

Ba(Fe_{0.5}Nb_{0.5})O₃ STUDIED BY MÖSSBAUER SPECTROSCOPY AND SQUID MAGNETOMETRY

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Abstract

The ceramic multiferroic barium iron niobate BaFe_{0.5}Nb_{0.5}O₃(BFN) studied in this work belongs to the single-phase perovskites exhibiting high value of dielectric permittivity [1].

The aim of our study was to clarify the transition temperature to magnetically ordered state from the temperature dependence of the hyperfine parameters and magnetic measurements.

The sample was prepared by the solid-state method. Scanning Electron Microscopy/Energy Dispersive Spectrometry (SEM/EDS) and X-ray fluorescence analysis (XRF) and X-ray diffraction (XRD) were employed for sample characterisation and check of the element and phase composition.

The Mössbauer measurements were carried out in the temperature range 4.2–300 K with the in-field spectrum taken in external field of 6 T at 4.2 K. Magnetic ordering transition was found in a relatively wide range of temperatures around 25 K. The in-field spectra indicate antiferromagnetic ordering.

ZFC and FC susceptibilities were measured by a SQUID magnetometer. The onset of the antiferromagnet phase is at about 28 K.

1. Introduction

Multiferroics—the name of a wide class of materials was introduced by H. Schmid in [2] as common designation of materials simultaneously exhibiting (ferro, ferri or antiferro)magnetic and ferroelectric ordering. These materials provide growing application potential and are widely used in electronics or sensors. But the interaction between magnetic and electric subsystems in the material is not fully understood yet.

BaFe_{0.5}Nb_{0.5}O₃(BFN) is an interesting highly dielectric lead-free material. It is a member of an extensive family of ABO₃ compounds with multiferroic properties and forms perovskite (like) crystal structure, where Ba ions occupy A sites, Nb and Fe share the B sites. BFN was first synthesized via solid-state reaction by Saha and Sinha in 2002 [3]. The only magnetic ions in the compound are the ferric ions; as they share the B sublattice with non-magnetic Nb the resulting disorder plays key role in magnetic properties [4]. The monoclinic (but close to cubic) structure at room temperature with $\beta = 89.93^\circ$ ($a = 4.020 \text{ \AA}$, $b = 4.0642 \text{ \AA}$ and $c = 4.0638 \text{ \AA}$) and a giant dielectric response with a dielectric relaxation has been reported [5]. BFN exhibits a ferroelectric phase transition (T_c) at $\sim 520 \text{ K}$ [6] and a transition to antiferromagnetic or weakly ferromagnetic phase (T_N) at $\sim 25 \text{ K}$ [7].

Influence of the magnetic moment ordering of ferric ions on the hyperfine fields of resonating nuclei ⁹³Nb, ¹³⁵Ba, ¹³⁷Ba in their proximity was observed in [8]. Effect of Ba

doping on magnetic properties of multiferroics $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ was also studied by EPR and magnetic methods [9].

In this work we present results of the measurement of temperature dependence of hyperfine parameters (^{57}Fe nuclei) carried out by Mössbauer spectrometry and macroscopic magnetic properties determined by SQUID magnetometry.

The sample in form of dark brown hard ceramic tablet (diameter ~ 12 mm, thickness ~ 1 mm) was prepared by solid-state reaction from high purity precursors BaCO_3 , Fe_2O_3 , Nb_2O_5 by Prof. I. P. Raevsky at Southern Federal University in Rostov, Russia [10].

2. Experimental results

a/ Chemical composition of the sample (SEM/EDS and XRF)

SEM/EDS analysis of the sample was done by electron microscope JEOL JSM-6510 (acceleration voltage 15 kV). Chemical composition was investigated on fractures of the sample, i.e. inside the tablet. The composition of the sample by EDX is close to the declared one: Fe(23.2%) : Nb(25.4) : Be(51.4%) and no impurity elements were found in the sample interior.

