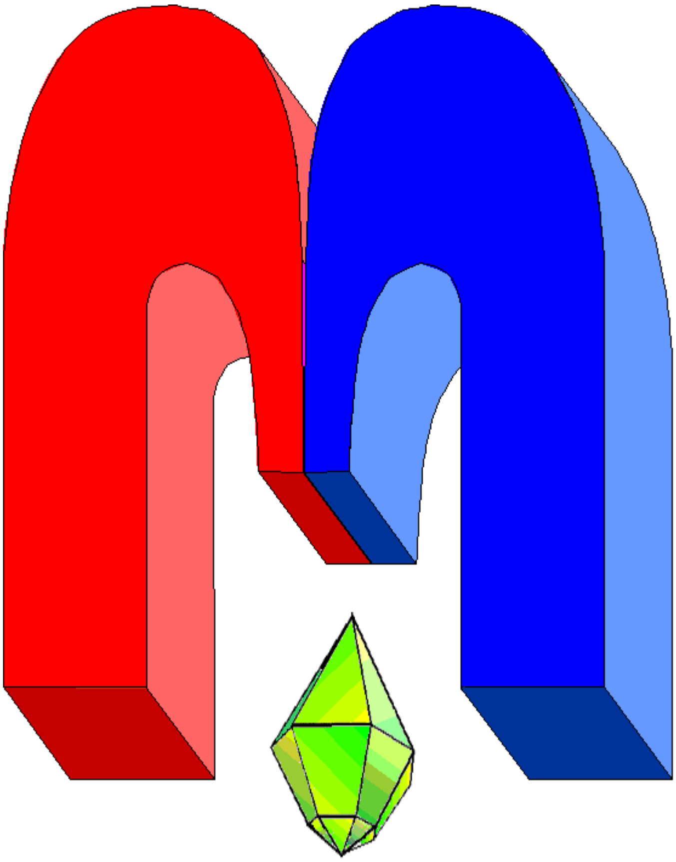
ISSN 2072-5981
doi: 10.26907/mrsej



Magnetic Resonance in Solids

Electronic Journal

Volume ***21***
Special Issue 3
Paper No ***19307***
1-7 pages
2019
doi: **10.26907/mrsej-19307**

http://mrsej.kpfu.ru
http://mrsej.ksu.ru

Established and published by Kazan University
Endorsed by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press (#015140),
August 2, 1996
First Issue appeared on July 25, 1997

"***Magnetic Resonance in Solids. Electronic Journal***" (**MRSej**) is a peer-reviewed, all electronic journal, publishing articles which meet the highest standards of scientific quality in the field of basic research of a magnetic resonance in solids and related phenomena.

Indexed and abstracted by
Web of Science (*ESCI*, Clarivate Analytics, from 2015),
Scopus (Elsevier, from 2012), *RusIndexSC* (*eLibrary*, from 2006), *Google Scholar*,
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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Magnetoelectric coupling in Y-type hexaferrite studied by a novel magnetic resonance technique

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(Received March 3, 2019; accepted March 10, 2019; published April 19, 2019)

Magnetoelectric materials with coupled and microscopically coexisting magnetic and electric polarizations have attracted great interest. The motivation behind this interest stems from the novel and interesting physical phenomena involved, but also from possible applications for novel electronic devices. Here we demonstrate the existence of magnetoelectric coupling at room temperature in ferrimagnetic Y-type hexaferrite $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ single crystal. By using a recently developed electrically modulated magnetic resonance spectroscopy, we determined quantitatively the magnetoelectric coupling strength in this compound. Obtained results show that Y-type hexaferrites belong to the rare class of materials with significant magnetoelectric coupling and large magnetic moment at room temperature.

PACS: 75.50.Gg, 75.85.+t, 76.50.+g.

Keywords: FMR, magnetoelectric, hexaferrites.

Preface

This paper is a contribution to the special issue of the journal *Magnetic Resonance in Solids* dedicated to the 85 years of Prof. Boris Kochelaev. One of the authors (A.S) has a pleasure and privilege to collaborate with Boris Ivanovich since many years. This collaboration started at the University of Zürich and continued after my return to Georgia. His deep knowledge of magnetic resonance in solid state and rare ability to reach quantitative results by using theoretical tools, allowed us together with Prof. Alex Müller to gain important insight on the microscopic phase separation and bipolaron clusters formation in cuprate high-temperature superconductors. On behalf of the Tbilisi State University magnetic resonance group I whole heartedly congratulate Boris Ivanovich with the 85th anniversary and wish him continuing good health and creativity for many more years.

