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Single crystal growth, structural characteristics and magnetic properties of chromium substituted *M*-type ferrites

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ABSTRACT

Two different types of fluxes, namely sodium based and chloride based fluxes were used to grow Cr substituted barium and strontium hexaferrite ferrite crystals, $(Sr,Ba)Fe_{12-x}Cr_xO_{19}$ at comparatively low temperatures of about 1300 °C. The sodium based flux led to growth of larger crystals up to 5 mm, but with only minor Cr contents $x \leq 0.07$. From the chloride based flux the obtained Cr contents are significantly higher with $x = 5.7$ (Sr) and $x = 3.4$ (Ba), however, crystals reach only sizes in the sub-mm range. X-ray absorption spectroscopy data support exclusively isovalent substitution of Fe^{3+} by Cr^{3+} even for very low Cr contents. ^{57}Fe Mößbauer spectroscopy reveals Cr to preferentially occupy the six-fold by oxygen coordinated site at $12k$ and, to a lower degree, $2a$ and $4f_2$ in space group $P6_3/mmc$. All characteristic magnetic properties drop upon Cr substitution, e. g., the Curie temperature from 728 K for pure $BaFe_{12}O_{19}$ to 465 K for $BaFe_{8.6}Cr_{3.4}O_{19}$, the saturation magnetization from 71 emu/g to 29.7 emu/g and the coercive field from 363 Oe to 45 Oe.

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1. Introduction

M-type hexagonal barium and strontium ferrites with magnetoplumbite structure and chemical formula $(Ba,Sr)Fe_{12}O_{19}$ are well known permanent magnetic materials, which are widely used in magnetic recording media, microwave devices and electromagnetic shielding fields [1,2]. These materials possess high Curie temperature, high coercive field and high magnetic anisotropy field, as well as high chemical stability and excellent resistance to corrosion [3,4]. These properties make such ferrites very attractive from a technological point of view. The *M*-type ferrites have shown very promising results for high density magnetic and magneto-optical recording media [5] and are also used as dielectric or magnetic fillers in electromagnetic attenuation materials [6,7]. Recently, a large room-temperature multi-ferroic effect has been observed in barium hexaferrite ceramics, which open up a wide range of potential applications such as multiple-state memory elements, novel memory media, transducers and new functional sensors [8]. Because of high technological interest *M*-type ferrites are being widely studied with the aim of modification of magnetic properties, which is required for different applications. Since $BaFe_{12}O_{19}$ is a material of increased technological interests for magnetic recording media many efforts have been devoted to improve the intrinsic magnetic characteristics both by substitution of Fe^{3+} cations with other paramagnetic or diamagnetic cations [9–11] and/or by developing different synthesis methods such as conventional solid state reaction [12], co-precipitation [13], glass-crystallization [14], hydrothermal synthesis [15], and ammonium nitrate melt techniques [16]. The purpose is to reduce the high magnetocrystalline anisotropy and the strong coercive field to levels suitable for

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magnetic recording media. Generally, the higher the coercive field of the magnetic material, the harder magnetization is to be disturbed by the demagnetization effect and the recording bit of information is more stable. On the other hand, the higher the coercive field, the larger magnetic field is required to change the magnetization in the recording process. In the case of the most intensively studied $BaFe_{12}O_{19}$ the high saturation magnetization ($M_s = 70$ emu/g at room temperature), strong uniaxial anisotropy ($K_1 = 6 \times 0.10^5$ erg/g at 300 K) and high coercive field ($H_c = 0.36$ T) [3,4] of this material can be reduced by substituting Fe^{3+} with a variety of different main group or transition metals like Al, Ti, Mn, Co, Ni, Cu, W, Zn etc. or their mixtures [17–24]. These substitutes are frequently used due to similarities in ionic radii or charges. It has been shown that the resulting magnetic properties of the cation-substituted material are strongly dependent on site preference-occupancy of the cations. In some cases cation substitutions for magnetic Fe^{3+} ions cause severe changes in the coercive field H_c, but they do not affect much the saturation M_s and remanent magnetization M_r. For example, with small substitution by manganese H_c increases by about 30% of magnitude, while M_s decreases by only few % [25]. However, for some substitutions considerable decrease of the saturation magnetization, restricting the use of the hexagonal ferrites for the magnetic recording media has been observed [26]. It is interesting to note that for $SrFe_{12}O_{19}$ the desired coercivity can also be attained without additives by heat treating Sr ferrite powder in the presence of nitrogen, hydrogen or carbon [8].

In this work we report the effect of Cr substitution on magnetic and structural properties of $(Ba,Sr)Fe_{12}O_{19}$ single crystals obtained from two different flux growth techniques. Despite the effect of Cr substitution has been studied earlier [9,27–30], the cation distribution and their effect on magnetic properties have not been completely solved, and satisfactory explanation of the magnetic properties of the Cr modified hexaferrites is still a matter of debate. In addition, the magnetic data available on Cr substituted *M*-type ferrites have been obtained on polycrystalline samples. Since the preparation techniques strongly influence the magnetic properties of this material it is important to study the effect of Fe replaced by Cr as a part of the fundamental investigations of the *M*-type ferrites using high quality single crystals. Therefore, the purpose of this paper is to study magnetic and structural properties of Cr substituted $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ single crystals over wide temperature and substitution ranges.

