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Dielectric and magnetic response of $SrFe_{12}O_{19}$–$CoFe_2O_4$ composites obtained by solid state reaction

Andrzej Hilczer[a,*], Katarzyna Kowalska[b], Ewa Markiewicz[a], Adam Pietraszko[b], Bartłomiej Andrzejewski[a]

[a] Institute of Molecular Physics Polish Academy of Sciences, M. Smoluchowskiego 17, Poznań 60-179, Poland
[b] Institute of Low Temperature and Structure Research Polish Academy of Sciences, Okólna 2, Wrocław 50-422, Poland

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ABSTRACT

Nanocomposites of hard magnetic $SrFe_{12}O_{19}$ hexaferrite and soft magnetic $CoFe_2O_4$ spinel with exchange spring interaction were obtained by simple solid state reaction during 8 h and 14 h at 1050 °C. The structure and morphology of the composites was characterized by X-ray diffraction, infrared spectroscopy and scanning electron microscopy. Dielectric and electric response of the composites were found to be similar to the behavior of other ferrites and can be well described within the Koops model of the ceramic consisting of highly conducting grains separated by poorly conducting grain boundaries. Single-phase magnetic hysteresis loops obtained for $SrFe_{12}O_{19}/CoFe_2O_4$ composites with weight ratio 4:1 containing ~1 wt.% hematite. The difference in magnetization below the temperature of irreversibility, measured in field cooling and zero field cooling experiments in fields exceeding doubled coercivity, was found to be greater for composites synthesized during 4–14 h than that obtained for 22 h.

1. Introduction

Nanocomposites of magnetic materials are recently of great interest since combining soft and hard magnetics in a nanoscale one can expect interfacial exchange coupling which may drastically modify the magnetic behavior [1–3]. Magnetic spring interactions based on exchange coupling in nanostructured soft and hard magnetic phases can result in high energy product $(BH)_{max}$ desirable for permanent magnets [4]. Moreover, the composites can exhibit wide-band microwave absorption which can be used to reduce the radar cross-section of targets and the pollution resulting from electromagnetic interference [5–11]. The magnetic spring behavior has been realized in various heterostructures, core–shell magnetic structures and magnetic composites [4,12–20]. It should be however noted that many hard magnetics used in the composites contained expensive rare earth metals [3,4,12–15] and therefore it appears an interest in nanocomposites with rare earth free hard magnetic materials [21]. The challenge is met by nanocomposites consisting of M-type hexaferrites as the hard magnetic phase [22] and the soft magnetic phase consisting of various spinel-type ferrites [5–11,23–33]. $NiFe_2O_4$, $ZnFe_2O_4$ and $(Ni,Zn)Fe_2O_4$ spinels were mainly used in the composites [6,8–11,23,24,26–28,30,31]. The cobalt spinel has been used in form of a shell in $SrFe_{12}O_{19}$ composite of core–shell structure [7] and in $SrFe_{12}O_{19}$@$CoFe_2O_4$ nanocomposites prepared by coprecipitation with high-temperature sintering [32] and in form of nanofibers [33]. The exchange coupling behavior of the composites was found to be dependent on the processing conditions i.e. the method, the temperature and time of synthesis, thermal treatment as well as on appropriate ratio of the soft and the hard magnetic phases. For instance composites prepared by mechanical mixing of separately synthesized $BaFe_{12}O_{19}$ and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanopowders were reported as two magnetically independent phases [11,26], whereas exchange spring behavior has been found for a nanocomposite obtained by mixing of $BaFe_{12}O_{19}$ and $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and adjusting the particle size of hard and soft magnetic phases by thermal treatment [24].

It should be observed that it is not easy to predict conditions for the exchange coupling between hard and soft ferrites since the magnetic properties of the composite are determined not only by the properties of constituent phases but also by the grain sizes and their shapes, as well as by the way in which the hard and soft magnetic phases are interconnected. A close contact required for interphase exchange coupling can be expected in the case of M-type hexaferrites as the hard magnetic phase and the soft

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* Corresponding author. Tel.: +48 618695154.
E-mail address: ahilczer@ifmpan.poznan.pl (A. Hilczer).

