

Magnetic Properties of Nanosized Ba₂Mg₂Fe₁₂O₂₂ Powders Obtained by Auto-combustion

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Abstract We studied the magnetic properties of nanosized Ba₂Mg₂Fe₁₂O₂₂ powder obtained by citrate auto-combustion synthesis. The powder consists of agglomerates with mean crystallite size of 100 nm. The magnetic properties of the powder were investigated at 4.2 K and at room temperature. The values measured of the magnetization M at a magnetic field of 60 kOe are 22.78 emu/g and 30.47 emu/g at room temperature and 4.2 K, respectively. The magnetic phase transition at 183 K is related to the ferromagnetic-to-spiral spin order and is a precondition for this material's exhibiting multiferroic properties.

Keywords: Y-type hexaferrite · Ba₂Mg₂Fe₁₂O₂₂ · Auto-combustion method · Magnetic properties

1 Introduction

Multiferroic materials in which long-range magnetic and ferroelectric orders coexist have recently been of great interest in the fields of both basic and applied sciences [1, 2]. In particular, those exhibiting a ferroelectric transition inducing a certain kind of magnetic ordering are of much interest, because in such systems the effects of coupling between magnetism and electric polarization are expected to give rise to new physical phenomena.

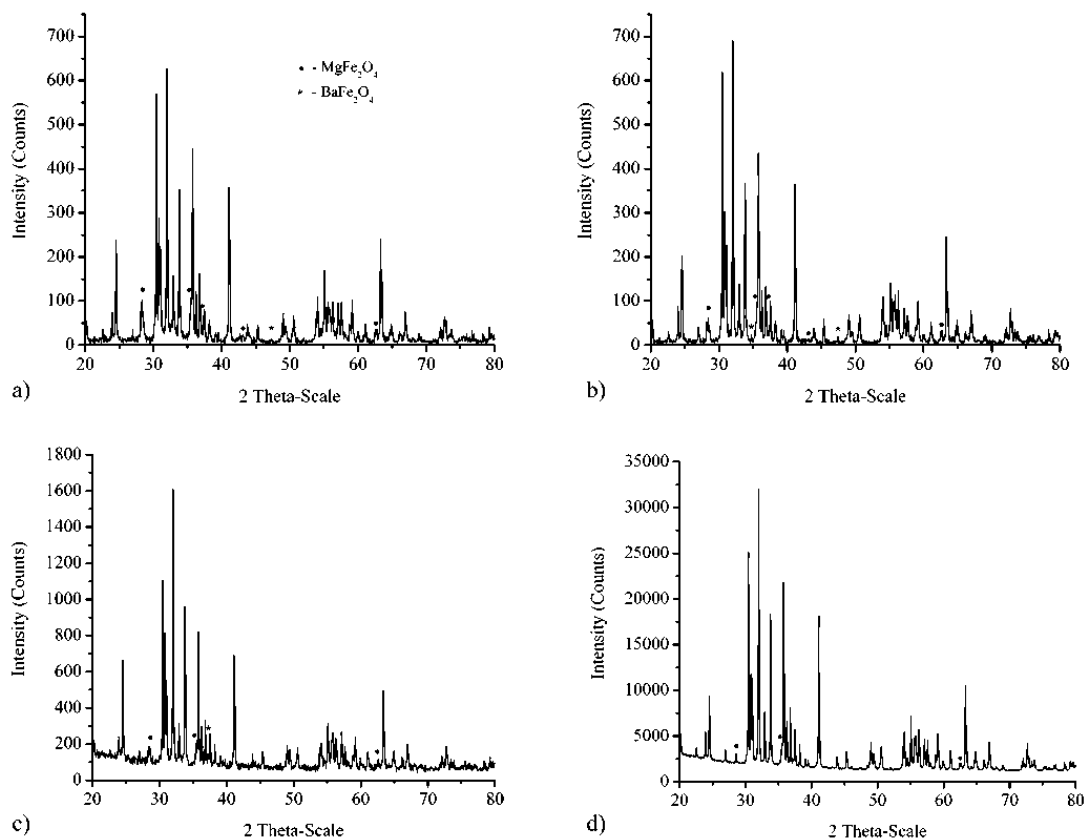
The Y-type hexagonal ferrites are an important type of high-frequency soft magnetic materials due to their strong planar magnetic anisotropy [3]. Owing to its planar magnetocrystalline anisotropy and high permeability, the Y-type hexaferrite is attractive for practical applications, such as microwave devices [4].