Chemical composition of the tablet surface was checked by XRF by equipment EAGLE III μ -Probe (rtg-tube voltage 40 kV). The data were taken at 5 different surface points and the result was obtained as the sum of these 5 measurements. Concentrations of Ba, Fe, Nb and more impurities are only approximately given by the semiquantitative method. The impurity elements Al ($\sim 7.8\%$), Ca ($\sim 0.3\%$) and Sr ($\sim 0.4\%$) were detected in the surface layer. The ratio of the main elements (Ba-Fe-Nb) was biased due to presence of impurities.

b/ X-ray diffraction

Diffraction patterns were collected from powdered sample with a PANalytical X'Pert PRO diffractometer with Co X-ray tube and K line in the range of 2θ from 30° to 130° - Fig. 1. Qualitative analysis was performed with the HighScorePlus software package (version 3.0.5), Diffrac-Plus software package (version 8.0) and JCPDS PDF-2 database [11].

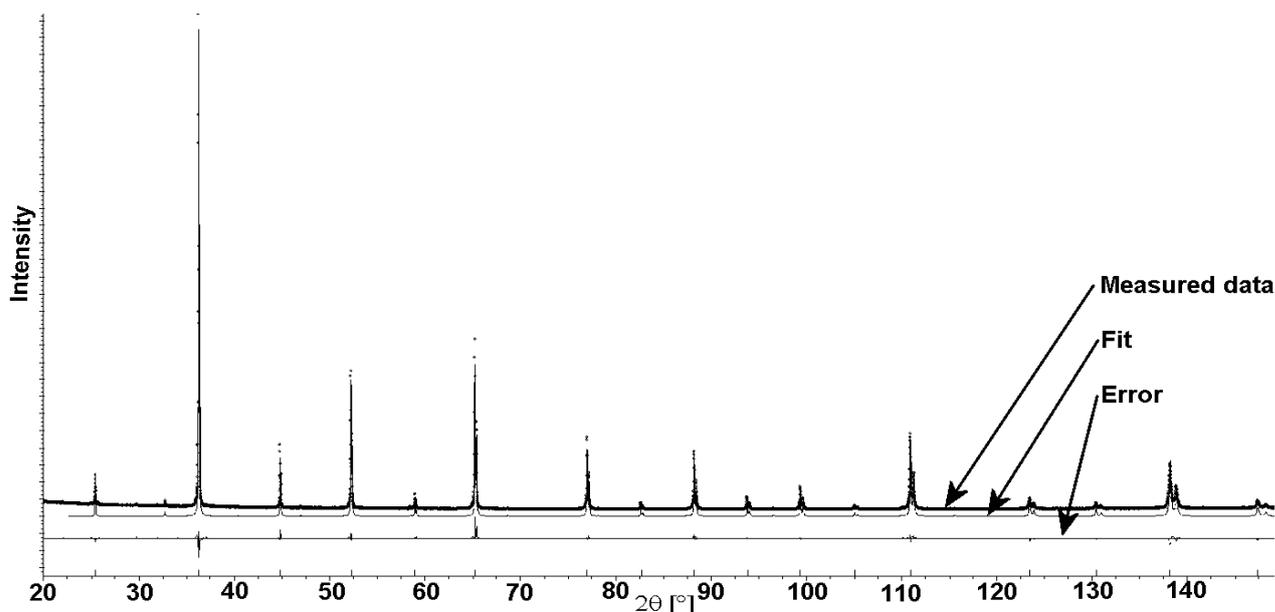


Fig. 1. Diffraction record of the sample

The space group of the sample is cubic (221, Pm-3m) with lattice constant $a \approx 6.062(6) \text{ \AA}$. The result is slightly different from [5], where the monoclinic structure with small tilt angle and close values of lattice constants a , b and c are reported. No phase impurities were detected in the sample.

c/ Magnetic measurements

The magnetic measurements were carried out using the SQUID magnetometers MPMS-5S and MPMS-XL (Quantum Design). The zero-field (ZFC) and field-cooled (FC) susceptibilities were measured for $H = 500 \text{ Oe}$. The ZFC and FC curves start to diverge at $T_g \approx 28 \text{ K}$. The maxima in ZFC susceptibility are typical for the spin or cluster glass behaviour. The Neel temperature can be better seen from the derivative of the FC temperature dependence. The onset of the antiferromagnetic phase is at about 28 K. (Fig. 2).

