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Novel method for low temperature sintering of barium hexaferrite with magnetic easy-axis alignment

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Abstract

Most applications of hexaferrites require sintered products, but sintering of hexaferrites at high temperatures degrades their magnetic properties and cannot be used as low-temperature co-fired ceramics. Additionally, due to the magnetic uniaxial anisotropy of hexaferrites, excellent magnetic properties are attained when the particles are aligned along the magnetic easy-axis. In order to overcome these problems, herein we suggest a new method to decrease the sintering temperature and improve the simultaneous alignment of magnetic particles along the easy-axis. NaCl-barium hexaferrite particles and NaCl-amorphous particles were sintered using the spark plasma sintering process. Using this method, a sintered body with a relative density of 92.5% and 70.2% alignment was fabricated at 800 °C for 5 min. In this method, the added NaCl played a significant role in facilitating the low temperature sintering and particle alignment. This method was found to be effective for low temperature sintering and nano-scale particle alignment.

Keywords: Hexaferrite; Low sintering temperature; Easy-axis magnetic alignment; Salt assisted ultrasonic spray pyrolysis; Spark plasma sintering

1. Introduction

Hexagonal ferrites, also called hexaferrites, are essential and useful magnetic materials for various industrial applications such as magnetic recording, data storage devices, microwave devices, and permanent magnets. The most well-known hexaferrite types are the M-type, Y-type, Z-type, W-type, X-type, and U-type.[1,2] Among them, M-type hexagonal ferrites have been studied extensively due to their excellent properties such as high electrical resistivity, high Curie temperature, magnetic uniaxial anisotropy, chemical stability, and large coercivity.[1–5] The M-type hexagonal ferrites have a chemical formula of $MeFe_{12}O_{19}$ (Me = Ba, Sr, Pb) with a magnetoplumbite structure that has strong magnetic properties with high magnetic uniaxial anisotropy along the c-axis.[6,7]

In most cases, the practical applications of hexagonal ferrites require a sintering process. However, sintering of M-type hexaferrites is conventionally performed at high temperatures ranging from 1100 °C to 1350 °C. These high temperatures increase the necking and grain growth of particles, and degrade the magnetic properties.[1,8,9] Meanwhile, sintering at higher temperatures impedes the electrical conduction of low-temperature co-fired ceramics (LTCCs) with Ag or Au metals because of their low melting temperature.[9–11]

Therefore numerous studies have been performed to determine how to lower the sintering temperature. The most common method is through addition of glass or oxides such as Bi_2O_3, B_2O_3, and SiO_2 that have a low melting point. This method is successful and convenient, but the use of additives leads to degradation of the magnetic properties.[10–15] Some researchers used spark plasma sintering (SPS) in order to lower the sintering temperature because it is the fastest sintering technique.[16,17] The SPS process was shown to be effective, but did not sufficiently prevent grain growth. The other studies were based on partial substitution of bivalent metals (Fe) with Cu and/or

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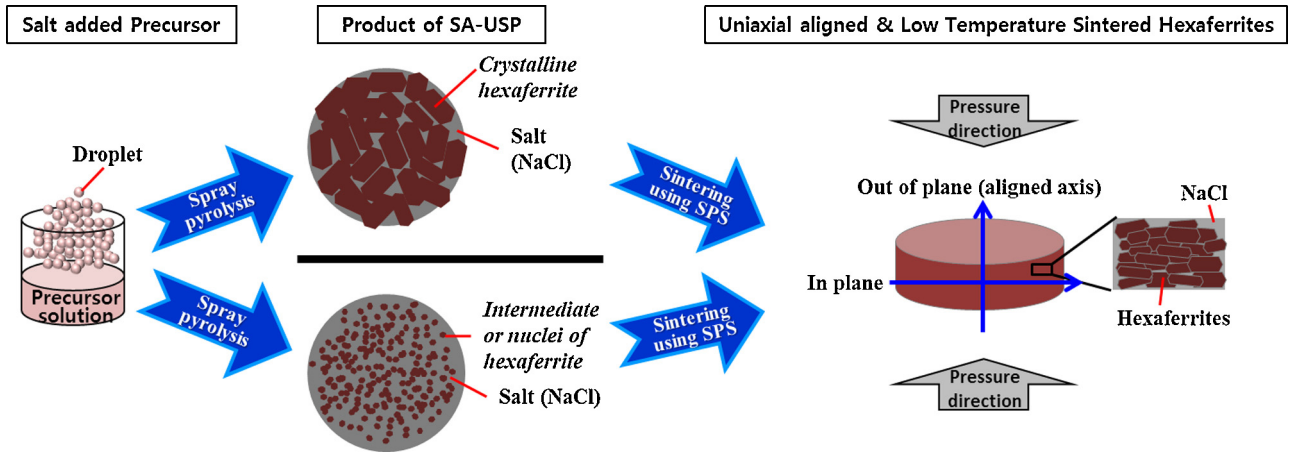

Fig. 1. Schematic illustration of a novel process for low temperature sintering and particle alignment.

on additives for a reactive liquid-phase for Z-, Y-, and M-type hexaferrites.[9,18,19] However, field of application for this substitution method is limited due to alterations in the magnetic properties.