The Y-type hexagonal ferrite Ba₂Mg₂Fe₁₂O₂₂ is a multi-ferroic material. It has a relatively high spiral-magnetic transition temperature (~ 200 K), shows multiferroic properties at a zero magnetic field, and the direction of the ferroelectric polarization can be controlled by a small magnetic field (< 0.02 T) [2]. Due to the fact that the Y-type hexaferrites are an intermediate phase during the synthesis of Z-type ferrites, which is suitable for multilayer chip inductors [5, 6], not much attention has been paid to their synthesis and magnetic investigation.

The Y-type Ba₂Mg₂Fe₁₂O₂₂ ferrite is constructed from basic units of hexagonal barium M-type ferrite and cubic spinel ferrites and has an easy axis of magnetization contained in a plane normal to the c axis direction. Ba₂Mg₂Fe₁₂O₂₂ consists of two magnetic sublattice blocks, L and S blocks, stacking alternately along [001], which bear, respectively, the opposite large and small magnetization M , causing ferrimagnetism even at high temperatures exceeding room temperature (below 553 K) and, below 195 K, the proper screw spin structure at $B = 0$ [7]. Magnetic measurements of single crystals have demonstrated the possibility of a transition to the longitudinal-conical spin state below about 50 K [8]; the prospects of applications as a multiferroic material prompted extensive studies of the structural, magnetic, and ferroelectric properties of single crystals of Ba₂Mg₂Fe₁₂O₂₂ [2, 8–12]. However, the properties of powder Ba₂Mg₂Fe₁₂O₂₂ have not been sufficiently explored.

In the paper, we present a study of the structural and magnetic properties of Ba₂Mg₂Fe₁₂O₂₂ powder synthesized by the sol–gel auto-combustion technique.

Fig. 1 X-ray diffraction patterns of Ba₂Mg₂Fe₁₂O₂₂ powders synthesized at 1080 °C for 5 (a), 1100 °C for 5 h (b), 1100 °C for 10 h (c), and 1170 °C for 5 h (d)

