Titanium and Manganese Doped Barium Ferrite for Electromagnetic Wave Absorbing Materials.

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M-Type Barium ferrites are of particular interest to Electromagnetic (EM) absorber applications above 10GHz due to the electromagnetic losses around the frequency of the ferromagnetic resonance (FMR) [1]. In the spinel and garnet type ferrites this FMR is below the GHz range however hexagonal ferrites have a comparatively higher magnetocrystalline anisotropy resulting in a FMR higher in the GHz range [2]. Current literature describes methods of manufacture [3] however parameters need to be optimised for each formulation. Our current work focuses on the manufacturing process to produce single phase hexagonal structure with doping parameters required for applications in the 16-28GHz range.

M-type hexagonal ferrites were produced via a conventional solid state ceramic manufacturing process from readily available metallic oxide and carbonate powders. Stoichiometric ratios of Iron oxide (Fe₂O₃), barium carbonate (BaCO₃), titanium oxide (TiO₂) and manganese carbonate (MnCO₃) precursor materials corresponding to a final composition of BaFe_{9.5}(Ti_{0.5}Mn_{0.5})_{2.5}O₁₉ were mixed for 8 hours in a rolling ball mill. The mixture then was calcined at 1000°C, milled for 3 hours, and sintered at 1250°C, 1300°C, 1350°C, 1400°C and 1450°C for 8 hours. Finally the resultant sintered material was crushed and ball milled for 20 hours to form a fine powder. The crystallographic structure of each ferrite sample was measured using a Brooker D X-Ray diffractometer with a cobalt source ($\lambda = 1.79$ Å).



Fig 1: XRD diffraction patterns of $BaFe_{9.5}(Ti_{0.5}Mn_{0.5})_{2.5}O_{19}$ powders after the 1000°C calcining step, post final sintering temperatures of 1250°C to 1450°C, and the precursor mixture.

Figure 1 shows the X ray powder diffraction spectrum for the samples with key peaks labelled. The calcining step at 1000° C is sufficient to eliminate the BaCO₃ precursor but Fe₂O₃ remains until the sintering step at 1250° C. A key take away is that the addition of substituting elements, titanium and manganese, did not significantly alter the crystal structure, nor prevent the formation of the hexagonal ferrite. There was only a slight increase in the unit cell size due to the larger ionic radii of Ti and Mn dopants than the Fe.



Fig 2: Scanning electron micrographs of doped Barium ferrite produced though the conventional ceramic route with a sintering temperature of (left) 1000°C and (right) 1300°C. Note the differing magnification factor.

Next stoichiometric ratios of the same precursors were mixed corresponding to $BaFe_{12-x}(Ti_{0.5}Mn_{0.5})xO_{19}$ samples at substitutions x = 2.0, 2.5, 3.0, and 3.5. M-Type barium hexaferrite was successfully produced for this range of dopants without the introduction of a secondary phase. This allows these ferrites to be tuned for use in passive EM absorbers.

^[1] Amin, M. B., & James, J. R. (1981). Techniques for utilization of hexagonal ferrites in radar absorbers. Part 1: Broadband planar coatings. *Radio and Electronic Engineer*, *51*(5), 209-218.

^[2] Pardavi-Horvath, M. (2000). Microwave applications of soft ferrites. *Journal of Magnetism and Magnetic Materials, 215*, 171-183

^[3] Syazwan, M. M., Azis, R. S., et al. (2017). Co-Ti- and Mn-Ti-substituted barium ferrite for electromagnetic property tuning and enhanced microwave absorption synthesized via mechanical alloying. *Journal of the Australian Ceramic Society*, *53*(2), 465-474.