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Microwave Sintering Effect on $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ Y-Type Hexaferrite

K. Rama Obulesu

Department of Physics, Government Degree College, Shanthinagar, Telangana- 509126, India.

Abstract:
Magnetoelectric multiferroic materials are promising for microwave tunable and memory device applications. Most well-known single-phase magnetoelectric multiferroic materials exhibit transitions in the low-temperature region. Here, I report the comparative magnetic and dielectric properties of magnetoelectric $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ hexaferrites obtained by microwave and conventional solid-state sintered method. XRD results showed that the prepared sample crystallized into a rhombohedral structure for both microwave- and conventionally sintered samples. Microwave sintering has a significant effect on the magnetic and dielectric properties. Samples exhibit an antiferromagnetic nature with Neel temperatures are 315 K and 305 K for conventional and microwave-sintered $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ ceramic. The ferromagnetic resonance signal is observed at 1734 and 1993 Oe for conventional and microwave-sintered samples. The prepared samples exhibit low dielectric loss making them promising for device applications.

Keywords: Hexagonal ferrite, Microwave Sintering, Magnetic properties, and dielectric properties.

1. Introduction

Magnetoelectric (ME) multiferroics have been an active field of research interest for the past two decades due to the coexistence of ferromagnetic and ferroelectric order in a single material. Recently, hexaferrite with helical spin order has been suggested as a promising candidate for room-temperature multiferroics. It was reported that Zn_2Y-type hexaferrite$Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ (BSZFO) exhibits a high ordering temperature of about 320K for the magnetic field-induced ferroelectricity around 1T [1-6]. The critical magnetic field in the range of 0.3-0.8T is required to induce the ferroelectricity in BSZFO samples [7-8]. Interestingly, it is reported that a fairly low critical magnetic field (1 mT–10 mT) is required to control the helical spin and induce polarization in Mg_2Y-type [9] and Al-doped Zn2Y-type hexaferrite [10]. Near room temperature ME effect was observed at the low-magnetic field in Co_2Z-type [11], M-type[12], U-type[13], W-type [14], and Co_2Y-type[15] hexaferrites. Moreover, Co_2Y-type, Co_2Z-type [16], Al-dopedZn_2Y-type [17], and CoZnY-type [18] hexaferrite responded to the electrical control of magnetization called the inverse ME effect at room temperature, emphasizing a large step towards technological device applications. However, there has been continuous research efforts are

under progress to decrease the critical magnetic field to induce the ferroelectricity of hexaferrite using developing novel and cost-effective synthetic methods.

The microwave sintering of ceramic materials has several potential advantages over conventional sintering in terms of sintering cycle time and energy efficiency. In this paper, we study the magnetic and dielectric properties of $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ hexaferrite prepared by the microwave sintering method, and the properties of the sample were compared with the conventional sintering method. The sample obtained through the microwave sintering method exhibits improved dielectric and magnetic properties as compared to the conventional sintering method.

2. Experimental Details

The $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ (BSZFO) samples were synthesized by the conventional solid-state reaction method. The stoichiometric proportions of $BaCO_3$, $SrCO_3$, ZnO, and Fe_2O_3 (Aldrich 99%) were mixed using a ball mill in isopropanol for 2h. These mixed powders were calcined at 1130 °C in air and then milled again for 3h. The resulting powders were pressed into pellets using a hydraulic press under a pressure of 250 MPa with 2 wt% polyvinyl alcohol as a binder. These pellets (diameter 8 mm and thickness 2 mm) were sintered at 1200 °C for 6 h in air and then cooled naturally. Subsequently, these samples were subjected to microwave sintering at 1150 °C for 30 min with a heating rate of 40 °C /min. The microwave sintering was executed using a 1.3 kW, 2.45 GHz multimode microwave furnace. The sample is placed in the casket and kept at the center of the cavity. An appropriate amount of silicon carbide can be used as a microwave susceptor around the sample to preheat the sample and compensate for the heat loss from the sample.