1. Introduction

Materials in which ferroelectric and magnetic orders coexist are called multiferroics. Recently, multiferroic materials have attracted unprecedented attention because such materials exhibit so-called magnetoelectric (ME) coupling [1, 2]. The ME coupling is of high technological relevance, since it implies that electrical properties are affected by a magnetic field or, conversely, that magnetic properties can be varied by an electric field. Especially, the electric field control of magnetism is a hot topic because it has multiple potential applications in magnetic memory storage, sensorics, and spintronics [3–5]. Therefore, the ME effect is one of the central subjects in contemporary condensed-matter science.

Finding multiferroic materials suitable for practical applications is a big challenge, however, because there are only very few known compounds which simultaneously display both electric and magnetic order at room temperature. Moreover, for ME effect both ferroic orders should be coupled. At present, of all multiferroic compounds, $BiFeO_3$ is one of the most interesting systems with antiferromagnetic order at Neel temperature $T_N = 650\,\mathrm{K}$ and a ferroelectric transition temperature at $T_C = 1100\,\mathrm{K}$ [6]. There were about 10000 publications devoted to $BiFeO_3$ in the past decade and it remains the leading candidate for room-temperature multiferroic single-phase devices. However, it is far from perfect: its magnetization is too small for many applications because of the antiferromagnetic order, and its dielectric loss and leakage current too large, despite efforts to dope it with various elements. Therefore the quest is to find compounds with large magnetization and sizable ME coupling at room temperature.

Recently iron oxide based materials called hexaferrites attracted attention due to their potential as high-temperature multiferroics [7]. Hexaferrites are ferrites with hexagonal structures. These are one of the oldest and the most extensively used magnetic materials providing endless potential for numerous applications due to their room-temperature ferromagnetic and insulating properties [8]. Depending on the chemical formula they are classified in six main types: M, Y, Z, X, U, W. Kimura et al. explored for the first time interesting ME properties of Y-type hexaferrite $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ [9]. The crystal structure of Y-type hexaferrite can be considered as an alternately stacked spinel (S) and tetragonal (T) blocks along the c axis. This crystal structure belongs to the space group $R\overline{3}m$, which does not allow spontaneous electric polarization. However, strong ME effect was demonstrated in $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ by applying magnetic field H and inducing electric polarization P [9].

Here we report the study of converse magnetoelectric (CME) coupling in Y-type hexaferrite $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$. The CME effect is defined as a change in the magnetization M in response to an applied electric field E. The CME coupling is important, since it provides a simple and efficient way toward manipulating the magnetization by electric fields, and thus can be potentially used to develop new low-power and high-speed spintronic or ME devices. By using the original electric field modulated ferromagnetic resonance technique we were able to detect and quantitatively measure the CME coupling in Y-type hexaferrite at room temperature.

2. Experimental details

The single crystal of Y-type hexaferrite $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ was prepared by flux growth method from high purity starting materials $BaCO_3$, $SrCO_3$, ZnO, Fe_2O_3, Na_2CO_3 in high purity platinum (99.9997 %) crucible. Crystals with sizes up to 3 mm were obtained. The structure and quality of grown single crystals were characterized by X-ray diffraction measurements using Rigaku Supernova single crystal diffractometer. The refined lattice parameters were found to be 5.85 Å and 43.42 Å in $R\overline{3}m$ space group with hexagonal settings. The crystal we used for magnetic measurements had the shape of the platelet with *c*-axis parallel to the crystal plane.

Magnetization measurements were performed using the Physical Property Measurement System equipped with VSM (Quantum Design PPMS and DynaCool).

The ferromagnetic resonance (FMR) measurements were performed with a standard X-band (9.6 GHz) Bruker ER 200D-SRC EPR spectrometer in the temperature range 160-450 K. In order to detect the ME effect, the sample was wrapped in a Scotch tape and placed in a capacitor-like structure between two copper electrodes. AC voltage of frequency 100 kHz from magnetic field modulation unit of the spectrometer after amplification to the necessary amplitude V_m was applied to electrodes. Two different FMR experiments were performed: with standard magnetic field modulation and electric field modulation.

