Journal of the European Ceramic Society 21 (2001) 149–153

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Microstructure characterization and properties of chemically synthesized Co_2Z hexaferrite

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Received 8 March 2000; received in revised form 1 June 2000; accepted 11 June 2000

Abstract

Powders having stoichiometric composition of Co_2Z ($Ba_3Co_2Fe_{24}O_{41}$) were prepared by gel self-propagating method and processed at different temperatures to study phase evolution process. Unlike other ferrites, Co_2Z hexaferrite was not synthesized directly by gel self-propagating technique, but was formed gradually from some intermediate phases due to its complicated crystalline structure. After Z-type phase formed at relatively low temperatures of 1200°C, the powders were annealed at temperatures lower than 1200°C. It was found that, once formed, this phase was quite stable. At the same time, the morphology and distribution of hexagonal particles was improved, and ceramic samples thus achieved from the relative powders presented excellent ultrahigh frequency magnetic properties. © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Co_2Z hexaferrite; Ferrites; Magnetic properties; Phase evolution; Self-propagating synthesis

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1. Introduction

Recently, with the rapid development of information and communication technology, multi-layer chip inductors (MLCI) applied in the hyper frequency regions have been rapidly developed as surface mounting devices (SMD).[1,2] MLCI is produced by coating ferrite and internal electrode pastes alternately and then co-firing. Since the multi-layer technology becomes mature, the properties of MLCI largely depend on the properties of the low temperature sintered ferrites. However, the low-fired ferrite has been a key problem of MLCI production. Much work has focussed on NiZn system ferrite[3–5] applied in frequency region of less than 300 MHz. As to hyper frequency regions (300–1000 MHz), there has been no ideal material so far. As an attempt, Co_2Z hexaferrite is expected to fill in this gap.

Crystallographically, Co_2Z ($Ba_3Co_2Fe_{24}O_{41}$) comprises basic units of hexagonal barium and cubic spinel ferrite in certain combination like other hexaferrites, such as BaM, Co_2Y and Co_2W.[6,7] Due to the sharing of many peak positions, the signals of small amounts of these compounds are extremely difficult to distinguish from the major phases in the very convoluted and similar XRD spectra of the hexagonal ferrite.[8] Studies on phase evolution of Co_2Z become extremely important.

However, its special plain-hexagonal structure is very complicated and only formed at rather high temperature[6,7] (1200–1400°C). Furthermore, the purity and stability of Z-type phase during sintering at low temperature is also a key problem.

In order to meet the increasingly demand for hyper-frequency MLCI, developing Co_2Z system ferrites become increasingly urgent. Various chemical methods have been proposed and proved to be effective to reduce the sintering temperature and get good properties for hexaferrites, such as BaM ($BaFe_{12}O_{19}$), Co_2Y ($Ba_2Co_2Fe_{12}O_{22}$) and Co_2W ($BaCo_2Fe_{16}O_{27}$).[9–11] But for Co_2Z, there has no been an effective way to prepare Co_2Z at low temperature. The authors developed a novel and economical method, namely of gel self-propating technique, to prepare ultra-fine and highly reactive powders. Consequently, the powders were used to synthesize Co_2Z ferrite at relatively low temperatures. Furthermore, a few issues involved in phase evolution, characterization and stability of Co_2Z hexaferrite were mainly discussed in this paper.

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0955-2219/01/$ - see front matter
PII: S0955-2219(00)00174-6

2. Experimental

2.1. Powder preparation

All reagents were chosen AR grades.

Stoichiometric amount of the starting materials including barium nitrate, cobalt nitrate, iron nitrate and citric acid monohydrate in proper molar ratio were dissolved in distilled water, respectively. Then the former salt solution was dissolved in the citric acid solution: a few minutes of moderate heating and actuating were necessary. When the blended solution cooled to room temperature, it was titrated quantitatively by concentrated ammonia solution until the solution was neutral or slightly alkaline (pH = 7–8). A few minutes later, a kind of completely homogeneous solution was achieved. The solution was slowly evaporated until a highly viscous gel was formed, which solidified without any segregation after being heated at 130–160°C. Introducing a little amount of ethanol ignited the organic matter. Later, the ignited gel slowly self-propagated for a few hours. The residual contained stoichiometric cation amounts and could be used to synthesize Co_2Z ferrites without calcing the obtained powders.