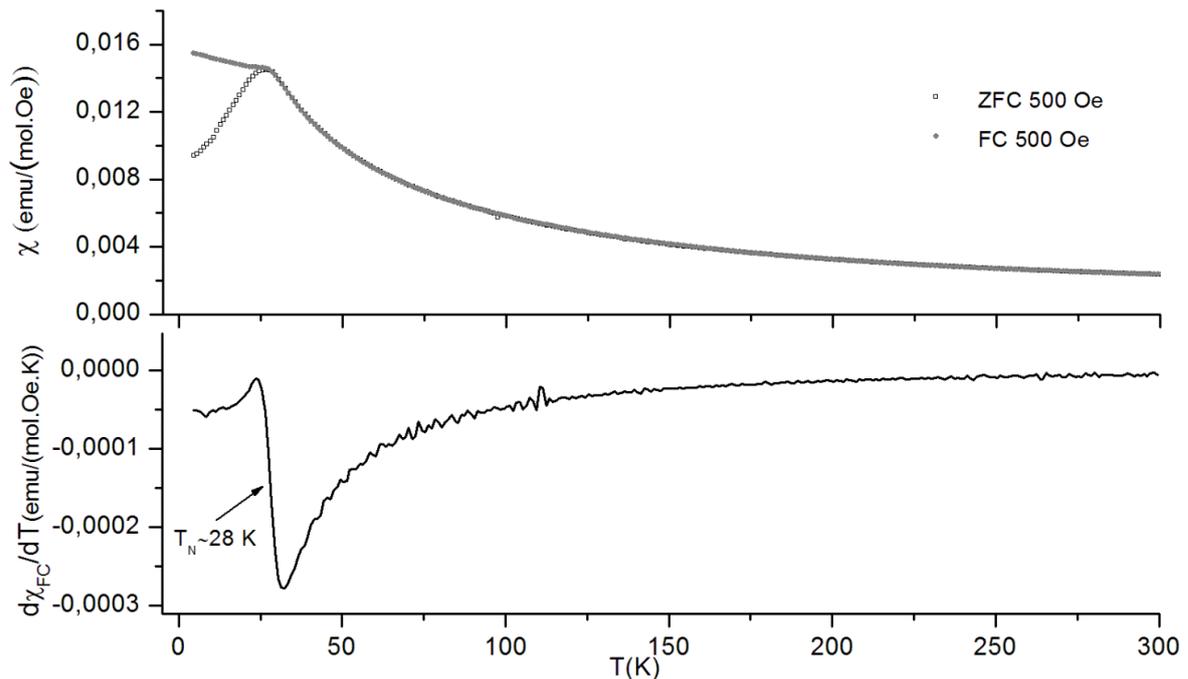


Fig. 2 ZFC/FC measurements for 500 Oe (top), derivative of the χ_{FC} temperature dependence (bottom)

d/ Mössbauer spectrometry

^{57}Fe Mössbauer spectra of the powdered sample were collected in transmission geometry using a constant-acceleration spectrometer equipped with a standard 50 mCi $^{57}\text{Co}/\text{Rh}$ source. The weight of the powder sample was about 15 mg at circular area of $\frac{1}{2}$ inch diameter. The calibration of the spectrometer was carried out using an α -Fe foil (thickness 12.5 μm) and isomer shifts are given with respect to its RT Mössbauer spectrum. The temperature-dependent spectra were acquired in Janis bath cryostat from 4.2 K to room temperature. The in-field spectrum was obtained at 4.2 K in magnetic field of 6 T oriented perpendicularly to the direction of the γ -ray. Spectra were evaluated using the current version of CONFIT [12] and MossWin@[13] fitting programmes.

Due to presence of the heavy ion (Ba) in the sample, it is difficult to obtain spectrum with sufficient quality in reasonable time. Spectra, especially at low temperatures under magnetic ordering temperature, display relatively high noise.

