Synthesis and Properties of Nanocrystalline δ -FeOOH

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Abstract. For fabricating pure δ -FeOOH, $\text{Fe}(\text{OH})_2$ was first precipitated by reacting $\text{FeCl}_{2(\text{aq})}$ with $\text{NaOH}_{(\text{aq})}$ and then oxidized by an oxidant, such as $\text{NaClO}_{(\text{aq})}$ or $\text{H}_2\text{O}_{2(\text{aq})}$. When using $\text{NaClO}_{(\text{aq})}$ as the oxidant, with various amounts of $\text{NaClO}_{(\text{aq})}$ and $\text{NaOH}_{(\text{aq})}$, four phase regions were found, i.e. (a) amorphous region, (b) α -FeOOH + δ -FeOOH + Fe_3O_4 phase region, (c) δ -FeOOH + α -FeOOH phase region, and (d) very high purity δ -FeOOH phase region. When using $\text{H}_2\text{O}_{2(\text{aq})}$ as the oxidant, with various amounts of $\text{H}_2\text{O}_{2(\text{aq})}$ and $\text{NaOH}_{(\text{aq})}$, three phase regions were found, i.e. (a) amorphous region, (b) δ -FeOOH + Fe_3O_4 phase region, and (c) δ -FeOOH phase region. The study on the microwave properties of pure δ -FeOOH showed that the electron spin resonance linewidth was 3 kOe and the external resonance magnetic field with the maximum absorption was at 2.5 kOe.

1 INTRODUCTION

Among the five forms of ferric oxyhydroxide, only hexagonal δ -FeOOH exhibits a significant magnetization at room temperature[1,2], whose properties are not yet fully understood, such as the controversial saturation magnetic moment (the reported values are among 20 to 40 emu/g) and microwave properties[3]. Normally, δ -FeOOH fine particles can be prepared using $\text{Na}(\text{OH})_2$ formed by mixing Fe^{2+} and NaOH aqueous solutions, which is then oxidized by an oxidant, e.g. $\text{H}_2\text{O}_{2(\text{aq})}$ or $\text{NaClO}_{(\text{aq})}$. However, there is as yet no sufficient information available about its preparation conditions, such as temperature, pH and concentration of oxidant during reaction. As an attempt to shed more light on this area, we investigated the preparation conditions for making pure δ -FeOOH and its magnetic properties.

2. EXPERIMENTAL

δ -FeOOH samples were prepared in the following procedures. First, ferrous hydroxide was precipitated by mixing a ferrous sulfate aqueous solution and a NaOH aqueous solution, followed by the addition of an oxidant, 5 wt% $\text{NaClO}_{(\text{aq})}$ or 35 wt% $\text{H}_2\text{O}_{2(\text{aq})}$, under nitrogen atmosphere at room temperature. Magnetic properties of δ -FeOOH powders were measured by a VSM and a SQUID. The phase identification were performed by XRD using $\text{CuK}\alpha$ radiation. The microwave absorption first derivative pattern was obtained with a Bruker ER 200D electron spin resonance (ESR). The frequency of the microwave generator was 9.782 GHz. The scanning external magnetic field, H_a , was from 0 to 10 kOe.

3. RESULTS AND DISCUSSION

According to the XRD analyses on the precipitates obtained by the oxidation of $\text{NaClO}_{(\text{aq})}$, it was found that the pure δ -FeOOH could only be obtained with large amount of $\text{NaOH}_{(\text{aq})}$ and $\text{NaClO}_{(\text{aq})}$. On the other extreme, when $\text{NaOH}_{(\text{aq})}$ and $\text{NaClO}_{(\text{aq})}$ were extremely insufficient, only amorphous phase could be formed. When the amount of $\text{NaOH}_{(\text{aq})}$ and $\text{NaClO}_{(\text{aq})}$ added was in between the aforementioned two extremes, δ -FeOOH, α -FeOOH, Fe_3O_4 and coexisted and high purity δ -FeOOH was difficult to obtain. Based on these data, as shown in Fig. 1, four phase regions can be found, i.e. (a) amorphous region where both NaOH and NaClO are insufficient; (b) α -FeOOH + δ -FeOOH + Fe_3O_4 phase region; (c) δ -FeOOH + α -FeOOH phase region, and (d) very high purity δ -FeOOH phase region obtained by enough amount of NaOH and NaClO .

From the above analysis, the amount of $\text{NaOH}_{(\text{aq})}$ added is the important factor that decides the resulting phases obtained, while the amount of $\text{NaClO}_{(\text{aq})}$ added decides the oxidation degree of Fe^{2+} . When the oxidant is insufficient, even though the amount of NaOH is sufficient, amorphous phase tends to be present. When the amount of oxidant is insufficient, even though NaOH is sufficient, the different kinds of oxides coexist. Therefore, to make the pure $\delta\text{-FeOOH}$, both NaOH and NaClO should be sufficient under nitrogen atmosphere.

Fig. 1 Phase diagram of samples prepared by the oxidation of $\text{NaClO}_{(\text{aq})}$, (a) amorphous phase region, (b) $\alpha\text{-FeOOH} + \delta\text{-FeOOH} + \text{Fe}_3\text{O}_4$ phase region, (c) $\alpha\text{-FeOOH} + \delta\text{-FeOOH}$ phase region, and (d) pure $\delta\text{-FeOOH}$ phase region

Fig. 2 Phase diagram of samples prepared by the oxidation of $\text{H}_2\text{O}_{2(\text{aq})}$, (a) amorphous phase region, (b) $\delta\text{-FeOOH} + \text{Fe}_3\text{O}_4$ phase region, and (c) pure $\delta\text{-FeOOH}$ phase region

When using $\text{H}_2\text{O}_{2(\text{aq})}$, as shown in Fig. 2, three phase regions can be found, i.e. (a) amorphous region where both H_2O_2 and NaOH are insufficient; (b) $\delta\text{-FeOOH} + \text{Fe}_3\text{O}_4$ phase region where H_2O_2 is insufficient; (c) $\delta\text{-FeOOH}$ phase region obtained by sufficient amount of NaOH and H_2O_2 . In this phase diagram, $\alpha\text{-FeOOH}$ is not found. It is thus thought that formation of $\alpha\text{-FeOOH}$ can be prohibited by using a stronger oxidant, e.g. $\text{H}_2\text{O}_{2(\text{aq})}$, in the synthesis procedure.

Magnetic properties of the high purity $\delta\text{-FeOOH}$ powders were carefully measured with a VSM calibrated against pure Ni. The pure $\delta\text{-FeOOH}$ samples obtained were superparamagnetic and the room temperature saturation magnetizations (M_s) were 20 ± 2 emu/g. The reported M_s values of up to 40 emu/g is believed to arise from Fe_3O_4 contamination. The true M_s ($T \rightarrow 0$, $H \rightarrow \infty$) of $\delta\text{-FeOOH}$ particles, as measured by a SQUID, was 39.4 emu/g. Fig. 3 shows the first derivative curve of a microwave absorption spectrum of $\delta\text{-FeOOH}$ particles. The result shows that the electron spin resonance linewidth, ΔH , is 3 kOe and the external resonance magnetic field with the maximum absorption, H_r , at 2.5 kOe.

Fig. 3 The first derivative curve of microwave absorption spectrum of pure $\delta\text{-FeOOH}$ particles

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