The x-ray diffraction (XRD) patterns of the samples were obtained by using a Brucker (D8 ADVANCED) x-ray diffractometer, using Cu-Kα radiation (λ=1.5405Å). The lattice parameters were determined using Rietveld analysis in TOPAS software. The density of the samples was estimated using Archimedes' principle. Surface morphology was studied by using a field-emission scanning electron microscope (FESEM, Carl Zeiss Ultra 55). The magnetic properties of the samples were measured by the physical property measurement system (PPMS) electromagnet was used in the vibrating sample magnetometer (VSM) mode (Quantum Design Model P525). Ferromagnetic resonance (FMR) spectra are recorded with X band ESR–JEOL spectrometer at room temperature. The frequency-dependent dielectric properties were measured using an impedance analyzer (Agilent 4329A) at a lower frequency (40 Hz- 2 MHz) range and room temperature.

3. Results and Discussion

X-ray diffraction patterns of conventional and microwave-sintered BSZFO samples are shown in Fig.1 (a, b). The XRD peaks were indexed and well-matched with the standard JCPDS file (File no: 79-0749). The unidentified peaks in the XRD pattern emerged from the $ZnFe_2O_4$phasewhich is commonly presented in Zn-rich ferrite samples [7]. The calculated lattice parameters are presented in Table 1. The value of lattice parameter '*a*' is low for microwave sintered (MS) samples as compared with the conventional sintered (CS) samples. The cation ionic radius of dopant strontium (0.127 nm) is close to

the Ba^{2+}(0.143 nm), which allows facile substitution of Sr at the cationBa^{2+}lattice site. As the dopant concentration of Sr^{2+} increases, the hexagonal crystal lattice changes lattice parameters due to different sizes of ionic sizes and modifies the superexchange interaction between Fe-O-Fe and the iron ions [8]. The theoretical density, measured density, and relative density of the MS sample are slightly less than the CS sample. The MS samples likely exhibited lower density than expected. Rapid heating may have caused insufficient densification, resulting in higher porosity. The microwave-sintered samples exhibited lower density and higher porosity, which likely contributed to the suboptimal microstructure. As seen from Fig. 2 (a, b) of the morphology of the samples, the conventional sintered sample, the FESEM image (Fig 2(a)) shows closely packed grains in a hexagonal plate shape. Meanwhile, the microwave-sintered samples (Fig 2(b)) show agglomerated particles and loosely packed grains with irregular shapes and pores between the grains. The majority of particles have elongated in size after microwave sintering. Similar observations are reported by Topal*et al.* [19] and Sozeri*et al.* [20] for $BaFe_{12}O_{19}$ samples. They found that the particles were also agglomerated in different sizes and shapes for microwave-sintered samples. The average grain size for a conventional specimen is ~1.5µm, which is larger than a microwave-sintered sample (~0.8 µm). The fast and short sintering duration might result in porosities and internal stress for microwave-sintered samples.

The magnetic field-dependant magnetization (M-H) curve of conventional and microwave-sintered $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ samples was measured in the field range ±2T at the room temperature and depicted in Fig. 3(a). The figure, observed a clear magnetic hysteresis loop with saturation magnetization signifies the ferromagnetic nature of both samples. However, the conventional sintered sample shows high saturation as compared to the microwave sintered sample. From the close observation of the M-H curve (inset of Fig. 3(a)) at low fields (±100Oe), the retentivity and coercivity of the samples were calculated. For CS and MSBSZF samples, the retentivity is calculated to be 0.086 and 0.33 emu/g, respectively. The retentivity enhancement of BSZFO samples is due to the following factors: (1) The magnetic structure of the $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ sample is composed of an alternating stacking of the L and S blocks along the c-axis; within these blocks, magnetic moments on Fe ions are collinearly aligned and ferromagnetically coupled. However, the magnetic moments between adjacent L and S blocks align non-collinearly. The resultant magnetic structure of $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ is a non-collinear screw spiral magnetic structure (propagation vector along the c-axis) in the absence of magnetic fields [6], (2) as the dopant concentration of Sr^{2+} increases, the crystal lattice changes, due to different size of ion by modifying the super exchange interaction between the Fe^{3+} ions (3) microwave sintering. The coercivity of the samples is measured as 10.8 and 22 Oe for the CS and MS samples. This type of behaviour has been reported by Junliang et al. [21] and Li et al. [22]. This high coercivity is mainly caused by the average grain size, porosity, and interaction of the microwaves with the material—longer sintering time results to have low coercivity [23, 24]. In contrast, the saturation magnetization value was higher for CS samples than for MS samples. This phenomenon was mainly caused by the bigger grain size of the sample [25].