2. Experimental

2.1. Synthesis

Two different types of fluxes have been used to grow Cr substituted $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$ single crystals. Iron oxide (Fe_2O_3), chromium oxide (Cr_2O_3), barium carbonate ($BaCO_3$) and sodium carbonate (Na_2CO_3) as flux served as starting materials to grow single crystals of *M*-type ferrites with low Cr content (3–7 at %). In this case, the optimal conditions for the crystal growth of non-substituted *M*-type barium hexaferrite $BaFe_{12}O_{19}$ were chosen accordingly to literature data [31]. Compositions of initial raw batches are collected in Table 1. The flux amounted up to 30 wt%.

The initial mixture was ground in an agate mortar and filled into a 30 mL platinum crucible. The crucible was placed in a resistance furnace equipped with a thermocouple PR-30/6 and a precision thermocontroller RIF-101. The specifically designed furnace was described in more detail earlier [32]. The furnace was heated from room temperature to 600 °C with 300 K/h and then to 1260 °C with 100 K/h. The mixture was homogenized in an open crucible in air at 1260 °C for 3 h followed by cooling to 900 °C with 4.5 K/h. At 900 °C the furnace was turned off. The obtained crystals with a size of up to 5 mm were separated from the solidified melt by leaching in hot nitric acid to remove all additional phases (Na_2CrO_4, $NaFeO_2$ according to XRD).

Single crystals with higher Cr content $SrFe_{6.3}Cr_{5.7}O_{19}$ and $BaFe_{8.6}Cr_{3.4}O_{19}$ were grown from $SrCl_2$ and $BaCl_2$ fluxes, respectively. For single crystal growth of Ba (Sr) bearing phases initial amounts of 2.6 (2.5) mmol Fe_2O_3, 2.1 (2.2) mmol Cr_2O_3 and 3.2 (3.0) mmol $BaCl_2$ ($SrCl_2$) were mixed and then pressed into pellets. The final pellets were heated to 1310 °C and kept at this temperature for approximately 40 h within lid-closed Al_2O_3 crucibles. Then the furnace was slowly cooled to room temperature. Black hexagonal platelets with maximal sizes of 1 mm and thickness of about 0.07–0.1 mm were mechanically extracted.

2.2. Characterization

Single crystal X-ray diffraction was carried out using a four-circle diffractometer NONIUS κ-CCD, Bruker AXS at ambient temperature with monochromatic MoK_α radiation. Powder X-ray diffraction analyses of powdered crystals was performed on a RigakuUltima IV diffractometer in the angular range from 10° to 80° with the speed of 0.5°/min using CuK_α radiation. Since we are unable to distinguish between those two 3*d* metal species by standard X-ray diffraction techniques due to the similar number of electrons, the compositions of all obtained crystals with respect to the Fe/Cr ratio were investigated by μ-probe using an electron microscope Jeol JSM7001F with an energy dispersive spectrometer Oxford INCA X-max 80 for elemental analysis.

A $^{57}Co/Rh$ source was available for the ^{57}Fe Mößbauer spectroscopic investigations. The sample was placed within a thin-walled PMMA container at a thickness of about 10 mg Fe/cm^2. The measurement was conducted in the usual transmission geometry at 78 K. Mößbauer spectroscopy was applied to determine the transition metal site occupancies and the related hyperfine fields.

The DC magnetization of $SrFe_{6.3}Cr_{5.7}O_{19}$ and $BaFe_{8.6}Cr_{3.4}O_{19}$ single crystals was measured over a temperature range 2–300 K in applied magnetic fields up to 5 T using a Quantum Design MPMS7 Magnetometer. Magnetic properties of powdered crystals with low Cr content (substitution level $x \leq 0.07$) were studied using a vibrating sample magnetometer LakeShore 7407 in magnetic fields up to 1.6 T at room temperature. Curie temperatures were determined using differential scanning calorimetry on a Netzsch 449C Jupiter thermal analyzer. The samples were placed into a crucible and heated in air at a rate of 2 K/min up to 800 °C. The phase transition temperature was determined using the peak positions in heating and cooling cycles.

The Cr and Fe–*K* edge X-ray absorption spectra (XAS) were measured at NSRRC 16a beamline in Taiwan, which is equipped with a double crystal Si(111) monochromator for the photon energy range from 2000 eV to 8000 eV. The energy resolution around Cr and Fe–*K* edges is about to 0.5 eV. The Fe-$L_{2,3}$ XAS spectra were measured at NSRRC 11a beamline in Taiwan. The energy resolution at the Fe-$L_{2,3}$ edge is set to 0.25 eV.

3. Results and discussion

3.1. Crystal growth and structure characterization

We have investigated two different approaches for flux-growth of Cr substituted magnetoplumbite $Ba(Sr)Fe_{12}O_{19}$ crystals, namely an alkali metal oxide-based flux and an alkaline-earth metal chloride-based flux both from reaction of iron(III) and chromium(III) oxides. By using these techniques the crystal growth temperature can be reduced to about 1300 °C, compared with

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