2.2. Thermal treatment of powders

Using the above-prepared powders were used to study the phase evolution processes, a series of powders were heat treated in air successively at temperatures from self-propagating to 1200°C, 4 h for each treatment. Specially, the powder treated at 1200°C/4 h was heat treated once again, and then was annealed in air at 1100 and 1000°C/4 h, respectively, with intermediate grindings to study the stability of Z-type hexagonal phase.

2.3. Sample preparation

The resulting powders were pressed in a stainless-steel die under a pressure of about 40 000 N/m^2 with 5% wt PVA as lubricant. The pressed pellets (10 mm outside diameter, 0.5–1.5 mm thickness) and toroidal samples (20 mm outside diameter, 10 mm inside diameter, about 3 mm thickness) were sintered at 1230°C/4 h in air and cooled in the furnace. After each sintering experiment, the weights and dimensions of the toroidal samples were calculated at room temperature to determine bulk densities.

2.4. Characterization

The phase evolution of the calcined powders was analyzed using X-ray diffractometry (XRD). Data collection was carried out using FeK_α radiation at 35 KV and 25 mA in the range of $2\theta = 35$–$55°$ with a scanning speed of 2°/min.

Transmission electron micrograph (TEM) was carried out to study grain morphology evolution, distribution and average grain size.

2.5. Property measurements

The DC resistivity of samples at room temperature was measured by HP4140B using silver-paste contacts. HP4191A impedance analyzer from 1 to 1000 MHz measured the frequency properties of ceramic samples.

The change of saturation magnetization (Ms) for Curie-temprature and magnetic hysterises curves were measured at LDJ9600 VSM (vibration sample magnetometer).

3. Results and discussion

3.1. Phase evolution and characterization

The XRD patterns of gel and powders treated between 700 and 1200°C are shown in Fig. 1. As to the self-propagating powder, a few kinds of single compounds can be identified as $BaFe_2O_4$, $CoFe_2O_4$ (spinel ferrite), α-Fe_2O_3 and this situation remained up to 900°C or so until BaM phase formed. However, at 1100°C the peaks of most BaM have been either replaced or hidden by the appearance of small amount of Co_2Y. The co-existence of these two phases of BaM and Co_2Y continued up to about 1180°C. By 1180°C, the BaM phase has disappeared due to the formation of $Ba_2Co_2Fe_{12}O_{22}$ (Co_2Y) ferrite, as seen in Fig. 1b. When the sintering temperature was raised to 1180, Co_2Z phase began to form. At 1200°C, besides the presence of small amount of Co_2Y, the majority phase was Co_2Z. One important phenomenon was that Co_2Z seemed not to be formed directly by simple oxides, but gradually transited from simple oxide or spinels to a mixture of BaM and Co_2Y, finally to Co_2Z. At present, there has been no relatively determined report on the crystallization process of Co_2Z without undergoing the co-existence of BaM and Co_2Y ferrites.

Fig. 2 illustrates the present phases in the sample powders, subjected to different heat treatment. The samples with the best Z-type phase characteristics were observed at 1200°C/4 h. Figs. 3 and 4 show the variation of saturation magnetization (Ms) for Curie-temperature and magnetic hysteresis curves of powders treated at different temperatures. All these indicate the transition characteristics of Z-type hexaferrite formation by reaction between some intermediate phases, such as spinel, $BaFe_2O_4$, BaM and Co_2Y.

In general, the intermediate phases S, $BaFe_2O_4$, M and Y are evident. The desired phase Co_2Z is only formed if the temperature arrives at 1200°C or higher. The optimal treatment for the Co_2Z phase formation is a repeated heat treatment at 1200°C/4 h.