The temperature-dependent magnetization was measured by sweeping the temperature from 5-350 K at a constant applied magnetic field of 500 Oe. From Fig. 3b, it is noticed that the samples exhibit an

antiferromagnetic nature with Neel temperature (T_N) above room temperature. The T_N has decreased from 315K of the CS sample to 305 K of the MS sample (see inset). The oxygen deficiency, small grain size, and high porosity of the MS sample result to have low saturation magnetization, high coercivity, and low T_N as compared to the CS sample [26].

The room temperature FMR spectrum of CS and MS BSZFO samples are shown in Fig.4a. The recorded spectrum is the first derivative of microwave power absorption concerning the static magnetic field. The calculated 'g' values are 3.745 and 3.25 for CS and MS$Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$hexaferrite samples. The resonance field (and line width) are estimated as 1734 (and 735) Oe and 1993 (and 896) Oe for CS and MS samples, respectively. In the CS sample, the first shoulder (up) is symmetric and homogeneous. Compared to the CS sample, the data of the MS sample has Lorentizian with better symmetry concerning the line. In both cases, the down shoulder of the Lorentizian exhibits in-homogeneous broadening. In NMR spectra, the line shape helps to determine the type of interactions between the spin systems, and line width is related to the strength of the interaction. In both cases, the 'g' values greater than 2 indicate that spin-orbital and spin-spin interactions are vital in deciding the type of interaction of the sample. The inhomogeneous broadening is observed because inhomogeneities in the dc field were observed by local spins, which means a strong internal field was present ('g' value tells) and dipolar interactions between the spins with different Larmor frequencies.

The variation of dielectric constant and dielectric loss (inset) with frequency for both CS and MS pellets are shown in Fig. 4b. The dielectric constant and loss showed the same trend, i.e. both the values are decreasing with increased frequency. It is significant to notice that the MS samples exhibit low dielectric constant and dielectric loss compared to the CS sample. The room temperature dielectric constant and dielectric loss values measured at 1 MHz are 135.55, 0.85 for CS, and 52.76, 0.26 for the MS sample. The responsible mechanism for the dielectric constant in ferrites is electrical polarization [27]. The existence of Fe^{2+} ions is expected to be low in the microwave-sintered sample—the other important factor affecting the dielectric constant such as porosity and grain size.

4. Conclusions

Conventional and Microwave sintering comparative results are shown in this paper. The actual results indicate that microwave sintering did not have the anticipated beneficial effects on the reaction time, microstructure, porosity, and dielectric loss of $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ ceramic samples. Instead, the results show the opposite, highlighting the importance of considering material-specific properties and optimizing the sintering process parameters. Conventional sintering, with its controlled and gradual heating, might be better suited for achieving the desired properties in this particular material. Magnetic measurements showed high field magnetization and magnetic retentivity values for the microwave sintered samples, whereas the antiferromagnetic Neel temperature is reduced by 10 K for the $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ sample.

Figure captions:

Figure 1: X-ray diffraction pattern of(a) conventional and (b) microwave-sintered samples.

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Figure 2: FESEM images of (a) conventional (b) microwave sintered $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ sample.
Figure 3: (Left) The magnetization – magnetic field (M-H) hysteresis loops of $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{12}$(black colour – conventional, red colour - microwave) sintered samples. (Right)Temperature dependence of magnetization at constant magnetic field 500 Oe of the $Ba_{0.5}S_{r1.5}Zn_2Fe_{12}O_{22}$ material (black colour – conventional, red colour - microwave).
Figure 4: (a) FMR spectra of conventional and microwave-sintered $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O22$ samples. (b) Dielectric permittivity variation with frequency for conventional and microwave sintered $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ samples.

Tables:

Table 1: The table shows the lattice parameters and theoretical density of conventional sintered and microwave sintered $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ ceramic samples.