The Mössbauer spectrum acquired at 4.2 K was fitted by 5 sextets (Fig. 3), with their relative intensities in fitting procedure adjusted to the assumed random distribution of Nb atoms in the nearest neighbourhood of Fe atoms respecting the equal concentration of Fe and Nb in the samples. Quadrupole splitting is close to zero for all sextets. The doublet D1 originates from traces of Fe in the Al foil, covering powder samples. The sextet S₅ with the lowest hyperfine field comes from the unresolved contribution of Fe atoms with 4 and more Nb n. n., provided their moments remain ordered.

Spectra measured at various temperatures are displayed in Fig. 4. The transition to magnetically ordered state occurs in a relatively wide temperature interval and Néel temperature TN could be estimated to about 25 K. Wide interval of transition temperatures indicates poor phase or chemical purity of the sample.

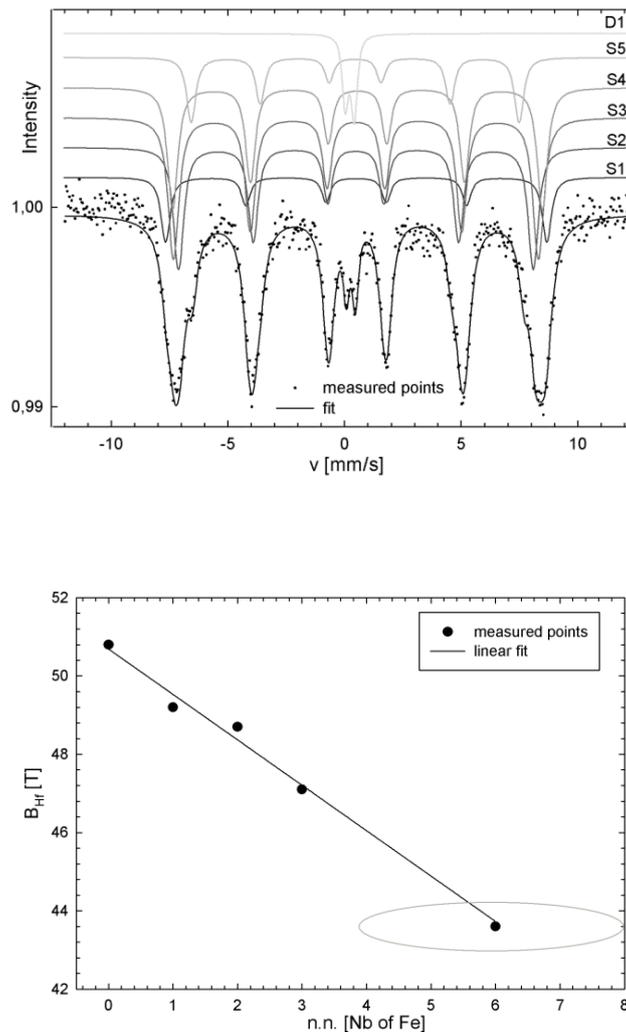


Fig. 3 Fit of the Mössbauer spectrum acquired at 4.2 K (upper) and dependence of B_{Hf} on number of Nb atoms in nearest neighbourhood of Fe atoms (lower).

