Nanocrystalline M-Type Hexaferrite Powders: Preparation, Geometric and Magnetic Properties

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Abstract- Co-Ti-Sn-Ge substituted M-type bariumhexaferrite powders with mean grain sizes between about 10 nm and about 1 μm and a narrow size distribution were prepared reproducibly by means of a modified glass crystallization method. At annealing temperatures between 560 and 580 °C of the amorphous flakes nanocrystalline particles grow. They behave superparamagnetically at room temperature and change into stable magnetic single domains at lower temperatures. The magnetic volume of the powders is considerably less than the geometric one. However, the effective anisotropy fields are larger by a factor of two to three.

I. INTRODUCTION

The application of micro- and submicrocrystalline M-type hexaferrite powders for permanent magnets and magnetic recording is well known. Such powders consist of individual single crystalline and single domain hexaferrite particles with diameters of about 40 - 400 nm, which can be produced in different way [1]. We believe that the glass crystallization method [1-6] gives the best particle ensembles [7-10]. In this paper we report on the reproducible preparation and the characterization of *nanocrystalline* Co-Ti-Sn-Ge substituted M-type bariumhexaferrite powders with sizes of a few lattice cells (diameter $\approx$ 10 nm) and a narrow size distribution. The powders have been prepared by means of a modified glass crystallization method. Our nanocrystalline hexaferrite particles behave superparamagnetically at room temperature; they change into stable magnetic single domains at lower temperatures - below the blocking temperature. Obviously, the smallest particles are already paramagnetic. Nanocrystalline hexaferrite powders can be applied e.g. [11] for new ferrofluids - the common ferrofluids consist of Fe or Fe_3O_4 suspensions.

Section II of this paper describes the preparation and the geometric properties of nanocrystalline hexaferrite powders. Structural characterization has been carried out by means of

X-ray diffraction, TEM, HRTEM, and BET. Section III is focused to some magnetic properties.

II. PREPARATION AND GEOMETRIC PROPERTIES OF NANOCRYSTALLINE HEXAFERRITE POWDERS

By means of glass crystallization [1-10] we prepared $BaFe_{12-2x}Co_xTi_{x-y-z}Sn_yGe_zO_{19}$ powders with x=0.8, y=z=0 (Co-Ti);
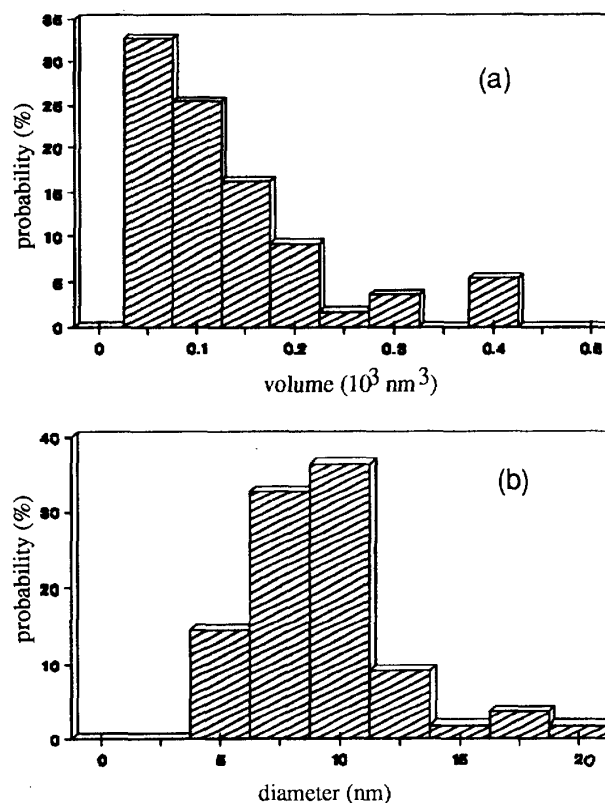
Fig.1. Volume (a) and diameter (b) distribution of the Co-Ti-Sn-Ge powder revealed by TEM