Figure (1):

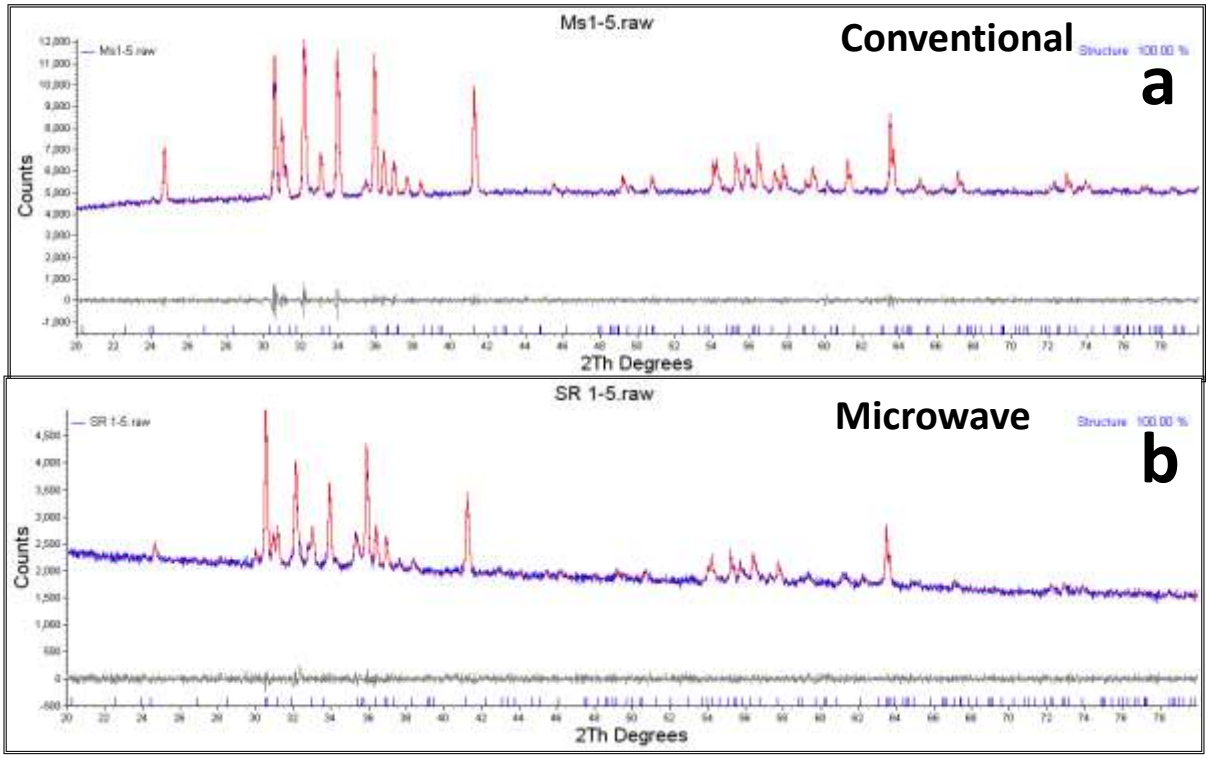

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Figure (2):

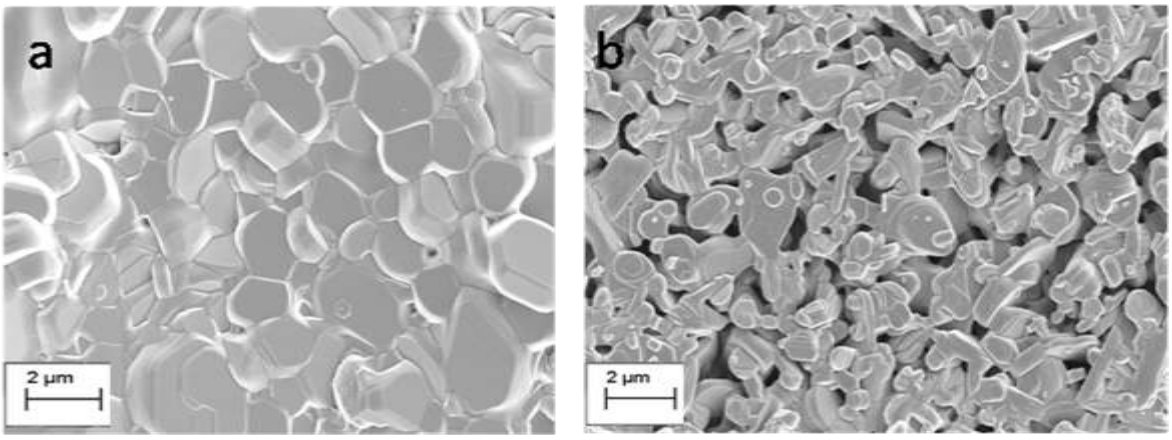

Figure (3):

