Infrared and magnetic characterization of the multiferroic Bi$_2$FeCrO$_6$ thin films in a broad temperature range

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Infrared reflectance spectra of an epitaxial Bi$_2$FeCrO$_6$ thin film prepared by pulsed laser deposition on LaAlO$_3$ substrate were recorded between 10 and 900 K. No evidence for a phase transition to the paraelectric phase was observed, but some phonon anomalies were revealed near 600 K. Most of the polar modes exhibit only a gradual softening, which results in a continuous increase of the static permittivity on heating. It indicates that the ferroelectric phase transition should occur somewhere above 900 K. Magnetic measurements performed up to 1000 K revealed a possible magnetic phase transition between 600 and 800 K, but the exact critical temperature cannot be determined due to a strong diamagnetic signal from the substrate. Nevertheless, our experimental data show that the B-site ordered Bi$_2$FeCrO$_6$ is one of the rare high-temperature multiferroics.

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I. INTRODUCTION

Magneto-electric multiferroic materials which exhibit simultaneously ferroelectric and magnetic order are promising for new generation of random access memories (RAM), where the information can be written by electric field and read non-destructively by magnetic sensing. Such memories avoid the weak points of the ferroelectric RAMs (destructive reading causes fatigue) as well as of magnetic RAMs (high electric current is needed for overwriting, which rules out high integration of magnetic RAMs). Unfortunately, there are not many magneto-electric multiferroics known up to now and only a few of them have both magnetic and ferroelectric critical temperatures above room temperature. Therefore there is nowadays an intensive search for magneto-electric multiferroic materials with high magnetization and spontaneous polarization above room temperature.$^{1-2}$

Baettig and Spaldin predicted from $ab$ $initio$ calculations that the chemically ordered double perovskite Bi$_2$FeCrO$_6$ (BFCO) will have - at zero temperature - a polarization of $\sim 80 \mu C/cm^2$ and a magnetization of $\sim 160 \text{emu/cm}^3$ (2 $\mu B$ per formula unit).$^{1}$ Such properties far exceed the properties of any known multiferroic. Nechache et al., for the first time experimentally prepared epitaxial thin film of BFCO which exhibited at room temperature (RT) a polarization of 2.8 $\mu C/cm^2$ and a saturated magnetization of 0.26 $\mu B$ per unit cell.$^{2}$ Recently Kim et al.$^2$ reported a remanent polarization of 60 $\mu C/cm^2$ at 77 K, for their BiFe$_0.5$Cr$_0.5$O$_3$ solid solution epitaxial film.$^2$ And Alexe even measured 70-80 $\mu C/cm^2$ at RT on the films grown by Nechache et al.$^2$ The magnetic $T_N$ and ferroelectric $T_c$ phase transition temperatures in ordered BFCO are not known up to now. Beattig et al.$^2$ predicted from first principles a Néel temperature $T_N$ near 100 K, which was not confirmed in the experiments performed by Nechache et al., who observed magnetic order at RT. Very recently Suchomel et al.$^2$ prepared BFCO ceramics and observed a magnetic phase transition below 130 K, but it is worth noting that their ceramics exhibited chemical disorder of the $\text{Fe}^{3+}$ and $\text{Cr}^{3+}$ cations on the perovskite B site, which reduces $T_N$. Thus it is not excluded that $T_N$ can be higher in ordered samples as in the case for the ordered BFCO films reported by Nechache at al.$^2$.

Determination of the ferroelectric phase transition temperature is not possible from the low-frequency dielectric measurements due to the too high DC conductivity of the BFCO film. The extrinsic leakage conductivity does not play an appreciable role in the THz dielectric response of the film, therefore high-frequency dielectric studies are advantageous. For this purpose we performed infrared (IR) measurements including investigation in hardly achievable far infrared (FIR) range below 200 cm$^{-1}$, which can give information about the complete phonon contributions to the static permittivity (note that in the case of displacive ferroelectrics only polar phonons are responsible for the dielectric anomaly near $T_c$). Moreover, IR spectra usually change at the ferroelectric (structural) phase transition temperature due to the change of selection rules for IR active polar phonons. Therefore the IR spectra (including FIR) of the BFCO film can help to estimate its $T_c$ as well as the symmetry of the high-temperature phase.