3.2. Stability of Co_2Z hexaferrite

Fig. 5 shows that crystallographically more pure Z-type hexaferrite formed when the powder (calcined at 1200°C/4 h) was repeatedly sintered at 1200°C/4 h with intermediate grindings. When annealed at 1000 and 1100°C/4 h, respectively, the formed Z-type reserved stable and no decomposition took place. Almost no any identified crystalline phases, but Z-type hexagonal phase was found from the background in Fig. 5.

Powders annealed at 1200, 1100 and 1000°C/4 h appeared to consist of sole Co_2Z. The results reveal that once the Co_2Z phase formed, it is stable, does not decompose and not produces some intermediate compounds yet. But it is thought unlikely that 100% pure Co_2Z had been formed, as the system is so complex and there are usually traces of Co_2Y from the formation process.[12,13]

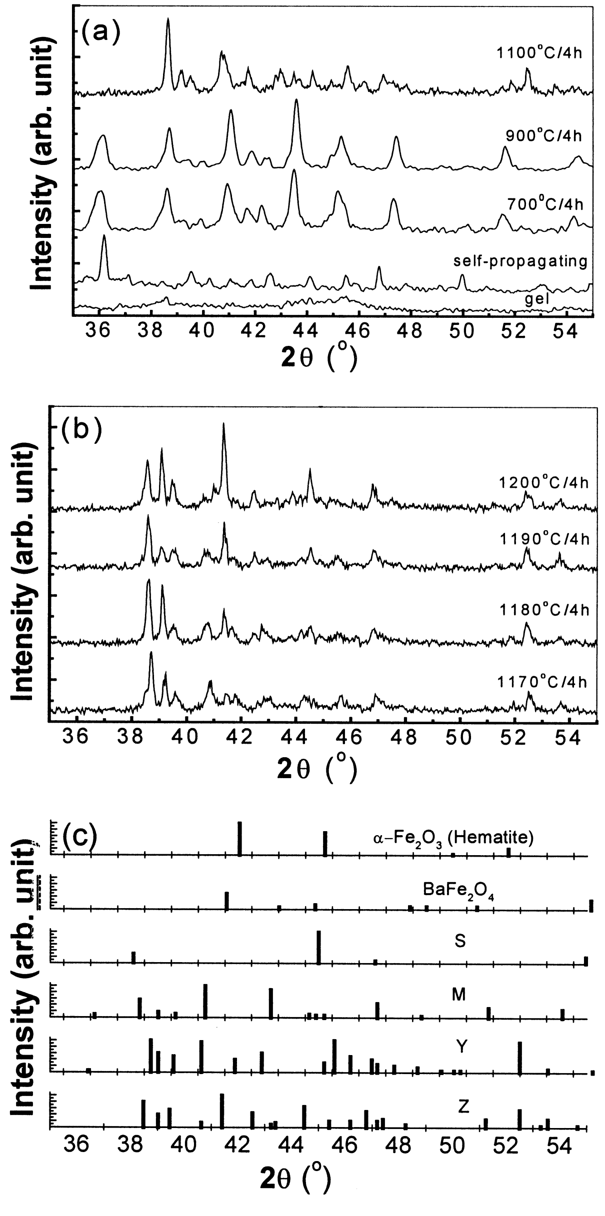


Fig. 1. XRD patterns of powders treated at different temperatures: (a) gel, 700, 900 and 1100°C/4 h; (b) 1170, 1180, 1190 and 1200°C/4 h; (c) the standard XRD spectra of different compounds (S, spinel; M, $BaFe_{12}O_{19}$; Y, $Ba_2Co_2Fe_{12}O_{22}$; Z, $Ba_3Co_2Fe_{24}O_{41}$).