TABLE I
GEOMETRIC AND MAGNETIC PROPERTIES OF Co-Ti, Co-Ti-Sn AND Co-Ti-Sn-Ge POWDERS

geometric properties	Co-Ti	Co-Ti-Sn	Co-Ti-Sn-Ge
TEM mean diameter (nm)	10.2	24.4	8.1
TEM mean thickness (nm)	-	5.3	-
BET specific surface (m²/g)	112	116	124
TEM specific surface (m²/g)	-	88	-
magnetic properties at RT			
specific magnetization at $H \to \infty$ (Gcm³/g)	17.3	21.4	15.0
coercivity (Oe)	8.5	68	15
remanence ratio $M_r/M_{s\infty}$	0.003 (?)	0.07	0.006 (?)
Curie temperature (°C)	360	348	342

x=0.85, y=0.4, z=0 (Co-Ti-Sn) and x=0.8, y=0.25, z=0.10 (Co-Ti-Sn-Ge) characterized in Table 1.

In order to get very small particles by glass crystallization we checked three possibilities: (i) suitable chemical glass compositions, which favour nucleation of barium borate and hexaferrite during annealing of the amorphous flakes [1] (ii) short enough annealing times, and/or (iii) as low as possible annealing temperatures.

Our experiments revealed that very short annealing times of flakes are not convenient in our system because nucleation and crystal growth by diffusion proceeds at higher temperatures ($\geq$ 700 °C) in less than 100 s and at lower temperatures iron oxide compounds are formed. Time intervals in the order of 100 s are too small for the formation of a homogeneous temperature distribution within the flakes. Nanocrystalline particles grow during annealing for longer times at temperatures of 560-580 °C depending on the chemical composition of the flakes. A reduction of the mean particle size by roughly a factor of four is achieved e.g. by Co-Ti substitutions [5,1].

Concerning the unsubstituted ferrites $BaFe_{12}O_{19}$ we improved the nucleation in the flakes by addition of small amounts ($\approx$1 mol%) of suitable compounds. These additions as well as the substitutions mentioned above decrease the temperature necessary for the formation of the hexaferrite phase. It is not sure whether or not such additions are incorporated into the hexaferrite particles.

Fig. 1 as well as Table 1 clearly show that the mean particle diameter reaches a value of about 8 nm. Electron diffraction and HRTEM studies on selected platelets prove the existence of the M-type structure in agreement with former results on microcrystalline particles [8]. The electron diffraction reflexes are slightly broadened because of the low particle sizes. Very small particles possess a spherical shape. The X-ray diffraction measurements disclose very broad peaks. Some reflexes disappear completely.

The specific surfaces of typical substituted nanocrystalline powders are in the range of 100-150 m²/g (see e.g. Table 1).

III. MAGNETIC PROPERTIES

We measured magnetic properties in dependence on temperature (2 - 300 K) as well as field ($\leq$ 50 kOe) and interpreted the experimental results in terms of theoretical models which were developed earlier. The ZFC (zero field cooled) and FC (field cooled) magnetization curves display the typical features of a small particle system [12] as shown in Fig. 2. The maximum of the ZFC magnetization at $T = T_M$ marks the transition from stable (Stoner-Wohlfarth) particles to superparamagnetic ones. $T_M = c<T_B>$ is proportional to the mean blocking temperature $<T_B>$, where $1 \leq c \leq 2$ depends on the width of particle distribution [13].
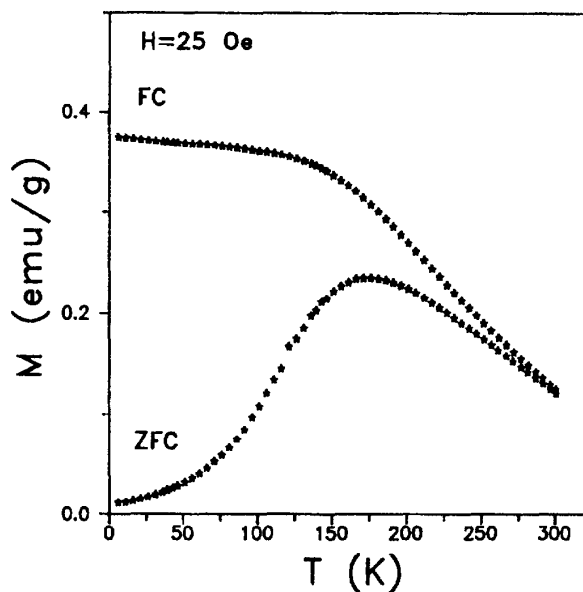