3. Results and discussion

Fig. 1 shows the temperature dependence of zero-field cooling (ZFC) and field-cooling (FC) magnetization of $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ single crystal in applied field $H = 100$ Oe. No difference was observed between ZFC and FC curves. Magnetization exhibits a pronounced peak at 331 K as can be seen in Fig. 1. Such a peak was observed previously in Y-type hexaferrites and was attributed either to ferrimagnetic transition [9,10] or to a transition from a collinear ferrimagnetic spin phase to a proper screw spin phase with decreasing temperature [11].

In order to clarify this question and to gain detailed insights into the development of the magnetic order in $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$, we performed FMR measurements. Strong FMR signals were observed below 400 K. Fig. 2 shows the FMR spectra at some selected temperatures for external magnetic field parallel to the *c*-axis. As can be seen in Fig. 2, below 350 K there is a pronounced shift of the resonance line to lower fields. This indicates that due to magnetic order an internal magnetic field builds up in the sample which adds to the external magnetic field and as a result resonance can be observed in smaller applied magnetic fields. Therefore one can conclude that in $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ the magnetic transition from paramagnetic to ferrimagnetic state takes place around 350 K. This conclusion is also supported by the temperature dependence of magnetic resonance intensity shown in Fig. 3. Below 350 K there is a strong increase of signal intensity. In contrast to EPR, FMR is the resonance of the total magnetization of the magnetically ordered sample. Therefore the strong increase of the resonance intensity is expected below the transition from para- to ferro/ferri-magnetic state. Based on FMR measurements one can conclude that in $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ ferrimagnetic order establishes below 400 K. Therefore the magnetization peak at 331 K shown in Fig. 1 is not due to ferrimagnetic transition, but is probably related to a transition from a collinear ferrimagnetic phase to a proper screw spin phase [11].

FMR signal shows strong angular dependence which was studied as a function of angle θ between magnetic field direction and the crystal *c*-axis. This is due to the magnetic shape anisotropy of the non-spherical sample as well as to the intrinsic magnetocrystalline anisotropy. The minimum of FMR resonance field was found in parallel orientation $\mathbf{H} \parallel c$ ($\theta = 0°$), which indicates that the *c*-axis is the easy axis direction in $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite. In this orientation the linewidth of FMR is also smallest. Away from the *c*-axis direction the FMR line shifts to higher magnetic fields and broadens significantly with maximum linewidth at $\theta = 90°$.

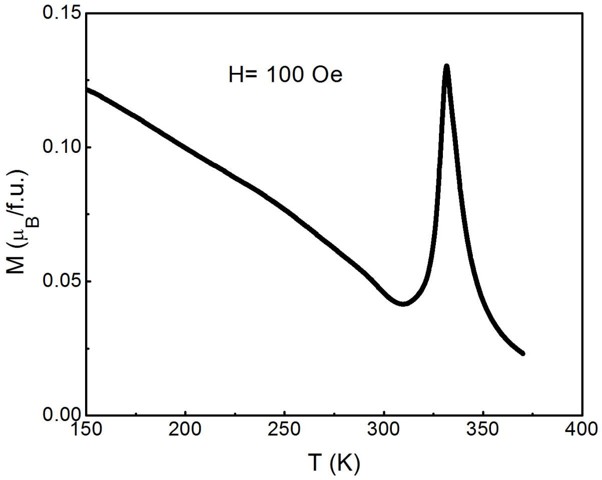

Figure 1. Temperature dependence of the ZFC and FC magnetization in a field of 100 Oe ($\mathbf{H} \perp c$ axis) for the single crystal of the $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite.