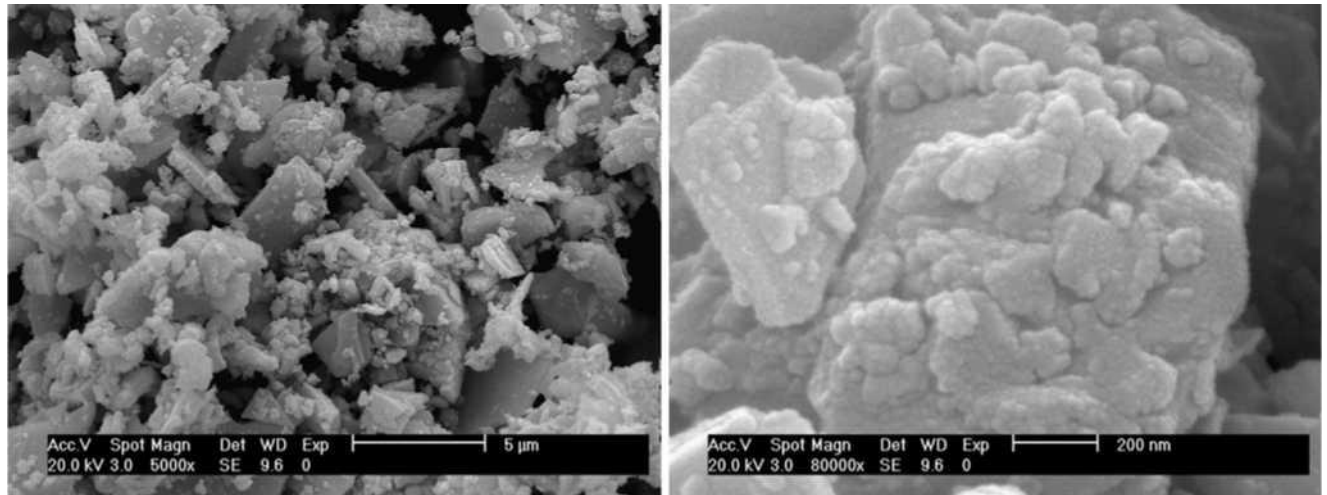


2 Experimental

The $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ powders were prepared following the citric acid sol-gel auto-combustion method. This method provides good control over the product homogeneity and microstructure. The corresponding metal nitrates were used as starting materials. A citric acid solution was slowly added to the mixed solution of nitrates as a chelator. The solution was slowly evaporated to form a gel. This gel was dehydrated at 120°C to obtain the barium-magnesium-iron citrate precursor. During the dehydration process, the gel turned into a fluffy mass and was burnt in a self propagating combustion manner. During auto-combustion, the burning gel expanded rapidly in volume. The auto-combusted powders were annealed at temperatures in the range $1080\text{--}1170^\circ\text{C}$ in air for different periods of time to study the effect of temperature and time on their formation.

The $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ powders were characterized using X-ray diffraction analysis with $\text{Cu-K}\alpha$ radiation and scanning electron microscopy (Philips ESEM XL30 FEG). The hysteresis measurements were carried out by a SQUID Quantum Design magnetometer at 4.2 K and at room temperature. The ZFC and FC measurements at a magnetic field of 100 Oe were performed on an Oxford Design 7000 susceptometer. The *ac*-magnetization was measured at *ac*-magnetic field with amplitude of 10 Oe and frequency of 1000 Hz while the temperature was slowly raised (0.05 K/min).

Fig. 2 SEM images of $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ powder synthesized at 1170°C for 5 h



3 Results and Discussion

Unlike the pure $\text{BaFe}_{12}\text{O}_{19}$ (M-type hexaferrite) preparation by the citrate precursor method, the Y-type phase powder can not be produced so easily due to the complexity of its structure, which imposes a progressive transformation through intermediate ferrites before achieving the required final structure. Figure 1 shows XRD spectra of samples annealed at temperature range 1080–1170 ° for different time periods.

The XRD patterns of the samples heat-treated at 1080 °C for 5 hours show the characteristic reflections of Y-type $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ as the main phase and some impurity phases, namely BaFe_2O_4 and MgFe_2O_4 . Figures 1b and 1c present the spectra of powders annealed at 1100 °C for 5 and 10 h, respectively. As can be seen, the intensities of the peaks of the impurity phases decrease as the temperature and the heat-treatment time are raised, while the intensities the $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ peaks increase. After an additional heat-treatment at a higher temperature (1170 °C for 5 h), the BaFe_2O_4 phase disappears and the peaks of MgFe_2O_4 phase are with very low intensity (Fig. 1d)—less than 2 mass%. The Rietveld refinement of the crystal structure of the $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ sample annealed at 1170 °C for 5 h revealed that in contrast to the $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ structure where the Zn^{2+} cations occupy only tetrahedral cation positions, the Mg^{2+} cations are distributed over all cation positions leading to mixed occupancies of positions in the cation sublattice. The occupancies obtained are close to the corresponding values given by Momozawa et al. [7] for single crystal $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$. The Rietveld refinement confirmed a rhombohedral symmetry of the structure with unit cell parameters ($a = b = 5.8694$ (1) Å and $c = 43.4962$ (1) Å; hexagonal setting). The unit cell parameters are in good agreement with the published values earlier [7, 8]. The mean crystallite size determined from the line broadening of diffraction lines is around 100 nm.