IR studies of ferroelectric thin films are rather rare in the literature and up to now almost only FIR transmission spectra of the films deposited on FIR-transparent substrates like Si, sapphire or MgO were investigated.
FIR transmission can give results only in a limited frequency range determined by the transparency window of the substrates, which is mostly very narrow, particularly at high temperatures (e.g., sapphire is partially transparent only below 150 cm\(^{-1}\) at 900 K). IR reflectance can yield results in a much broader spectral range, but its sensitivity is limited a) by the thickness of the film, b) by the strengths of polar phonons in the IR spectra and c) by the IR properties of the substrate. Our experience shows that the substrates with buffer electrodes are not suitable due to the negative permittivity of the buffer layers, which reduces the sensitivity of the method. Therefore, dielectric substrates, which do not show any strongly temperature-dependent IR reflectivity spectra, are the most suitable for reflectance studies of thin films. Nevertheless, IR reflectance spectra of the thin films deposited on the substrate are strongly influenced by the substrate, since the thin films are partially transparent for the IR wavelength. Therefore both IR spectra of the bare substrate and of the film on the substrate should be measured at the same temperatures and the film properties are evaluated from the spectra fits to such a multi-layer system. This method was used only twice in the literature for room or low-temperature IR studies of SrTiO\(_3\) films.\(^{12,13}\) Here, we will use this method for the first time above room temperature and up to 900 K.

In this paper we shall show that the static permittivity of the BFCO thin film, determined from the polar phonon contributions, increases monotonically on heating to 900 K, due to the phonon softening. Some phonon anomalies, probably connected with a magnetic phase transition, were observed near 600 K, but no dramatic changes, such as those usually related to a ferroelectric phase transition, were observed. Therefore, it seems that the phase transition to the paraelectric phase in BFCO thin film occurs above the highest investigated temperature of 900 K. We shall also report on our study of the magnetic properties of the BFCO film up to 1000 K and we shall show that the magnetic phase transition occurs between 600 and 800 K.

### II. EXPERIMENTAL

BFCO films were grown directly on (100)-oriented SrTiO\(_3\) substrates doped with 0.5 wt\% of Nb (abbreviated STO:Nb) as well as on a (100)-oriented LaAlO\(_3\) substrate, better suited for IR measurements. An epitaxial 210 nm thick film deposited on the conducting STO:Nb substrate was used for Mössbauer spectroscopy and vibrating sample magnetometry studies. XRD and TEM data have shown that the film is epitaxial. Weak superlattice spots showed evidence of partial chemical order of the Fe and Cr cations.\(^{10}\)

The SrTiO\(_3\) substrate exhibits a strongly temperature-dependent FIR spectra due to the presence of an optic soft mode, which gives large inaccuracies in evaluation of the FIR properties of the thin film. We therefore studied FIR spectra of the BFCO film deposited on non-conducting LaAlO\(_3\) substrates with the size 5x10x0.5 mm. Since polar phonons are rather weak in BFCO, we investigated a 600 nm thick film. The relaxed film on LaAlO\(_3\) substrate (orientation (001)) was epitaxial with orientation (100), but it revealed only very weak superlattice spots, so its chemical order in the B site was only partial. XRD analysis of the film on LaAlO\(_3\) revealed a slight Bi-deficiency in the BFCO phase as well as about 5% of Cr-doped Bi\(_2\)O\(_3\) secondary phase, which were not observed for the films on SrTiO\(_3\).

The unpolarized FIR and IR reflectance spectra were taken using a Bruker IFS 113v FTIR spectrometer at temperatures between 10 and 900 K with the resolution of 2 cm\(^{-1}\). An optistat CF cryostat from Oxford Instruments equipped with polyethylene windows was used for cooling the sample down to 10 K, while a commercial high temperature cell SPECAC P/N 5850 was used for heating it up to 900 K. A helium-cooled Si bolometer operating at 1.6 K was used as a detector at low temperature measurements, while pyroelectric DTGS detectors were used for the IR measurements above RT.

Magnetic properties of the BFCO films on substrates 3x3 mm in size were investigated using a PPMS 14 vibrating-sample magnetometer (Quantum design) between 3 and 1000 K.

The Mössbauer spectrum measurement was carried out in the Conversion electron Mössbauer spectroscopy (CEMS) mode with \(^{57}\)Co diffused into an Rh matrix as a source moving with a constant acceleration. The spectrum was accumulated for 7 days. Classical Mössbauer spectroscopy in transmission mode could not be used due to the small volume of the investigated thin films. The Wissel spectrometer was calibrated by means of a standard \(\alpha\)-Fe foil, and the isomer shift was expressed with respect to this standard at 293 K. The fitting of the spectra was performed using the NORMOS program. The CEMS method requires a conducting sample, therefore we investigated the thin film deposited on a conducting STO:Nb substrate, while the films deposited on non-conducting LaAlO\(_3\) were more suitable for the IR studies.