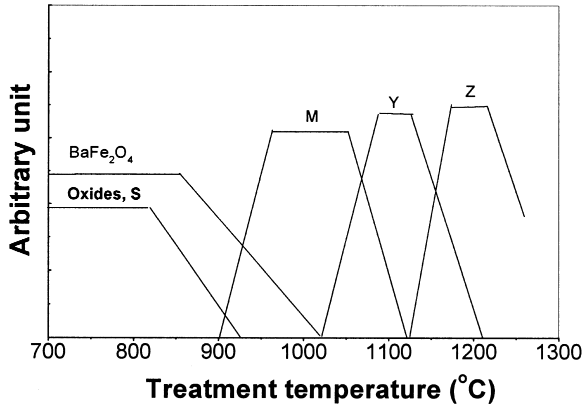


Fig. 2. The evolution of different phases in the sample powders subjected to different heat treatment temperature.

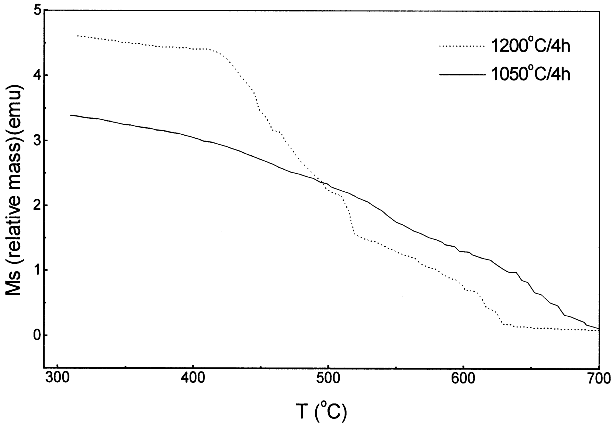


Fig. 3. The variation of saturation magnetization for Curie-temperature.

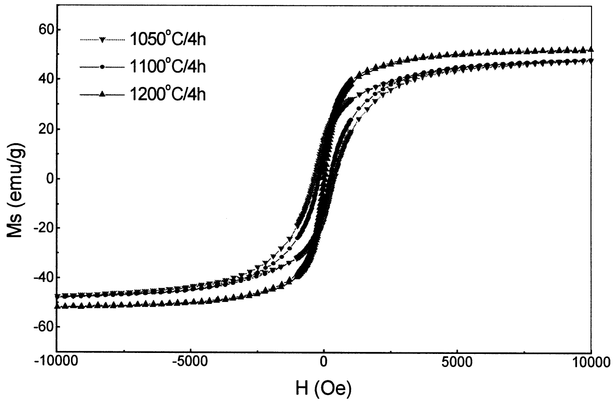


Fig. 4. The magnetic hysteresis curves of powders treated at 1050°C/4 h and 1200°C/4 h.

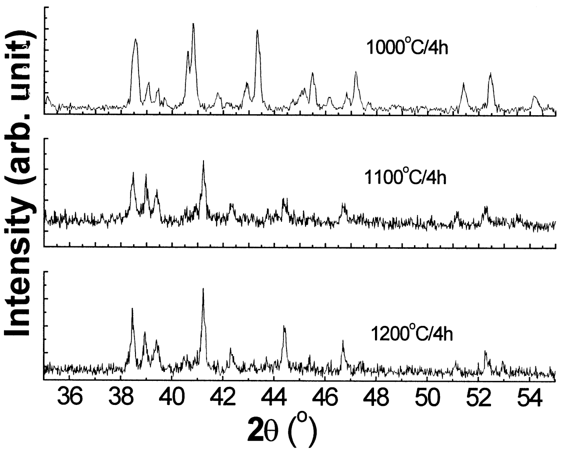


Fig. 5. XRD patterns of Co_2Z powders annealed at 1200, 1100 and 1000°C/4 h, respectively.