Scanning electron microscopy was used to examine the morphology of the sample synthesized at 1170 °C for 5 h (Fig. 2). The SEM images show that the hexaferrites are well agglomerated to form clusters of different sizes and shapes. Some of the clusters formed have a plate-like shape. The high degree of aggregation seen is due to the strong magnetic attraction forces.

We only present here the magnetic properties of $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ powder synthesized at 1170 °C for 5 h due to the fact that the main phase is Y-type hexaferrite and the trace of MgFe_2O_4 did not affect the powder's magnetic properties.

The hysteresis loops of the powder at room temperature and 4.2 K are shown in Fig. 3. The magnetic parameters, namely, the magnetization at 60 kOe, remanent magnetization (M_r) and coercivity field (H_c) obtained from the curves, are listed in Table 1. The value measured of the magnetization M at a magnetic field of 60 kOe is 22.78 emu/g and 30.47 emu/g at room temperature and 4.2 K, respectively. The magnetization value at room temperature is very close to that reported for a single crystal (23 emu/g) [13]. The inset in Fig. 3a shows a triple hysteresis loop at 4.2 K in low magnetic field range that indicates the presence of two kinds of ferromagnetic states with different magnetization values.

The ZFC and FC magnetization measurements of $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ powder at a magnetic field of 100 Oe are presented in Fig. 4. One can see the change in the magnetization behavior at temperatures near 183 K and 40 K, which is related to magnetic phase transitions. The exact values of the phase-transition temperatures were determined by following the variation of the powder's ac differential magnetization as the temperature was raised in an ac magnetic field with frequency 1000 Hz and amplitude 10 Oe (Fig. 5). The change at 183 K is brought about by a phase transition from ferromagnetic state to spiral spin order state. This transition determines the multiferroic

properties of $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$. We believe that the transition at 40 K is related to spin reorientation along the c axis into a longitudinal conical state.

Fig. 3 Magnetic measurements of $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ powder at 4.2 K (a) and 300 K (b)

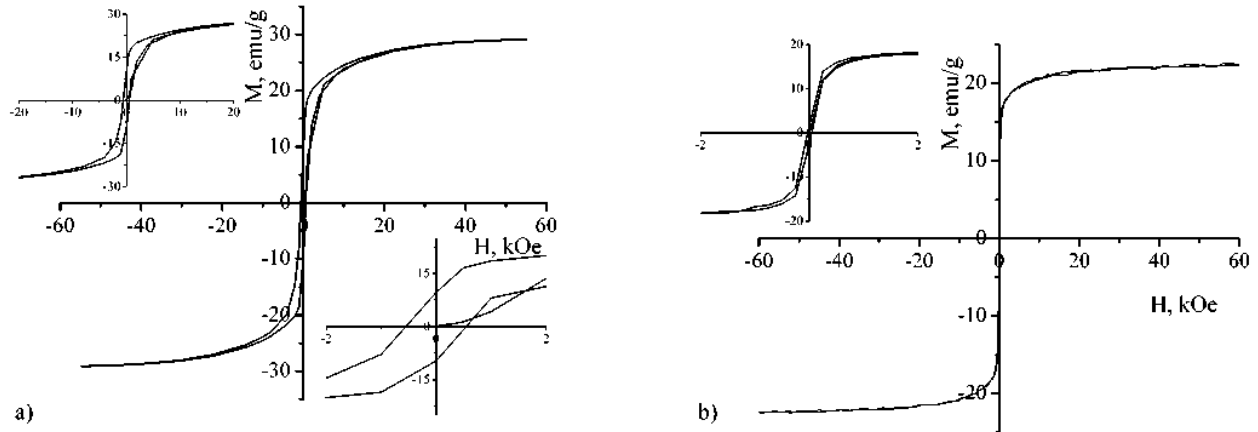


Table 1 Magnetic properties of $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ powder synthesized at 1170 °C for 5 h