### III. RESULTS AND DISCUSSION

Fig. 1 shows IR reflectance spectra of both a pure LaAlO\(_3\) substrate and a BFCO thin film (deposited on LaAlO\(_3\)) at selected temperatures between 10 and 900 K. Only small temperature dependence of the reflectivity spectra of the LaAlO\(_3\) substrate can be seen, mostly due to an increase in phonon damping with temperature. Also the sharp peaks near 500 and 600 cm\(^{-1}\) gradually disappear due to a second order structural phase transition in LaAlO\(_3\) from trigonal to cubic phase at 800 K.\(^{14}\)

IR reflectance spectra of the semitransparent BFCO film deposited on the opaque LaAlO\(_3\) substrate exhibits more pronounced changes with temperature mainly near 100, 250 and 550 cm\(^{-1}\) (marked by arrows in Fig. 1). For
the detailed analysis we evaluated the complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ of the film (see Fig. 2) using the following procedure: The reflectivity $R(\omega)$ of the bare substrate at each temperature was first fitted using the formula

$$R(\omega) = \left| \frac{\sqrt{\varepsilon^*(\omega) - 1}}{\sqrt{\varepsilon^*(\omega) + 1}} \right|^2,$$

where for the $\varepsilon^*(\omega)$ the factorized form of the complex permittivity was used

$$\varepsilon^*(\omega) = \varepsilon_\infty \prod_j \frac{\omega_{\text{LO}j}^2 - \omega^2 + i\omega\gamma_{\text{LO}j}}{\omega_{\text{TO}j}^2 - \omega^2 + i\omega\gamma_{\text{TO}j}}.$$

$\omega_{\text{TO}j}$ and $\omega_{\text{LO}j}$ denote the frequencies of the j-th transverse and longitudinal phonon, respectively, and $\gamma_{\text{TO}j}$ and $\gamma_{\text{LO}j}$ denote their corresponding damping constants. The high-frequency permittivity $\varepsilon_\infty$ results from the electron absorption processes and from the phonon contribution above 600 cm$^{-1}$. Then the spectrum of the two-slab system (film + substrate) was fitted using the full formula for the coherent reflectance of a two-layer system, where the oscillator parameters of the substrate were fixed, in order to determine the oscillator parameters of the polar phonons in the film. We note that for the film IR spectra we used the classical Lorentz model of the damped harmonic oscillators instead of Eq. (2)

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\Delta \varepsilon_j \omega_{\text{TO}j}^2}{\omega_{\text{TO}j}^2 - \omega^2 + i\omega\gamma_{\text{TO}j}}.$$  (3)

where $\Delta \varepsilon_j$ means the contribution of the j-th mode to the static permittivity. The rest of the parameters in Eq. (3) have the same meaning as in Eq. (2). Eq. (3) is more suitable for the reflectivity fits of phonon spectra with a large TO-LO splitting, when both kinds of phonon modes have different damping. Such a model was necessary to use for a good fit of the LaAlO$_3$ substrate. Eq. (3) is more appropriate for fitting of the reflectivity spectra of phonons with a small TO-LO splitting and/or transmission spectra which do not show up anomalies at LO frequencies. It has fewer parameters and gives acceptable physical results, while the former model can sometimes yield un-physical negative dielectric losses, when the parameters are not properly chosen.

Complex dielectric spectra of BFCO film obtained from the above described fit of the IR reflectance spectra displayed on Fig. 1 are plotted in Fig. 2. The temperature dependence of TO phonon frequencies is plotted in Fig. 3. One can clearly see the shift of most of the phonon modes to lower frequencies on heating (phonon softening). It causes the gradual increase of the static permittivity with rising temperature (see inset in Fig. 2).