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magnetic ferrites of spinel structure, which may fit the S blocks of the hexaferrites [14].

To get a commercial impact and tailor the microstructure for exchanged coupled hexaferrite/spinel ferrite nanocomposites simple chemical reaction and sintering conditions are required. Among the methods used to prepare the nanocomposites one can list the solid state reaction [5], sol–gel technique followed by self-combustion [6,23,26,28,30], modified flux method [8], chemical co-precipitation [10,28], mechanical mixing of hard and soft phases followed by thermal treatment [24], hydrothermal synthesis [30] and one-pot synthesis with ethylene diamine tetraacetic acid [11–27]. The one-pot synthesis route seems to be the most promising because of simplicity and cost-effective due to low-temperature of calcination. We propose solid state reaction in which by tuning the sintering time good magnetic exchange coupling can be obtained in $SrFe_{12}O_{19}/CoFe_2O_4$ nanocomposites. The nanocomposites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and their magnetic and dielectric response was studied in wide temperature range. As the magnetic properties of $CoFe_2O_4$ are determined by magnetic interactions among the cations in tetrahedral and octahedral positions of the spinel structure we studied also the distribution among the cations in tetrahedral and octahedral positions using infrared spectroscopy.

2. Experimental

2.1. Sample preparation

The exchange coupling of the nanocomposites is determined by the weight/molar ratio of the magnetic hard and soft phases, as mentioned in Section 1. The optimum weight ratio of 4:1 has been reported for $BaFe_{12}O_{19}/NiZnFe_2O_4$ composites [24], $BaFe_{12}O_{19}/MgNiZnFe_2O_4$ composites [26] an as well as for $BaFe_{12}O_{19}/CoFe_2O_4$ and $BaFe_{12}O_{19}/MgFe_2O_4$ composites [29]. Our work was aimed at obtaining $SrFe_{12}O_{19}/CoFe_2O_4$ nanocomposites with the weight ratio of magnetic hard to soft phase close to the optimum using simple solid state reaction. $SrFe_{12}O_{19}/CoFe_2O_4$ ferrite nanocomposites were prepared from Co_3O_4 (0.06753 g; Alfa Aesar), Fe_2O_3 (0.806186 g; POCH) and $SrCO_3$ (0.186031 g; Sigma–Aldrich) by solid state synthesis. The substrates were mixed in a home-made ball mill during 6 h and synthesized at $T_s = 1050\,^{\circ}C$ during various time $t_s = 4$, 8, 14 and 22 h in the air. A part of the obtained powders was pressed (0.6 GPa) into pellets ~1 mm thick and for dielectric measurements the samples were covered with Au sputtered electrodes.