3.3. *Microstructure characterization of powder particle*

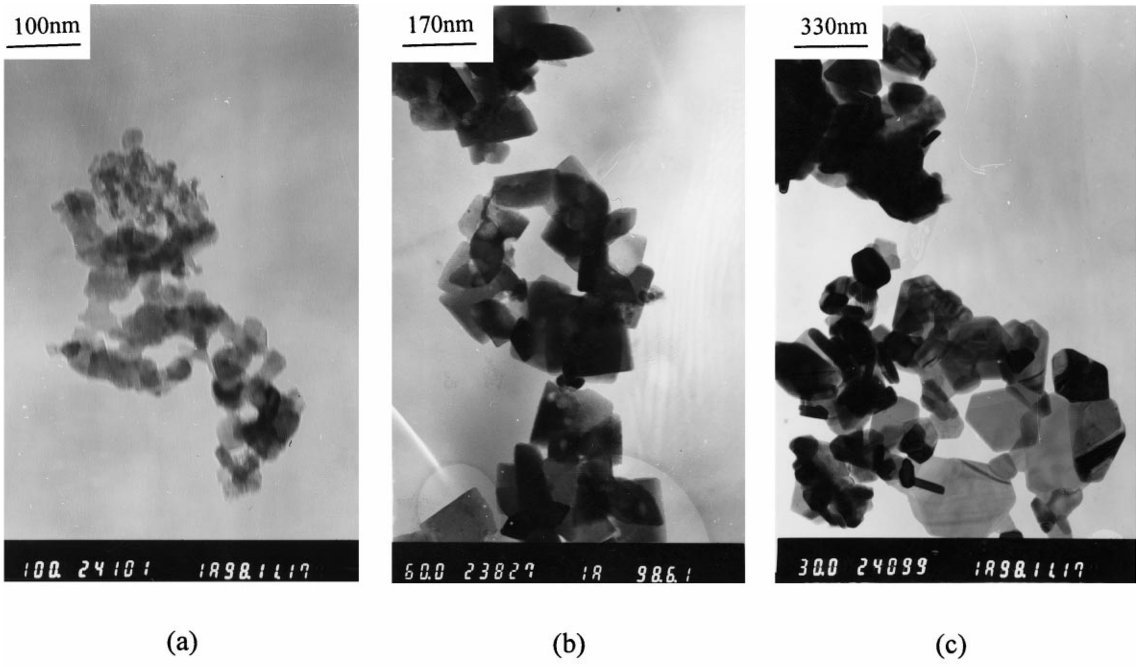
As seen from Fig. 6, the morphology of the self-propagated powder treated under 1200°C was almost agglomerate due to magnetism. The average crystallite sizes from X-ray line broadening are found to be in the range of 40–100 nm, seen in Fig. 6a and b. Beyond 900°C, platelet grains of BaM hexaferrite possibly appeared (Fig. 6b). With the rise of treating temperatures, the number of typical platelet grains (mean size: about 200 nm) that belong to Co_2Z increase more and more (Fig. 6c) and are relatively well disagglomerate.

It can be observed that a rapid increase in particle size and a great change in crystalline structure had already been observed above 900°C/4 h from not only TEM observation but also the identification of X-ray. The microstructure (sintering temperature bellow 1100°C) consists of what appeared to be a mixture of small cubic spinel and large hexagonal plates. At higher temperature, there possibly co-exist M and Y grains. Finally, at about 1200°C, larger and more homogeneous hexagonal platelet particles appeared. Accompanying the creation of hexagonal plates was a rapid and exaggerated form of crystal growth, as observed from Fig. 6c. It is understood that the rate of crystallite growth in the plane perpendicular to the *c*-axis is much higher than that in the direction of *c*-axis and implies that grain growth mainly proceeds in two dimensional manner. As to the mechanisms involved in mass transporting and crystalline structure change during treatment process is now under investigation.

When the powders synthesized at 1200°C were annealed, powder particle size increased rapidly and no obvious change in microstructure distribution occurred, as seen in Fig. 7a and b. With the increase of annealing temperature, larger hexagonal platelet particles took on more homogeneous distribution. At the same time, the number of particles with regular hexagonal platelet shape became more and more.

3.4. *Properties of ceramic samples*

Ceramic samples thus achieved from self-propagating powder presented better magnetic properties than those made from solid-state reaction method. The initial permeability and quality factor are shown in Fig. 8. As seen



(a) (b) (c)

Fig. 6. TEM micrographs of powders treated at (a) self-propogating, no heat treatment; (b) 900°C/4 h; (c) 1200°C/4 h.