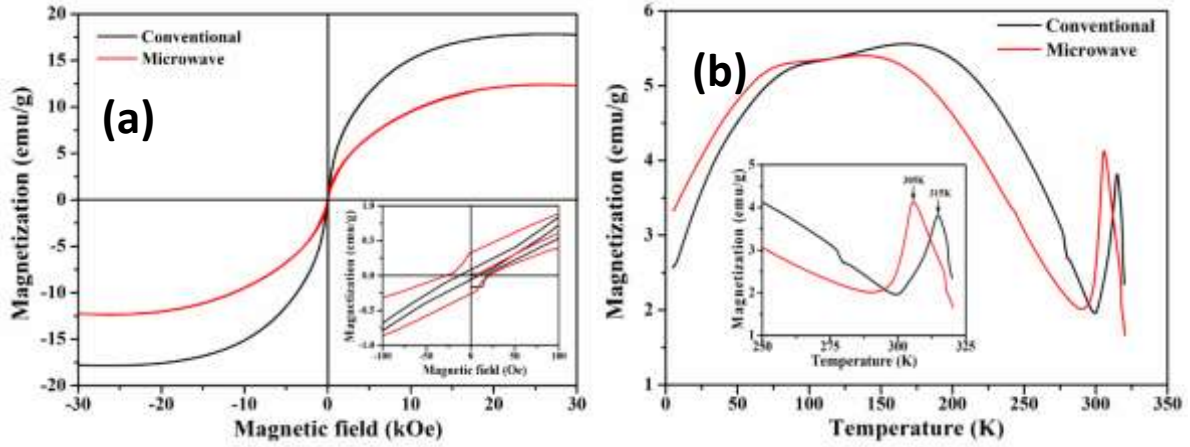

Figure (4):

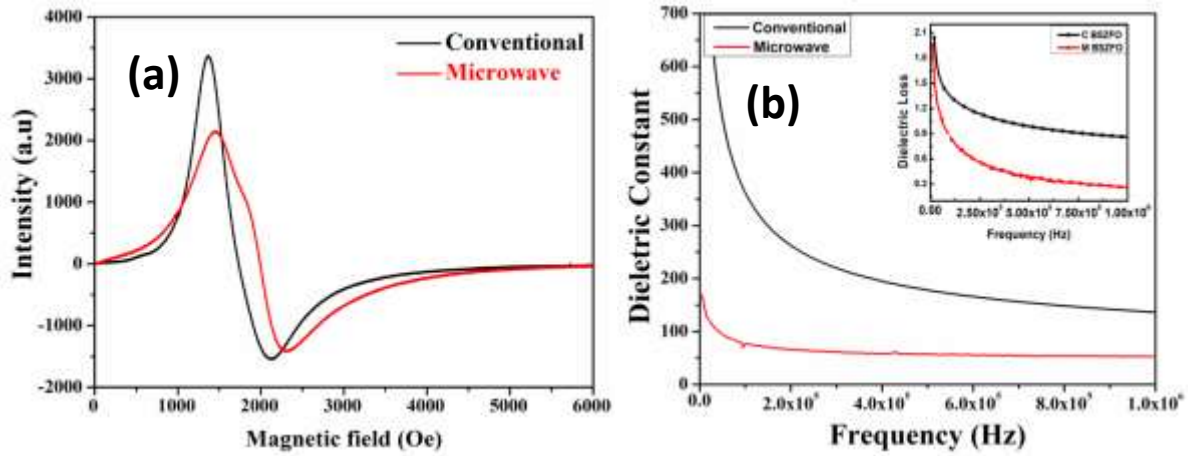

Table:

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Compound	a (A°)	c (A°)	Theoretical Density (g/cm^3)	Measured Density (g/cm^3)	Relative Density (%)	Porosity (%)
C-$Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$	5.855	43.76	5.189	4.96	92.5	4.45
M-$Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$	5.84	44.18	5.164	4.90	90.5	5.13

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