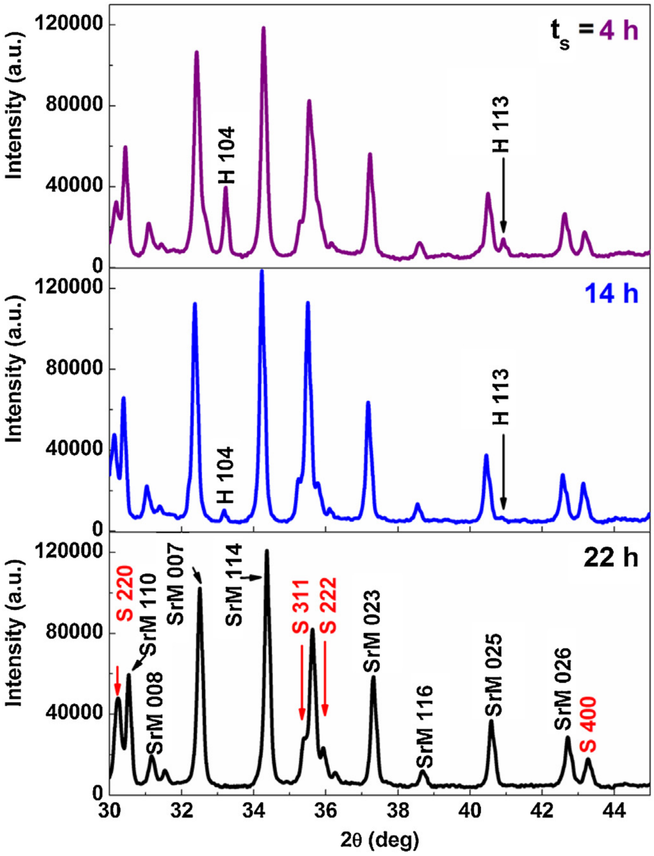

Fig. 1. XRD spectra of powders synthesized at $T_s = 1050\,^{\circ}C$ during $t_s = 4$, 14 and 22 h. SrM denotes $SrFe_{12}O_{19}$ hexaferrite, S stands for $CoFe_2O_4$ spinel and H for Fe_2O_3 hematite.

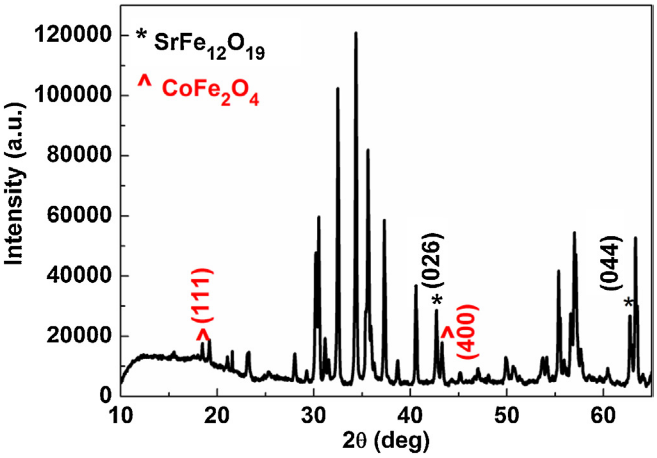

Fig. 2. X-ray diffraction pattern of powder synthesized at $T_s = 1050\,^{\circ}C$ during $t_s = 22$ h.

2.2. Sample characterization

The structure of the powder synthesized by solid state reaction at $T_s = 1050\,^{\circ}C$ and various synthesis time $t_s = 4$, 8, 14 and 22 h was controlled by room-temperature X-ray powder diffraction. The diffraction patterns were collected during 16 h in the reflection mode at Bragg–Brentano geometry in 2-theta range from 10° to

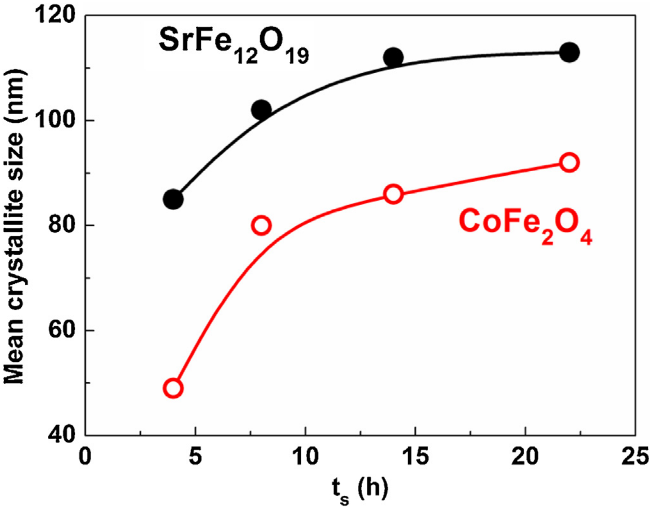

Fig. 3. Mean size of $SrFe_{12}O_{19}$ and $CoFe_2O_4$ crystallites in powders synthesized at $T_s = 1050\,^{\circ}C$ versus the synthesis time t_s.