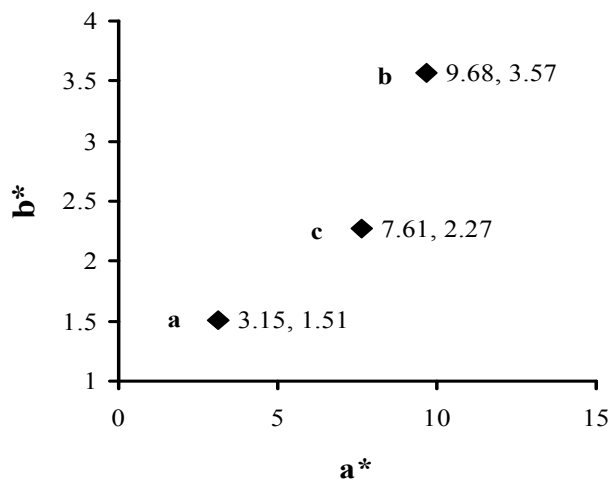

Fig.7 Color tone a* and b* of the samples at the composition of Fe:Nd equal to a) 100:0 b) 95: 5 and c) 90:10 at% at 1150°C

In Fig.7, the a* axis stands for red tone, and the b* axis for yellow. In this case, the particle sizes and reflective indices of the pigment produced brighter yellowish-red color tone when Nd^{3+} ion added to the hematite in between 1100 and 1200°C temperatures that is primarily caused by the various absorption processes. Samples contained 5 at% Nd^{3+} ion in initial solution exhibited wide range of brighter yellow-reddish pigment. Due to the addition of more Nd^{3+} ion into the hematite at 1100°C and above, particle size decreased and the color tone turned into dark rapidly. But an interesting observation is that by comparing with the almost same particle sizes of pure α-Fe_2O_3 obtained by identical condition, it was found that neodymium substituted hematite by co-precipitation method exhibited brighter color tone than that of pure hematite (a* = 6.90 and b*= 2.25).

4. CONCLUSION

Hematite substituted with Nd^{3+} ion (i.e. $Fe_{2-x}Nd_xO_3$) was prepared by co-precipitation

method at 1100°C and above. Several Fe:Nd atomic ratios were used to study the effect of substitution on lattice parameters, crystalline size, morphology and color tone of the Nd^{3+} substituted hematite. XRD patterns were shifted towards the lower angle by comparing with internal silicon standard evidenced the Nd^{3+} ion substitution in to the α-Fe_2O_3. The unit cell parameters and cell volume of $Fe_{2-x}Nd_xO_3$ were found to be expanding also clearly established the incorporation of larger Nd^{3+} ion into the α-Fe_2O_3. Crystalline size and grain growth of the samples were found on the decrease by increasing the amount of Nd^{3+} ion added to the hematite. Morphological study of the particles proved the suppression of particle growth by the presence of Nd^{3+} ion. Compared with different compositions and temperatures, it was found that the yellowish-red color tone of $Fe_{2-x}Nd_xO_3$ than that of pure hematite increased. $Fe_{2-x}Nd_xO_3$ is suggested to be formed by solid state reaction between α-Fe_2O_3 and Nd_2O_3 at 1100°C - 1200°C. Yellowish-red color tone of $Fe_{2-x}Nd_xO_3$ was also found brighter than that of sample obtained at lower temperatures (α-Fe_2O_3 and Nd_2O_3) and that of pure α-Fe_2O_3 contained almost same particle size obtained by identical condition.

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