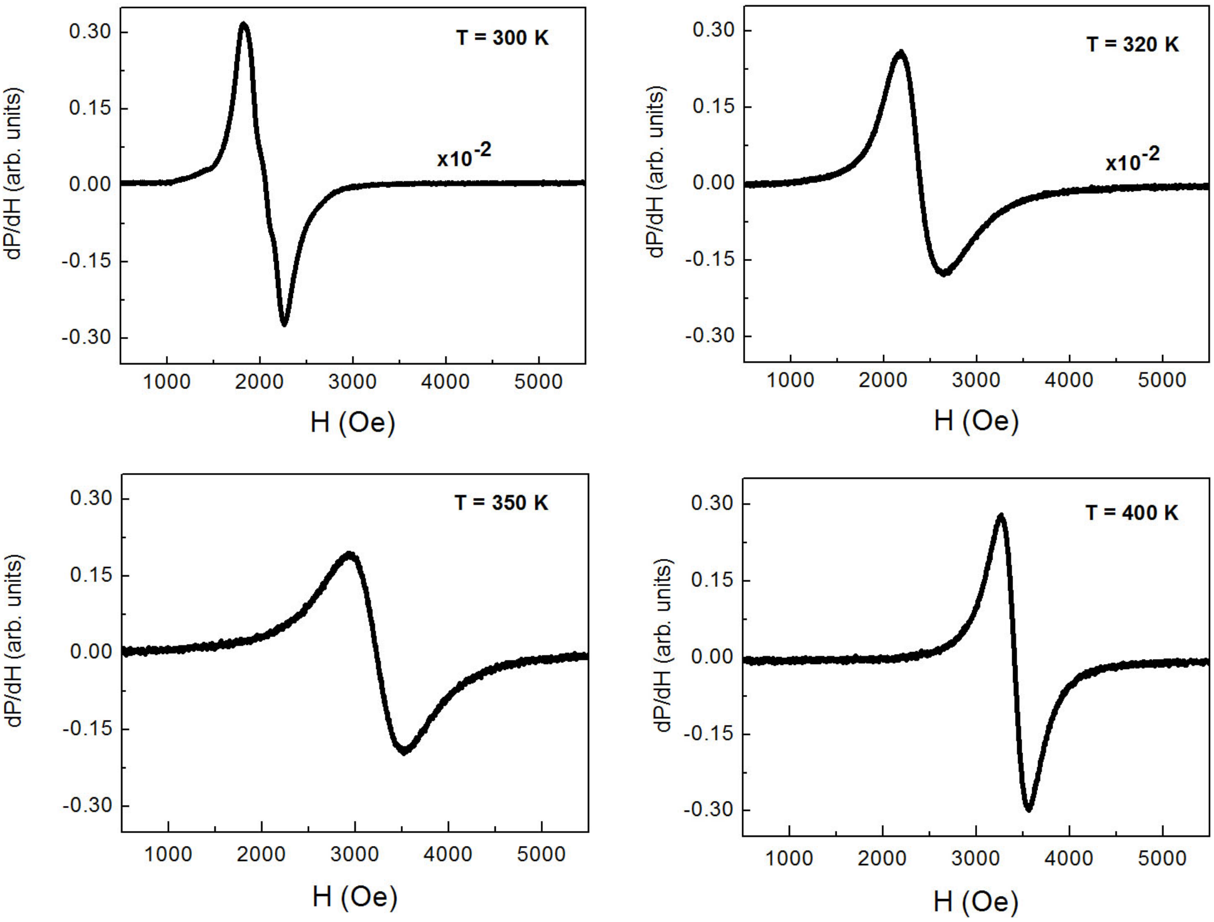

Figure 2. Exemplary FMR spectra of $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ hexaferrite single crystal at selected temperatures for external magnetic field applied parallel to the *c*-axis.

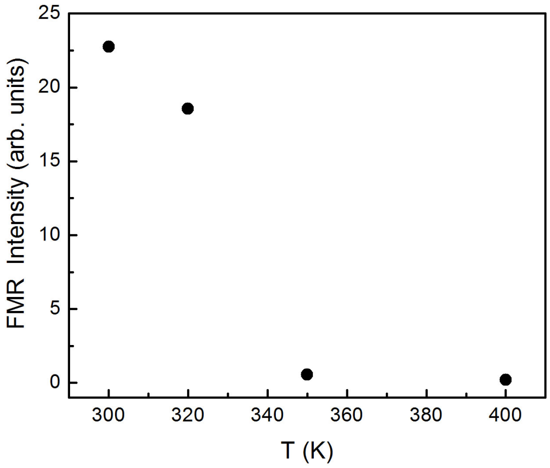

Figure 3. Temperature dependence of the FMR signal intensity in $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$.

