Magnetic Behavior of Nanostructured and Nonequilibrium Ferrites

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It is widely appreciated that the performance of ferrites (*e.g.*, MFe$_2$O$_4$, MeFeO$_3$, MFe$_{12}$O$_{19}$; where *M* and *Me* are divalent and trivalent metal cations, respectively) is closely related to the ways, in which they are processed. The conventional solid-state (ceramic) synthesis of ferrites requires prolonged treatment at considerably high calcination temperatures, often causing the loss of metal cations due to their high volatility. This results in the formation of multiphase products and, consequently, in the degradation of microstructural and functional properties of ferrites. Among the many types of preparation and processing techniques, the nonconventional mechanochemical route (mechanosynthesis) has been recognized as a powerful method for the one-step production of nanostructured & nonequilibrium ferrites [1].

In the present work, a one-step complete synthesis of nanocrystalline ferrites of various chemical compositions and structural types via mechanochemical processing of mixtures of corresponding educts at room temperature is reported. In addition to the XRD method being sensitive to medium- and long-range structural order, the mechanically induced evolution of powdered mixtures is followed by ^{57}Fe Mössbauer spectroscopy. The well-resolved Mössbauer subspectra of the Fe-containing educt and product phases enables us to monitor the single-step mechanosynthesis route to various ferrites and to accurately determine the degree of conversion of mechanochemical reactions. Furthermore, Mössbauer spectroscopy reveals partial superparamagnetic state of the as-prepared ferrites at room temperature. Ferrite nanoparticles prepared by mechanochemical routes are found to be roughly spherical, consisting of a crystalline inner core surrounded by a structurally disordered surface shell/interface region. Both, a high degree of spin canting and a far-from-equilibrium structural state (*e.g.*, nonequilibrium cation distribution) are found to be characteristic features of surface shell/interface regions of mechanosynthesized nanomaterials. The macroscopic magnetic behavior of the as-prepared nanoferrites (enhanced magnetization, enhanced coercivity, reduced magnetic moment, shifted hysteresis loop, *etc.*) is discussed in detail and is attributed to the effects of spin canting and nonequilibrium structural states located in the surface shell/interface regions of nanoparticles.

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[1] V. Šepelák, A. Düvel, M. Wilkening, K.-D. Becker, P. Heitjans, *Chem. Soc. Rev.* 42 (2013) 7507.