Sample	T (K)	M (60 kOe) (emu/g)	M_r (emu/g)	H_c (Oe)
$\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$	300	22.78	1.74	31.35
$\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$	4.2	30.47	9.69	545

Fig. 4 ZFC and FC measurements of $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ powder

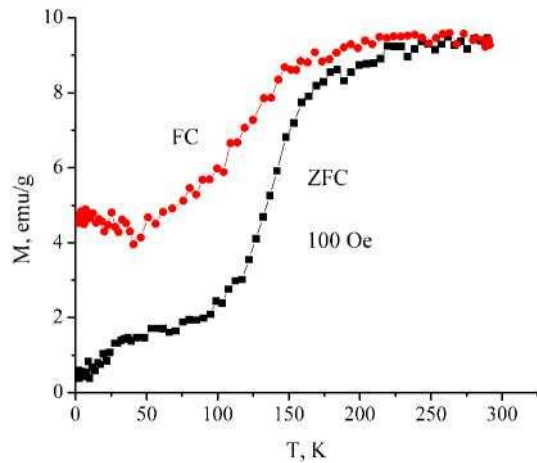
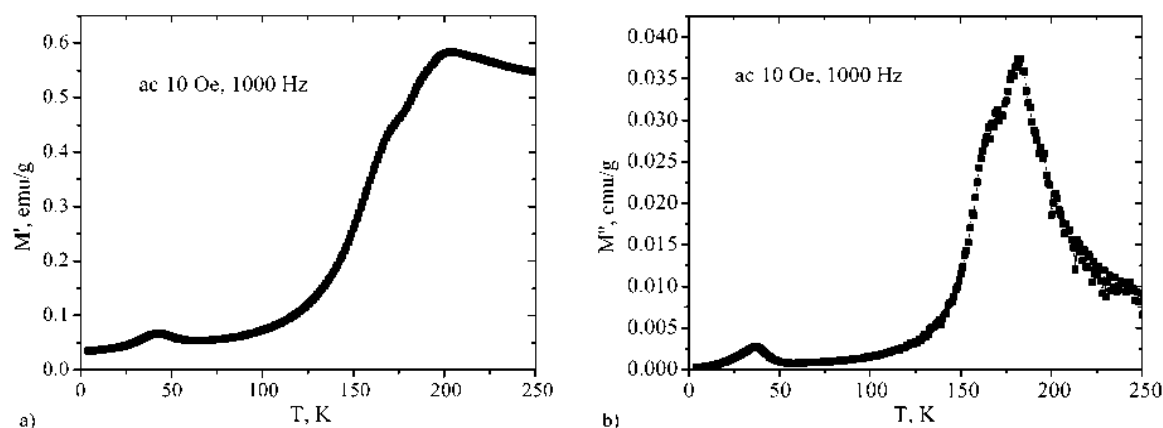


Fig. 5 Temperature dependence of the ac differential magnetization of $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$ in an ac magnetic field with amplitude 10 Oe and frequency 1000 Hz: (a) $M'(T)$ —the real part of the differential magnetization; (b) $M''(T)$ —the imaginary part of the differential magnetization



4 Conclusion

Ba₂Mg₂Fe₁₂O₂₂ powders with mean crystallite size of 100 nm were prepared by means of the sol-gel auto-combustion method. The structural studies demonstrated that the Mg²⁺ cations occupy both the octahedral and the tetragonal sites in the Ba₂Mg₂Fe₁₂O₂₂ crystal lattice. A phase transition from ferromagnetic to spiral spin order was observed at 183 K, together with a transition to longitudinal-conical spin state below 40 K. The presence of these two effects is important for the realization of Ba₂Mg₂Fe₁₂O₂₂ as a multiferroic compound.

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