Preparation of Co$_2$Z-Ferrite Fine Powder by Gel-Combustion
Shinichi KIKAWA, Daiki KUBO and Takashi TAKEDA
Faculty and Graduate School of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo 060–8628, Japan

Gel-combustion synthesis was used to synthesize a fine powder of Co$_2$Z-ferrite (Ba$_3$Co$_5$Fe$_2$O$_{19}$). Either citric acid or glycine was added, as a peptizer, to the mixed aqueous solution of Ba(NO$_3$)$_2$, Co(NO$_3$)$_2$·6H$_2$O and Fe(acac)$_3$. The product gel was ignited at 150°C and then fired again in a temperature range of between 500°C and 1200°C. The ignited product was a mixture of CoFe$_2$O$_4$ and Ba(NO$_3$)$_2$ when citric acid was used as a gelling agent. Its fired product was a mixture of Co$_2$Z-, CoY-, BaM-ferrites and BaFe$_2$O$_4$. A higher temperature was attained during the ignition of the glycine gel rather than the citric acid gel. The ignited product of the glycine gel was a mixture of CoFe$_2$O$_4$ and BaFe$_2$O$_4$. Pure Co$_2$Z-ferrite fine powder was subsequently obtained by firing this ignited product at 1000°C. This temperature is much lower than the firing temperature of 1300°C required by the solid state reaction. Its crystallite and average particle sizes were 42–48 nm and 180–200 nm, respectively. Saturation magnetization was 45–47 emu/g and coercivity was 0.59–0.90 kOe.

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Introduction

In order to get higher speed and larger capacity in signal processing, the frequency of various kinds of digital equipment is shifting to a higher region, namely MHz to GHz. Noise generated from this equipment is also reaching to this frequency region. It may interfere with the operation of computers, industrial machinery, medical equipment and so on. A noise wave absorber is required to remove this electro magnetic interference. Magnetic ferrites with high magnetic permeability have been used as radio wave absorbers. However, the ferrites commercially available have a low efficiency of wave absorption in the GHz region.

The crystal structure of magnetoplumbite (M–) type ferrite BaFe$_2$O$_4$ (hereafter called as BaM) is an alternate stacking of spinel and rock salt-blocks. Several kinds of derivatives are known for this ferrite with slightly different layer stackings and chemical compositions; W’(BaCo$_3$Fe$_9$O$_{27}$); Z(BaCo$_2$Fe$_2$O$_{19}$); Y(BaCoFe$_2$O$_{11}$) [hereafter called such as CoW, CoZ and CoY, respectively]. Co$_2$Z-ferrite has a large magnetic permeability and hence is able to absorb high frequency waves. It is difficult to obtain a phase pure sample of this compound because of the existence of closely related derivatives. The effective firing temperatures of these have been reported, respectively, to be 800°C for BaM, 1100°C for CoY, and 1300°C for Co$_2$Z-ferrites.

Grain growth occurs in high temperature firing. Therefore, the firing temperature should be as low as possible to obtain fine powder of any multinary oxides. Preparation from solution allows the starting materials to mix homogeneously with each other. Lower firing temperatures, which can therefore be used, may lead to a formation of new metastable compounds. We have been studying on the preparation of multinary oxides from aqueous solution using either citric acid or glycine as a gelling agent. Combustion reactions occur when metal nitrates are used as starting materials. Fine powders, 20 to 100 nm in diameter, of (ZnO)$_2$In$_2$O$_3$ transparent conductor, BaM-ferrite, and Y$_2$O$_3$·Eu phosphor have been synthesized. Their fine powders are required to obtain sintered bodies and, after first being dispersed in resin or paint, thin films.

The citrate precursor method had been applied to obtain the Co$_2$Z-ferrite in a relatively low temperature firing of between 1150°C and 1200°C. The precursor was prepared by adding an ammonia solution to a mixed aqueous solution of iron nitrate, cobalt nitrate, barium nitrate and citric acid. The gel self-propagation method had also been applied for its preparation. A stoichiometric mixture of metal nitrates was dissolved in distilled water with citric acid. The solution was neutralized with ammonia and evaporated until a viscous gel was formed. Its ignited product was a mixture of CoFe$_2$O$_4$ and CoY$_2$O$_3$. The majority phase was Co$_2$Z-ferrite with a small amount of CoY-ferrite impurity when the product was fired at 1200°C. The use of iron acetylacetonato or iron ethylene diamine as the iron source was very effective to obtain BaM-ferrite in a low temperature firing of the ignited products at 800°C. These iron complexes reduce the hydrolysis of the ferric ion to form its hydroxide.

In the present investigation, a similar gel-combustion reaction was used to obtain fine crystals of, the high frequency wave absorber, Co$_2$Z-ferrite.

