

Mechanochemical Synthesis of Zinc Ferrite, $ZnFe_2O_4$

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Abstract

Mechanochemical synthesis of zinc ferrite, $ZnFe_2O_4$, was attempted from a powder mixture of iron (III) oxide, $\alpha\text{-Fe}_2\text{O}_3$ and zinc (II) oxide, ZnO . Nanocrystalline zinc ferrite, $ZnFe_2O_4$ powders were successfully synthesized only by milling for 30 hours. Evidence of the $ZnFe_2O_4$ formation was absent for the powders milled for 10 and 20 hours; the milling lowered the crystallinity of the starting materials. Heating after milling enhanced the formation of $ZnFe_2O_4$, crystal growth of $ZnFe_2O_4$ and the unreacted starting materials. The unreacted starting materials decreased their amounts by heating at higher temperatures.

Keywords : Zinc ferrite, $ZnFe_2O_4$, mechanochemical synthesis, nanocrystal

1. Introduction

Zinc ferrite ($ZnFe_2O_4$) is being investigated as a magnetic material, gas sensor, photocatalyst [1-5] and hot-gas desulfurization absorbent [6]. The mechanochemical synthesis of $ZnFe_2O_4$ was usually attempted using vials and balls made of stainless steel instead of expensive ceramics, since the contamination of iron or iron oxide during the milling process was not thought to be serious.

Ito et al. [7] needed heating at 660°C after the milling of zinc (II) oxide, ZnO and iron (III) oxide ($\alpha\text{-Fe}_2\text{O}_3$) in order to measure the formation rate of $ZnFe_2O_4$. Šepelák et al. [6, 8] interpreted a weak diffraction peak of the as-milled powder mixture as $ZnFe_2O_4$ although the broad peak can also be interpreted as Fe_2O_3 . Yang et al. [9] recently interpreted the exothermic DTA peak of the amorphous as-milled powder as the formation reaction of $ZnFe_2O_4$ (an exothermic reaction) and/or the crystallization of the amorphous phase. These results indicate that it seems difficult to prepare the crystalline $ZnFe_2O_4$ phase only by milling.

The present study attempted the mechanochemical synthesis of crystalline $ZnFe_2O_4$ by a long-time operation of a high-energy ball mill; a high-power X-ray diffraction instrument was used for the identification of the phases. Heating of the as-milled powders was also systematically executed.

2. Experimental and Results

Powders of ZnO (purity 99.0%; particle size, 0.8 micron; Hokusui Chemical) and $\alpha\text{-Fe}_2\text{O}_3$ (purity, 99.9%; particle size, 1.0 micron; Kojundo Chemical) were mixed at a molar ratio of 1:1. The powder mixture (50 g) was mechanochemically processed in air using a mill (model CM01; Zoz bmGH) whose rotational axis was horizontally disposed. The cyclic rotation (1200 rpm for 4 min and 900 rpm for 1 min) is expected to remove the powders stuck on the wall surface. Steel balls (diameter, 5 mm; total mass, 1 kg; DIN 17230; Cr, 1.35-1.65%) were hit by the rotators against the inner wall of the housing which was cooled with water. The powders were examined by X-ray diffraction analysis (Cu rotating target, 40 kV, 300 mA; model, RINT2500V; Rigaku); silicon was used to calibrate the lattice constant. The powders were pressed at 200 MPa into a pellet before heating (the heating rate; 10°C/min) at 500-900°C for 1 hour in air.

The X-ray diffraction spectra of the as-milled powders (without heating) with various milling times showed a remarkable peak broadening. A ZnO peak at 31.7° decreased its intensity by milling and completely disappeared after a 30-hour milling time. A peak of Fe_2O_3 at 33.0° decreased its intensity although it remained after milling for 30 hours. Another peak of Fe_2O_3 at 35.5° still remained at 20 hours. A weak trace of the $ZnFe_2O_4$ peak at 29.9° was observed at 10 hours and drastically increased the intensity at 30 hours. Another $ZnFe_2O_4$ peak at 35.2° clearly

appeared at 30 hours. This peak might be duplicated at the peak of Fe_2O_3 at 35.5° . A shoulder at 36.8° (30 hours) should be attributed to ZnFe_2O_4 . These results indicated that the formation of crystalline ZnFe_2O_4 occurred without the post-milling heat treatment.

