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Influential diamagnetic magnesium (Mg^{2+}) ion substitution in nano-spinel zinc ferrite ($ZnFe_2O_4$): Thermal, structural, spectral, optical and physisorption analysis

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Abstract

Nano-spinel zinc ferrites ($ZnFe_2O_4$) with substitution of diamagnetic magnesium (Mg^{2+}) ions were synthesized using solution-gelation (sol-gel) self ignition route. The thermal, structural, spectral, optical and N_2-physisorption properties of the prepared Zn–Mg ferrite nanoparticles were analyzed by standard characterization techniques. The temperature dependent spinel phase formation and percentage weight loss was studied by thermogravimetric and differential thermal analysis (TG-DTA). The analysis of the room temperature X-ray diffraction (XRD) patterns showed the formation of cubic spinel structure with single phase in the Zn–Mg ferrites. The crystallite size decreasing from 27 nm to 20 nm with Mg^{2+} substitution confirmed the nanocrystalline formation of the Zn–Mg ferrites. The two characteristics vibrational modes of interstitial sub-lattice sites corresponding to the spinel structure were observed within the desired wavelength range of the FT-IR spectra. The optical band gap values estimated from the UV–Visible data analysis is found to be in the scope of 1.96 eV–2.39 eV. The photoluminescence (PL) spectra showed the broader emission band in the visible region (around 525 nm) for all the samples of Zn–Mg ferrites. The BET isotherms were recorded by the N_2 adsorption-desorption and the surface area, pore volume, average pore radius etc surface parameters were deduced. The BET surface area and average pore radius values were obtained in the range of 5.6–24.8 m^2/gm and 2.61–4.52 nm respectively.

Introduction

Recent advances in the material science field enabled the research community to prepare and test the nano scaled materials with different compositions, sizes and shapes for their applicability in the diverse applications [1,2]. Amongst the nano scaled materials, ferrites are proving themselves as a promising candidate for various practical applications due to their dual natured magnetic and electrical properties [3,4]. Ferrites at the nano level acquire the distinguishable physical and chemical properties than their bulk forms. These distinguishable and remarkable properties lead to the applicability of ferrites in different fields ranging from electronics industry to the biomedical field [[5], [6], [7], [8]].

Chemically ferrites are nothing but the combination of iron oxide (Fe_2O_3) and the metal ions (Co, Zn, Mg, Mn, Ni, Y, Ba etc.) which can be designated in three forms viz. MFe_2O_4 (Spinel ferrite), MFe_5O_{12} (Garnet) and $MFe_{12}O_{19}$ (Hexaferrite). Among these types, spinel ferrites are the simplistic form of the ferrites which poses cubic lattice structure and are chemically more stable [9]. The unit cell of spinel ferrites with generic formula $M^{II}Fe_2O_4$ (where M is divalent transition metal ions) contains the one metal ion, two Fe^{3+} ions and four O^{2-} ions resulting in the face centered cubic (F.C.C.) structure. The allotment of metal ions and Fe ions over the available two lattice sites viz. tetrahedral interstitial site (A) and octahedral interstitial site [B] decides the spinel lattice structure i.e. whether it is normal or inverse or mixed [10]. For example zinc ferrite is a normal spinel structured ferrite (as zinc ions accommodate only (A) site) whereas cobalt ferrite is an inverse spinel structured ferrite (as cobalt ions accommodate only [B] site). The pristine spinel lattice structure can be modified by incorporation of guest metal ions which subsequently modify and improve the properties of spinel ferrites [11,12].

Zinc ferrite (ZNF) having normal spinel lattice structure with a chemical formula as $(Zn^{2+})^A\ [Fe_2{}^{3+}]^B\ O_4{}^{2-}$ is one of the excellent member of the nanoscale ferrites family due to its simple crystal structure, better chemical activity and thermal stability [13,14]. Due to these properties, they are extremely used in the electro-optical devices [15], transducers [16], photo-catalytic systems [17], contrast enhancers [18], hyperthermia therapies [19,20] and so on. Apart from the ZNF, magnesium ferrite (MGF) having inverse spinel structure with a chemical formula as $(Fe^{3+})^A\ [Mg^{2+}\cdot Fe^{3+}]^B\ O_4{}^{2-}$ is also a outstanding member of ferrites family due to its better magneto-electric properties [21]. As same as the ZNF, the MGF are also applicable in the electronics and biomedical areas [22,23]. Thus, the combination of these two variant lattice structures i.e. ZNF (normal spinel) and MGF (inverse spinel) results in a formation of mixed spinel lattice structure which gives rise to a superior properties than their individual parts.