Experimental

0.02 mol of citric acid was dissolved in 50 dm$^3$ distilled water. A stoichiometric mixture of iron acetylacetonato (0.01 mol), cobalt nitrate hexa hydrate (0.00083 mol) and barium nitrate (0.00125 mol) was added to the citric acid aqueous solution. It was condensed to a gel and ignited in a furnace at 200°C for 1 hour. The ignited product was pulverized, pelletized and again heated to either 500°C, 800°C, 1000°C, or 1200°C, at a rate of 10°C/min and kept at the respective temperature for 1 hour. In further reaction, 0.666 g, 1.332 g or 1.998 g of ammonium nitrate was also added to the mixed aqueous solution as an oxidizer. This series of experiments was repeated but with citric acid substituted with glycine. The amount of glycine used was either equal to, double, triple or five times the total molar amount of metal salts used.

Results and discussion

The ignited product of the gel prepared from the citric acid aqueous solution was X-ray amorphous with a small amount of CoFe$_2$O$_4$ and Ba(NO$_3$)$_2$, as shown in Fig. 1(a). The amount of CoFe$_2$O$_4$ increased and Ba(NO$_3$)$_2$ disappeared following its firing at 500°C. A small amount of BaM-ferrite also appeared. A mixture of CoY-, BaM- and BaFe$_2$O$_4$ ferrites was obtained by a firing at 800°C. Co$_2$Z-ferrite appeared as a mixture with these ferrites from the firing at 1000°C, as
represented in Fig. 2(a). Pure Co$_2$Z-ferrite was obtained at 1200°C. This temperature is 100°C lower than the firing temperature required to obtain this compound in solid state reaction. The formation of CoFe$_2$O$_4$ leads to an inhomogeneous mixing during the ignition because the attained temperature was low. The temperature was also too low to decompose Ba(NO$_3$)$_2$, which decomposes at its melting point of 592°C.$^{11}$ Various amounts of ammonium nitrate were added to the mixed aqueous solution as an oxidizer. The ignited products were mixtures of CoFe$_2$O$_4$ and Ba(NO$_3$)$_2$ as shown in Fig. 1 (b). There was not much change with the amount of ammonium nitrate. Only the amount of CoFe$_2$O$_4$ in the post fired product at 500°C differed with the amount of ammonium nitrate in the starting material. Its concentration, in mixtures with BaM-ferrite and BaFe$_2$O$_4$ increased slightly with the nitrate amount. There was no difference with the nitrate amount in the fired products above 800°C. All the fired products at 1000°C were mixtures of CoY- and BaM-ferrites and BaFe$_2$O$_4$ as shown in Fig. 2(b). Co$_2$Z-ferrite did not appear from the firing at 1000°C.

Glycine was then substituted for citric acid. The former generates much more exothermic heat in very short duration in its combustion with nitrate than the latter. The amount of glycine in the starting gel affected the ignited products. They were a mixture of CoFe$_2$O$_4$, BaFe$_2$O$_4$ and BaCO$_3$ when the amount of glycine was more than twice that of total metal salts as shown in Fig. 1(c). Only a small amount of BaFe$_2$O$_4$ and BaCO$_3$ was detected on the ignited product of the equimolar mixture because a relatively high temperature was attained during the ignition. Barium nitrate, which was observed in the ignited products of the gel formed with citric acid, was not present. However, there was no difference among the post fired products of the ignited samples with various amount of glycine. The fired products at 500°C were mixtures of BaM-ferrite, CoFe$_2$O$_4$, BaFe$_2$O$_4$ and Fe$_3$O$_4$. The fired products at 800°C were mixtures of Co$_2$Z-, CoY-, BaM- and BaFe$_2$O$_4$ ferrites. Pure Co$_2$Z-ferrite was obtained by firing at 1000°C, as shown in Fig. 2(c). Very reactive conditions were achieved during the glycine ignition including the generation of large amount of exothermic heat that was sufficient to decompose barium nitrate.

Magnetic property measurements were carried out on the Co$_2$Z-ferrites obtained in this investigation. The product from the citric acid route had a saturation magnetization of 45.4 emu/g and a magnetic coercivity of 0.25 Oe. The products from the glycine route showed similar values each other, independent of the amount of glycine used. Saturation magnetization values were in a range of 45.0 to 47.1 emu/g and magnetic coercivities were in a range of 0.59 to 0.90 Oe. The observed saturation magnetization values are about 90% of its theoretical value. The coercivity changed with the crystallite size. The product from citric acid, which was fired at 1200°C, with crystallite size of 87 nm showed a smaller coercivity than the products from glycine fired at 1000°C with crystallite size of 42–48 nm. During the firing the hexagonal platelets of Co$_2$Z-ferrites sintered together. Their dispersion would be required for subsequent application.

In conclusion, Co$_2$Z-ferrite with crystallite size of less than 50 nm was obtained by firing a precursor prepared through the combustion of a glycine-nitrate gel. The firing temperature was 1000°C, which is much lower than the 1300°C required in the solid state reaction. It was also much lower than the previous preparations using citrate.$^{9,10}$ In the powder XRD pattern of the ignited product there were several low angle (2θ < 20°) diffraction peaks that could not be assigned to any compounds. They might be assigned to a Co$_2$Z-ferrite precursor.

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References