Main purpose of the present study was to detect and quantitatively determine the CME effect in Y-type hexaferrite $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ single crystal. In order to detect the ME effect, sensitive and reliable experimental techniques are required, since this coupling is generally quite small. Usually, for the determination of the ME and CME couplings either the electric polarization is measured as a function of magnetic field or the magnetization is studied as a function of an applied electric field [2]. Recently we developed a novel microscopic method for the direct determination of the ME effect based on the standard Electron Paramagnetic / Ferromagnetic Resonance (EPR/FMR) technique combined with electric field modulation (EFM) [12]. Below we briefly describe this method.

In a standard EPR spectrometer, an external magnetic field is swept and the resonance absorption of microwave energy by a Zeeman-split spin system is registered. In addition, to increase the sensitivity, the applied magnetic field H is modulated: $H = H' + H_m \sin(2\pi\nu_m t)$, where H' is the static applied magnetic field, H_m is the modulation amplitude, and ν_m is the modulation frequency. As a result, while sweeping the magnetic field H', the detected microwave absorption power $P(t) = P_m \sin(2\pi\nu_m t)$ is also modulated with the frequency ν_m. The amplitude P_m is proportional to the slope of the absorption signal $P(H)$ as illustrated in Fig. 4. Further amplification and lock-in detection of $P(t)$ results in the EPR derivative signal dP/dH. In the EFM EPR/FMR measurements an oscillating electric field instead of magnetic modulation is applied to detect the resonance absorption. In a spin system without ME effect no modulated signal $P(t) = P_m \sin(2\pi\nu_m t)$ will occur. However, if the ME effect is present, modulation by an electric field $E(t)$ will lead to a modulation of the magnetic field in the sample $B(t)$. In this case the EPR/FMR signal which is proportional to the ME coupling, may be detected as was demonstrated in different compounds [12–14].

For EFM-FMR measurements the hexaferrite crystal was placed in a capacitor-like structure between two copper electrodes. Experiments were performed in two steps. First usual FMR signals were detected using magnetic modulation. Afterwards magnetic modulation cable was removed from the cavity and an AC voltage of a frequency of 100 kHz from the magnetic field modulation unit of the spectrometer after amplification to the necessary amplitude V_m was applied to copper electrodes.

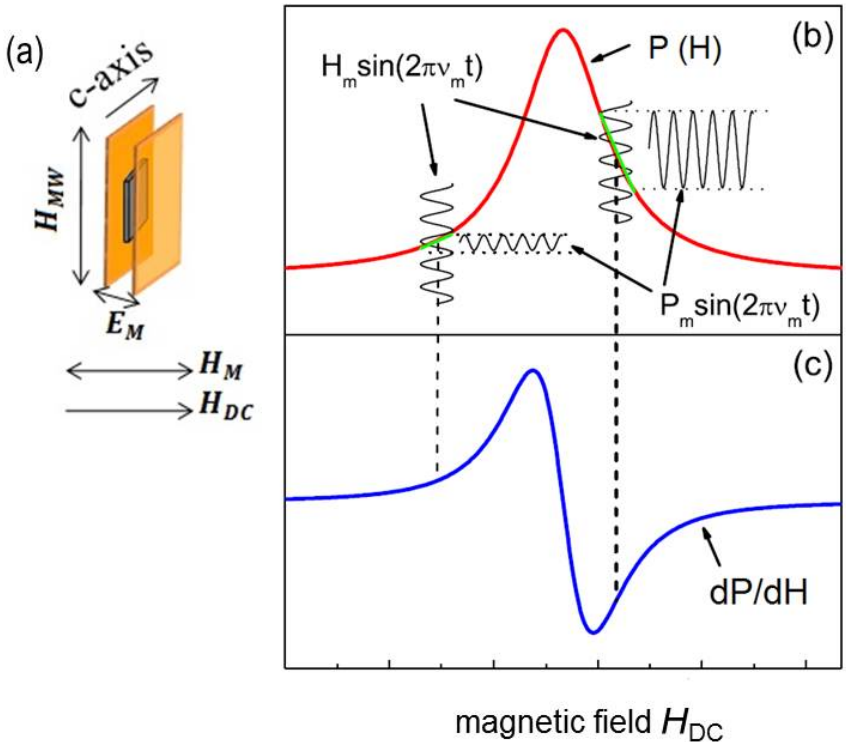

Figure 4. (a) Schematic view of the sample and the magnetic or electric field configuration. The sample is sandwiched between two copper plate electrodes. (b) Basic principle of EPR signal detection. Red curve represents the EPR absorption line $P(H)$. (c) First derivative dP/dH signal of the EPR absorption line $P(H)$ after lock-in detection.