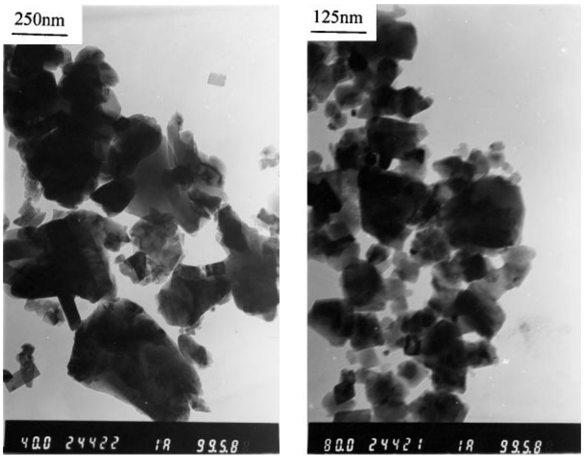


Fig. 7. TEM micrographs of powders annealed at (a) 1000°C/4 h; (b) 1100°C/4 h.

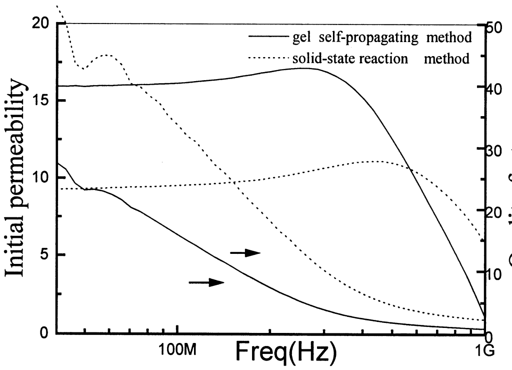


Fig. 8. Frequency dependence of magnetic properties for $Ba_3Co_2Fe_{24}O_{41}$ ferrite samples.

in Fig. 8, there was an obvious change as a function of the applied frequency, the initial permeability and quality factor of samples increased greatly, but the applying frequency revealed a little decreas. However, the sintering density (increase much more due to the grain growth resulting from the recrystallization at sintering tempratures) and DC resistivity arrived at 5.08 g/cm^3 and $2.89\times10^7\Omega$ cm, respectively, much more improved than those made from solid-state reaction method.

3.5. Discussion

Due to the preparation of ultra-fine and highly reactive particles, Co_2Z could be synthesized at 1200°C, about 150°C lower than that of conventional ceramic method. On account of the complexity of the phase structure of Co_2Z, the synthesizing temperature of this ferrite was impossible to further decrease like other ferrites. Nevertheless, the Z-type phase is stable and if additives or modifying components are introduced, Co_2Z ferrite may be sintered at temperature lower than 1000°C and meet requirements for low temperature sintering of MLCI like NiZnCu ferrites. The relative experimental results of ceramic samples thus achieved from the powders will be reported carefully in the forthcoming papers.

4. Conclusions

1. Unlike spinel ferrites, Co_2Z hexaferrite with planar hexagonal structure could not be synthesized directly by gel self-propagating method, but could be formed gradually by reaction between some intermediate phases, such as spinel, $BaFe_2O_4$, BaM and Co_2Y.
2. Co_2Z hexaferrite can steadily exist and take on more homogeneous distribution in typical hexagonal particle when subjected to different annealing treatment, although the grain size increased obviously. This makes it hopeful to be adopted in fabricating MLCI applied in hyper-frequency of 300–1000 MHz.
3. Ceramic samples sintered from the powder synthsized at 1200°C exhibit excellent frequency properties and sintering properties.

Acknowledgements

The authors were indebted to the financial support from the High Technology and Development Project of PR China (Grant: 715-Z33-006-0050), National Natural Science Foundation of PR China (Grant: 59995523) and the Ceramic Technology Center, Motorola, Inc., USA.

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