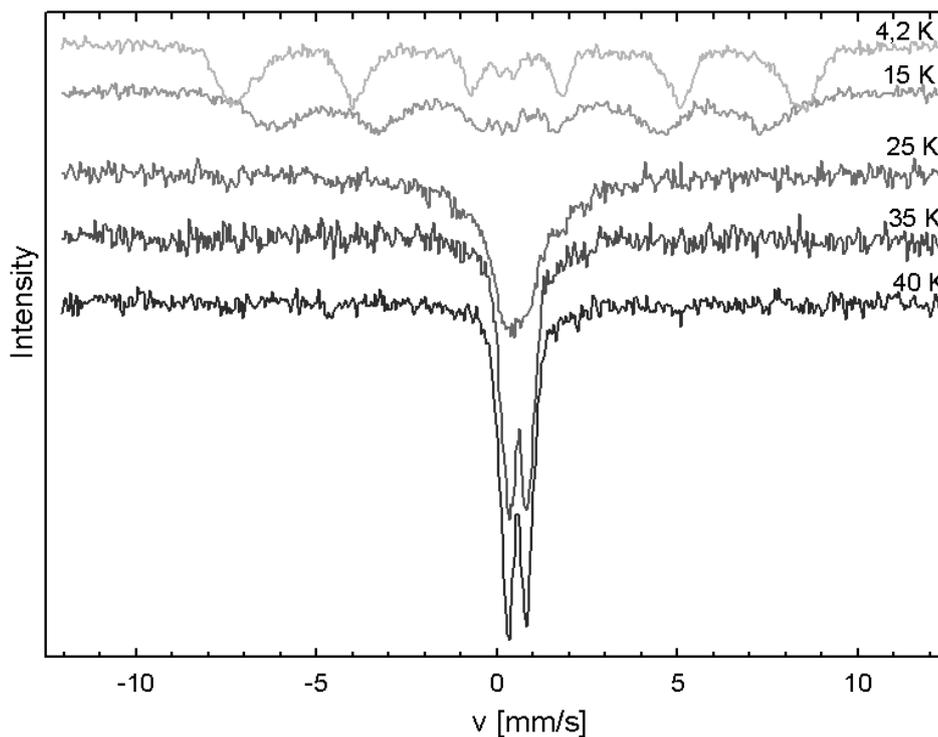


Fig.4 Temperature dependence Mössbauer spectra around the magnetic ordering transition

Comparison of the in-field spectrum acquired at 4.2 K in external magnetic field $B_{\text{app}} = 6 \text{ T}$ with the spectrum at 4.2 K without magnetic field indicates the type of magnetic arrangement (Fig. 5). The behaviour of the spectra in an applied magnetic field B_{app} and without field is typical for an antiferromagnetic state, but allowing for weak ferromagnetism.

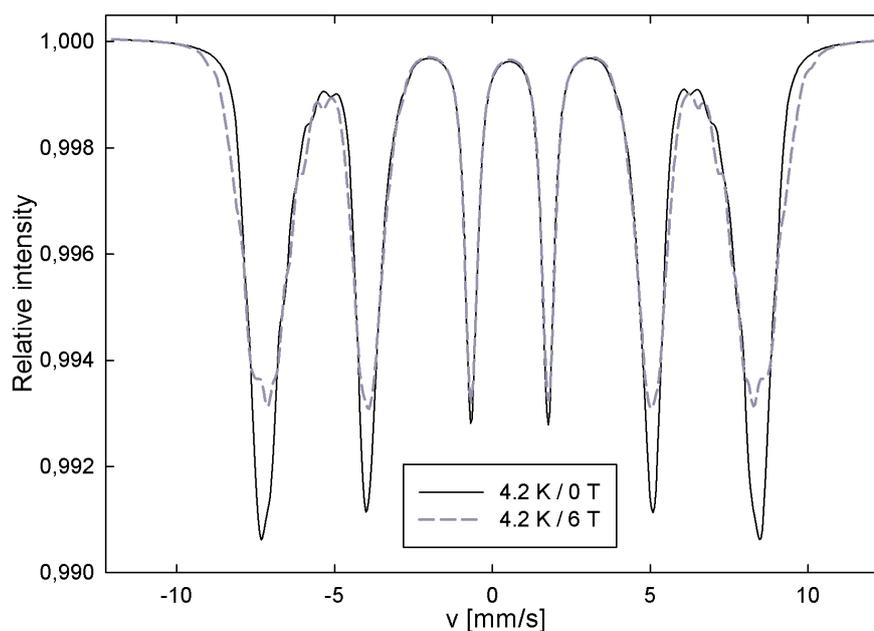


Fig. 5 Comparison of the fits of the in-field spectrum (6 T) and spectrum without external magnetic field recorded at 4.2 K

Conclusions

From the temperature dependence of the Mössbauer spectra of the BFN sample a broad magnetic ordering transition was found at temperatures around 25 K in reasonable agreement with the transition observed in magnetic susceptibility. The Mössbauer spectrum at 4.2 (well under the magnetic ordering temperature) is consistent with the anticipated random distribution of Fe and Nb atoms. Behaviour of the spectra of the BFN sample in external magnetic field indicates an antiferromagnetic ordering (allowing for weak ferromagnetism) in agreement with the results of the magnetic measurements.

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