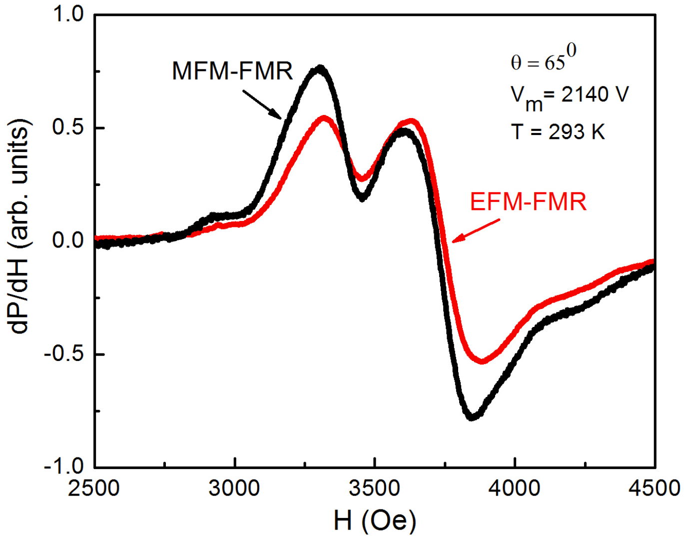

Figure 5. FMR spectra measured in $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ single crystal at room temperature by using MFM (black line) and EFM (red line) techniques.

Fig. 5 shows the FMR signals measured at room temperature by using magnetic (black) and electric (red) field modulations, with a dc magnetic field applied at angle $\theta = 65°$ to the crystal c-axis. This angle was chosen because at $\theta = 90°$ FMR signal was very broad as was mentioned above and it becomes very difficult to extract information about ME coupling at this angle. One can see a clear EFM-FMR signal detected in $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$. Observation of the EFM-FMR signal unambiguously proves the existence of ME coupling in $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ since no signal can be observed in materials that do not possess ME coupling [12].

The ME coupling strength γ can be determined quantitatively from the ratio of the EFM and MFM-FMR signal intensities [12, 13]:

$$\gamma = \frac{I^{\text{EFM}}}{I^{\text{MFM}}} \frac{\mu_0 H_m d}{V}, \tag{1}$$

where I^{EFM} and I^{MFM} are FMR signal intensities detected by electric by magnetic modulations respectively, $\mu_0 H_m$ is the field used in the MFM experiment, V is applied voltage and d is a distance between electrodes. Using Eq. 1 we obtained the ME coupling strength $\gamma = 2.4 \times 10^{-5}$ Oe/V/mm. This is close to the value 2×10^{-5} Oe/V/mm reported for prototypical ME compound Cr_2O_3 at room temperature [15].

4. Summary and conclusions

In summary, magnetic and magnetoelectric properties of Y-type hexaferrite $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ single crystal were studied. It was found that this compound orders magnetically with ferrimagnetic order below about 350 K. A large magnetization peak was observed in small applied magnetic fields at 331 K, which can be attributed to a transition from a collinear ferrimagnetic phase to a proper screw spin phase with decreasing temperature. Microscopic magnetic properties of $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ were investigated by measuring FMR in a broad temperature range. From angular dependence of FMR resonance field it was found that the c-axis is the easy axis direction in this compound.

ME coupling in $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ was studied by using a novel EFM-FMR method. It was shown that this Y-type hexaferrite has significant ME coupling even at room temperature. The ME coupling strength was determined quantitatively and it is comparable to that of the prototype single phase magnetoelectric Cr_2O_3. However, Cr_2O_3 is antiferromagnetic and therefore its total magnetization is too small for many applications, while $Ba_{0.6}Sr_{1.4}Zn_2Fe_{12}O_{22}$ has a large magnetization due to ferrimagnetic order. Obtained results show that Y-type hexaferrites belong to the rare class of materials which combine significant ME coupling and large magnetic moment at room temperature. There is a potential to further increase ME coupling strength in these materials by adjusting their chemical composition.

Acknowledgments

This work was supported by the Shota Rustavely National Science Foundation of Georgia under grant No. FR17_325.

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