In the accessible literature reports, some researchers made and attempt to study the properties of nanoscale zinc-magnesium ferrite (ZMF). Recently, E. Petrova et al. (2019) studied the impact of synthetic roots on the structural and magnetic properties of ZMF powders in the nanoform [24]. He successfully obtained the nanopowders of ZMF via three different routes viz. spray pyrolysis, co-precipitation and combustion reaction. He concluded the correlativity to prepare the ZMF with predefined properties. H. M. El-Sayed et al. (2017) reported the ZMF nanoparticles to study the effect of thickness of magnetic dead layer on the magnetic properties [25]. Pamela Y. Rodriguez et al. (2017) carried out the synthesis of ZMF nanoparticles with wide compositions and studied their structural and magnetic properties [26]. Their out comings indicated that, the prepared materials are capable material for hyperthermia therapies. S. B. Singh et al. (2016) studied the magnetic exchange interface among the ZMF nanoparticles prepared by wet chemical co-precipitation route [27]. He deduced the outcomes based on the cationic re-distribution supposing variation in the exchange interface energy. The effect of heat treatment on the properties of ZMF nanoparticles was carried out by K. Nadeem et al. (2015) [28]. His conclusions showed that, heat treatment significantly affects the structural and magnetic properties of ZMF ferrites.

In addition to these reports, various synthetic routes viz. hydrothermal [29], micro-emulsion [30], co-precipitation [31], spray pyrolysis [32], sol-gel [33], ball milling [34] etc were applied to prepare the nano scale spinel ferrites. The solution-gelation (sol-gel) method with self ignition reaction is favorable among these methods as it involves simple setup, low reaction temperature and time, low cost with maximum yield and homogeneity [35]. Though there are sufficient reports are available on the structural and magnetic properties of ZMF nano particles, the promising reports on thermal, optical and surface related properties are lacking. In light of this fact, the present work is focused on the sol-gel self ignition synthesis of ZMF nanoparticles and the study of synergic effect of diamagnetic magnesium (Mg^{2+}) substitution on the thermal, structural, infrared, optical and surface analysis of zinc ferrite ($ZnFe_2O_4$) nanoparticles. All the outcomes show the synergistic effect of diamagnetic Mg^{2+} ions on nano-spinel zinc ferrites drawing the noteworthy changes in thermal, structural, infrared, optical and surface parameters. Among all the ZMF samples, the sample ($Zn_{0.5}Mg_{0.5}Fe_2O_4$) with equal amounts of Zn^{2+} and Mg^{2+} ions in zinc spinel ferrite matrix showed the enhanced properties. Thus, the equi-amounted ZMF sample is promising for diverse range of bio-applications such as magnetic fluid hyperthermia therapies (MFHT) for cancer treatment and contrast enhancing agents in magnetic resonance imaging (MRI).

Section snippets

Experimental details

Magnesium (Mg^{2+}) substituted zinc ferrite nanoparticles (ZMF) with compositional formula of $Zn_{1-x}Mg_xFe_2O_4$ (where x=0.0, 0.3, 0.5, 0.7 and 1.0) were prepared by well known and effectual sol-gel self ignition route. The raw source materials for the respective metal ions i.e. Zn^{2+}, Mg^{2+} and Fe^{3+} were procured from Merck in the form of nitrates with maximum purity of 99.9%. For the chelating of metal nitrate ions, citric acid was used as a fuel. The ratio as Metal nitrate: Fuel: 1 : 3 was chosen…

Thermal analysis (TG-DTA)

The impact of the heat treatment on the prepared ZMF nanoparticles was analyzed by the weight reduction due to the thermal response recorded by TG-DTA. Fig. 2 (a) and (b) demonstrates the thermogravimetric (TG) curves and the differential thermal (DT) curves for the prepared ZMF nanoparticles. Normally, it can be noted from Fig. 2 (a) that, in the initial temperature range (i.e. 27 °C–400 °C) the weight loss was occurred in very slow manner and further the sudden weight loss was appeared within …

Conclusions

Diamagnetic Mg^{2+} ion substituted nano-spinel zinc ferrite (ZMF) samples were successfully synthesized by high yielding solution-gelation self ignition route. The in detailed thermal, structural, infrared, optical and surface analysis of the prepared ZMF samples was prolifically carried out. Thermal studies revealed the minimum weight loss with spinel phase formation by combustion process. XRD analysis showed the formation of cubic spinel structure with single phase for all the ZMF samples. The…

Declaration of competing interest

There are no conflicts of interest connected to the present work.…

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