The formation of crystalline ZnFe_2O_4 for the as-milled (unheated) powders milled for 30 hours were confirmed by twelve diffraction peaks. Four weak peaks assigned to Fe_2O_3 indicated that a very small amount of crystalline Fe_2O_3 coexisted in the specimen after milling for 30 hours. No ZnO peak was observed. The lattice constant of ZnFe_2O_4 (0.8438 nm) was approximately equal to that (0.8440 nm) of the above-mentioned specimens heated at 900°C without milling. The broad diffraction peaks indicated the formation of nanocrystalline ZnFe_2O_4 whose crystallite size was 26.3 nm.

The specimens heated after milling for 10 hours showed broad XRD peaks of the as-milled powders of the starting materials (Fe_2O_3 and ZnO); this indicated poor crystallinity. The spectrum after heating at 600°C showed three coexisting phases, i.e., the formation of ZnFe_2O_4 and the re-crystallization of Fe_2O_3 and ZnO. The width of the ZnFe_2O_4 and Fe_2O_3 peaks decreased by heating at 600°C ; crystal growth (grain growth) occurred by heating. Heating at a higher temperature (700°C) eliminated ZnO, decreased Fe_2O_3 and accelerated the crystal growth of ZnFe_2O_4 . The results by milling for 20 hours are not indicated but were approximately identical with those for 10 hours.

The X-ray diffraction spectra of the specimens heated after milling for a longer time (30 hours) showed the spectrum of the as-milled powders indicated ZnFe_2O_4 and a small amount of unreacted Fe_2O_3 without a trace of ZnO. Heating at 500°C , which is lower by 100°C than that milled for 10 hours, enhanced the crystal growth (grain growth) of ZnFe_2O_4 and Fe_2O_3 . Heating at a higher temperature (600°C), which is lower by 100°C than that milled for 10 hours, decreased the amount of Fe_2O_3 and accelerated the crystal growth of ZnFe_2O_4 . Thus the prolonged milling time lowered the heating temperature necessary to form the highly crystalline ZnFe_2O_4 . The lattice constant (0.8440 nm) after heated at 600°C was approximately equal to the as-milled condition (0.8438 nm) and the reported value (0.8441 nm).

The diffraction peaks of ZnFe_2O_4 heated at 600°C after milling for 10 hours were sharper than those after milling for 30 hours even heated at the same temperature. The former should be understood that relatively large ZnFe_2O_4 powders were formed at 600°C via solid-state reaction between ZnO and Fe_2O_3 powders. The latter should

be attributed to insufficient grain growth of mechanochemically-synthesized ZnFe_2O_4 powders.

3. Summary

The mechanochemical synthesis of ZnFe_2O_4 (zinc ferrite) was attempted from the powder mixture of Fe_2O_3 and ZnO. The following results were obtained:

(1) Milling for 30 hours: Nanocrystalline ZnFe_2O_4 powders were mechanochemically synthesized without heating after milling. The formation of crystalline ZnFe_2O_4 was confirmed by twelve broad peaks in the X-ray diffraction spectrum. A small amount of unreacted Fe_2O_3 coexisted. The crystallite size determined by the peak width of the X-ray diffraction was 26.3 nm.

(2) Milling for 10 and 20 hours: The mechanochemical processing lowered the crystallinity of the starting materials (Fe_2O_3 and ZnO). Clear evidence of the ZnFe_2O_4 formation was absent.

(3) The heating after milling: Heating after milling enhanced the formation and crystal growth of ZnFe_2O_4 . The crystal growth of the unreacted starting materials was also accelerated by heating. Heating at higher temperatures decreased the amount of the unreacted starting materials.

4. References

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