Furthermore, in order to exploit the strong magnetic properties conferred by magnetic uniaxial anisotropy, the M-type hexaferrite particles must be aligned along the c-axis of the crystalline direction, which corresponds to a magnetically easy-axis, and perpendicular to the plane in a hexagonal platelet shape. Wet pressing is the conventional method for magnetic alignment of micron-scale M-type hexaferrites,[20] and some other methods have been investigated, including a screen-printing process with a magnetic field,[21] a magnetic field with polymer network-assisted-alignment process,[22] and an electrophoretic deposition and magnetic field method.[23] Apart from wet pressing, these processes were used primarily for film-type hexaferrites, but not for bulk magnetic ceramics.

In this study, we suggest a novel method for simultaneously lowering the sintering temperature and inducing magnetic alignment of hexaferrites. To achieve these aims, salt-assisted ultrasonic spray pyrolysis (SA-USP) was adopted for synthesizing the salt added hexaferrite particles, and SPS was used as the subsequent sintering process. The SA-USP is known to achieve non-agglomerated nanoparticles[24,25] as the added salt acts as a separating material to prevent agglomeration. The nanoparticles were obtained after washing the product from the SA-USP with water in order to remove the added salt. The SPS process was employed for instant sintering to prevent grain growth and necking of the particles. In our study, the added salt was not removed, because it played a significant role as an additive for achieving a low sintering temperature and served as a medium for the movement of particles during the SPS process. Once the reaction temperature of the SPS process reached the melting temperature of the added salt, alignment of hexagonal platelet particles with their plane direction was expected perpendicular to the pressing direction due to flux of the molten salt and uniaxial pressure.

Herein we investigated the influence of added salts in terms of lowering the sintering temperature and uniaxial arrangement of barium hexaferrite (BaM) nanoparticles. The particles prepared by SA-USP were classified as crystalline and amorphous types and their influence on the final product after the SPS process was determined. The density and magnetic properties of the sintered body were also evaluated.

2. Experiments

Salts included BaM were prepared using SA-USP according to a process described elsewhere.[24] Two different precursor solutions were prepared with added salt concentrations of 3 wt.% and 5 wt.%, respectively. The precursor was prepared by dissolving 60 mmol of iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$, 99.9%, Kojundo, Japan) and 5 mmol of barium nitrate ($Ba(NO_3)_2$, 99%, Kojundo, Japan) in 200 ml of distilled water. Subsequently 2.94 mmol or 5 mmol of sodium chloride (NaCl, 99%, Samchun, South Korea) was dissolved in the precursor solution, depending on the desired final concentration. Each solution was atomized in a furnace and the obtained salt included BaM. To obtain crystalline and amorphous particles, the temperatures of a two-stage furnace were controlled at 800/400 °C (inlet/outlet) and 750/250 °C, respectively. The atomized droplets were transferred to a tubular furnace with O_2 as a carrier gas at a flow rate of 1 L/min. The reaction time (passing the droplet through the heating stage) was only about 20 s. The crystalline and amorphous particles synthesized using SA-USP were dubbed XC-BaM and XA-BaM, respectively (where X is the content of added salt). The prepared particles were sintered to a disk shape using the SPS process. The sintering temperatures were 700 and 800 °C, respectively, and a pressure of 60 MPa was applied over 5 min to the particles set in a carbon mold with a 7 mm internal diameter and a thickness of 3–3.5 mm. The sintered bodies were dubbed XC-BaM-Y and XA-BaM-Y, respectively (where Y is the sintering temperature). A schematic illustration of the process is shown in Fig. 1.

The composition and phase of the synthesized particles and sintered body were determined using an X-ray diffractometer (XRD, D/MAX-2500/PC, Rigaku) with Cu Kα radiation operating at 40 kV and 100 mA. Sintered bodies were analyzed to the out-of-plane direction of the disk. Densities of the sintered bodies were measured by the Archimedes method. The relative