Fig. 2. Magnetization M as a function of the temperature T for the Co-Ti-Sn-Ge powder of Fig. 1 measured under zero field cooled (ZFC) and field cooled (FC) conditions
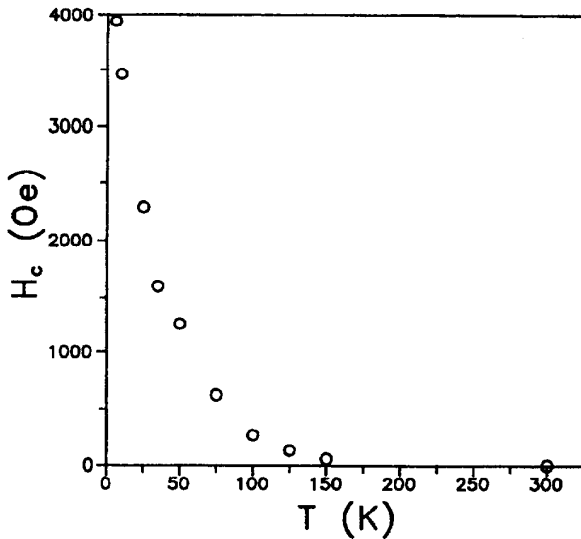
Fig.3. The coercivity H_c of the Co-Ti powder in dependence on the temperature T

The transition "stable" → "superparamagnetic" is presented as well in the temperature dependence of the coercivity given in Fig. 3.

The occurrence of superparamagnetism at room temperature illustrated by the coercivities and the remanence ratios given in Table 1 can be understood easily by the well known relation for the time dependence of the remanent magnetization

$$M_R(t) = M_R(0) \exp(-t/\tau) \qquad (1a)$$

with the reciprocal relaxation time

$$\tau^{-1} = f_0 \exp(-K_{\text{eff}}V/k_BT). \qquad (1b)$$

For $BaFe_{12}O_{19}$ at room temperature the effective anisotropy constant $K_{eff} \approx 3\times10^5$ J/m^3 and the frequency $f_0 \approx 8\times10^9$ s^{-1} are valid; k_B is Boltzmann's constant. As usual we set $\tau = 100$ s and get the critical volume $V = V_c \approx 380$ nm^3 for superparamagnetism. Our actual volumes presented in Fig.1a are smaller. In fact, the K_{eff} values of the Co-Ti substituted barium hexaferrites are even less by roughly a factor of three - however, the K_{eff} values of nanocrystalline particles are larger by a factor of two to three [15]. The effective anisotropy field of the Co-Ti substituted nanocrystalline powder characterized in Fig. 3 amounts 16 kOe at a temperature $T \to$ 0 K.

The magnetic volume and therefore the magnetization of all powders (cf. Table 1) is considerably less than the geometric one caused by effective "dead layers" parallel to the crystallographic c- surfaces of the particles with thicknesses δ

= 1,3 nm for $BaFe_{12}O_{19}$ and δ = 0.7 nm for $BaFe_{10.2}Co_{0.9}Ti_{0.9}O_{19}$ [8]. These data are in good agreement with a value of Kurisu et al. [14], who found δ = 0.8 nm for $BaFe_{10.26}Co_{0.87}Ti_{0.87}O_{19}$. Obviously, the smallest particles are even paramagnetic.

IV. CONCLUSIONS

- Nanocrystalline Co-Ti-Sn-Ge substituted M-type bariumhexaferrite powders with sizes of a few lattice cells (diameter $\approx$ 10 nm) and a narrow size distribution can be reproducibly prepared by means of a modified glass crystallization method.
- The magnetic volume of the powders is considerably less than the geometric one caused by effective "dead layers" parallel to the crystallographic c- surfaces of the particles. The smallest particles are even paramagnetic.
- The Co-Ti substituted nanocrystalline powders exhibit unexpected large effective anisotropy fields of about 16 kOe (at $T \to$ 0 K) measured with different methods. This anisotropy field is larger by a factor of two to three compared with microcrystalline ones.

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