Controlled microwave-assisted synthesis of nano-crystalline zinc ferrite

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Controlled synthesis of nanocrystalline spinel ferrites are of immense importance owing to their interesting magnetic characteristics at nanoscale that leads not only to study the process of magnetization in them at that scale but also to use them for the development of various functional devices. Among largely-favoured low-temperature solution-based processing methods, as demonstrated in our earlier work[1], microwave-irradiation-assisted synthesis technique (MAST) offers rapid way to obtain pure crystallites with very narrow size distribution. However, the use of surfactant and the need of post-synthesis anneal was unavoidable in order to control distribution and growth of particle size. In this work we will demonstrate surfactant-free and anneal-free synthesis of zinc ferrite nanocrystallites with tunable physical and chemical properties by same MAST but with slightly altered synthesis conditions. Furthermore we will also show the effect of processing conditions on their properties.
For the synthesis of zinc ferrite by MAST, metalorganic complexes such as $Zn(acac)_2$ and $Fe(acac)_3$ were chosen (in stoichiometric ratio) as precursors and taken in a solvent mixture containing ethanol, 1-decanol, and a small quantity of de-ionized water (5:8:1) and stirred mildly until a clear solution resulted. The clear solution was then transferred to a Pyrex glass vessel, designed for 'Discover SP' system (Microwave reactor, CEM Corp., US), and placed inside the microwave cavity for the exposure of microwave irradiation (2.45 GHz, 300 W) for just 10 minutes so as to complete the reaction that resulted in pure nanocrystalline zinc ferrite powder (sample name: N10x) as precipitate at the bottom of the vessel. 1-decanol, being a high boiling point solvent, pushed the overall boiling point of the solution mixture near to 200 °C, while serving the purpose of surfactant due to its high viscosity. Therefore, the inclusion of 1-decanol was found to be crucial to control shape and size of the nanocrystallites. The purity and crystallinity of the samples were confirmed through powder X-ray diffraction (PXRD; Fig. 1) and X-ray photoelectron spectroscopy (XPS). Scanning electron microscopy (SEM) image of the crystallites revealed mono-dispersed particles of ~ 5-7 nm diameters in agglomerated state. Magnetization of these nanocrystallites, measured at low (3 K) temperature by using SQUID magnetometer, revealed (Fig. 3) hysteresis with saturation magnetization (M_S) and coercivity of 30 emu/g and 400 Oe respectively. Zinc ferrite – a normal spinel, which ideally is antiferromagnetic (below T_N=10 K) in bulk, displayed superparamagnetism even at room temperature (Fig. 1c). This observation is a clear evidence of process-induced distribution of cations in the lattice that in turn enables ferrimagnetically coupled superexchange interactions among the Fe^{3+} ions present both in tetrahedral and octahedral sites. It is also to be noted that the inversion was infused in the crystal structure only at ~190 °C and is believed to be influenced heavily by the presence of microwave irradiation. Prolonged exposure (1 hour; sample name: N10 x-1H) of microwave irradiation, however, resulted in a little reduction in M_S (23 emu/g), while uniform growth of nanocrystallites up to 20 nm was observed (Fig. 1 and 2). Therefore, an anneal-free alternative to crystal growth was evidenced.

Reference

1) R. Sai *et al*, J. Mater. Chem., **22**, 5 (2012), 2149.

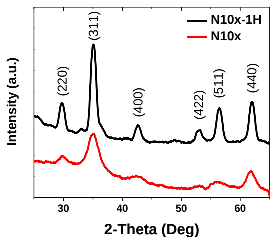

Fig. 1: XRD patterns of N10x and N10x-1H

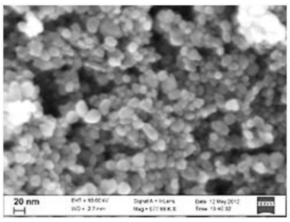

Fig. 2: SEM image of N10x-1H

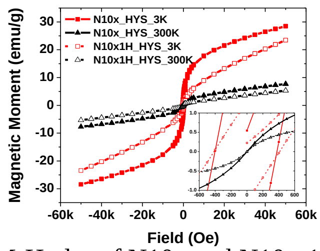

Fig. 3: M-H plot of N10x and N10x-1H measured at 3 K and 300 K