Six modes (respectively seven below 200 K) were necessary for the fits. Let us compare the number of observed polar modes with the prediction of factor group analysis. BFCO crystallizes in the rhombohedral space group $R3 - C_3^1$. Bi, Fe and Cr cations have the site symmetry $C_3(1)$, while oxygen ions have the $C_1$ site symmetry. Factor group analysis of the lattice vibrations based on tables published by Rousseau et al. yields the following optic phonons

$$\Gamma_{R3} = 9A(z, x^2 + y^2, z^2) + 9E(x, y, x^2 - y^2, xy, xz, yz).$$  (4)

It means that the $9A$ and $9E$ modes are both Raman and IR active. The analysis gives also additional $1A + 1E$ acoustic modes. The modes with the $A$ symmetry are active in spectra with the electric vector $E$ of the IR wave parallel to the $z$ axis, while the $E$ modes are active in $E \parallel x, y$ spectra. The rest of symbols $(z^2, xy$ etc.) in brackets of the group analysis in Eq. 4 shows components of Raman tensors, in which the phonons are Raman active. Our epitaxial BFCO film is (001) oriented and since we measure the in-plane response, we see mostly the $E$ symmetry modes in our FIR spectra. We resolved 7 modes in the low-temperature spectra although 9 $E$ modes are
allowed. This is quite reasonable, if we take into account that some of the modes have small intensity or they may overlap with other modes. It is worth to note that the TO phonon frequencies in BFCO correspond very well to the E symmetry TO phonon frequencies in chemically and structurally related BiFeO$_3$.

One mode near 50 cm$^{-1}$ disappears from the FIR spectra above 200 K (see black solid squares in Fig. 3). Such change could be a hint of some structural phase transition, but the FIR spectra near 50 cm$^{-1}$ are rather noisy at high temperatures, so we cannot exclude that the mode is present in the spectra also at higher temperatures, but we do not resolve it due to lower sensitivity of the high-temperature FIR experiment. The absence of any other phonon anomalies at higher frequencies also does not give some phase transition near 200 K.

Interesting phonon anomalies are seen near 600 K (see Fig. 3). Some mode frequencies show relatively large temperature changes and splitting of the modes near 490 and 550 cm$^{-1}$ that almost disappears above 600 K. However, it is important to stress that no mode from the doublet disappears above 600 K. Both modes remain in the spectra with similar frequencies near 520 cm$^{-1}$ up to 900 K. Suchomel et al. observed decomposition of BFCO ceramics on heating above 400 °C. This effect could be also responsible for the phonon anomalies seen near 600 K in our film, but we have to emphasize that we did not observe any decomposition in our sample (placed in a vacuum chamber of the spectrometer), because the IR spectra and magnetic properties (see below) were reproducible before and after the thermal cycling.

Phonon anomalies near $T_N = 640$ K, similar to ours in Fig. 3, were observed in Raman spectra of BiFeO$_3$ and they were explained by spin-phonon coupling. We will discuss this possibility below together with the magnetic data.

The phonon frequency changes seen near 600 K can be a consequence of some phase transition, but probably not a ferroelectric one because we see a gradual increase of the static permittivity $\varepsilon'(0)$ (from phonon contributions) on heating (see inset in Fig. 2), while for a ferroelectric transition a maximum in $\varepsilon'/(T)$ should be seen near $T_c$. It seems that the ferroelectric phase transition in BFCO lies above 900 K, like for BiFeO$_3$. Note that BiFeO$_3$ has
a rhombohedral $R3c$ structure with a structural phase transition (according to earlier literature) to cubic paraelectric $Pm\bar{3}m$ phase near 1120 K. Very recent structural studies\textsuperscript{23} revealed an intermediate orthorhombic phase with the space group $C_{2h}^1 - P2mm$ or $C_{2h}^{11} - C2mm$ at temperatures between $\sim 1100$ and $\sim 1200$ K and probably only above $\sim 1200$ K BiFeO$_3$ transforms into the cubic and simultaneously conducting phase.\textsuperscript{23}

If we assume that the structural phase sequence in BFCO is the same as in BiFeO$_3$, than the following factor group analysis of the optic phonons applies in the orthorhombic phase

$$\Gamma_{P2nm} = 10A_1(x, x^2) + 4A_2(xy) + 7B_1(x, xz) + 6B_2(y, yz).$$

(5)

It means that instead of the 18 modes in the rhombohedral structure, 23 IR active modes (13 in $E \parallel x, y$) should be seen in the IR spectra of the orthorhombic phase. Unfortunately, no new mode appears in our FIR spectra, so we do not see any evidence for a phase transition into the orthorhombic phase at temperatures below 900 K.

On the other hand, in cubic paraelectric phase the following optic modes are expected:

$$\Gamma_{Pm\bar{3}m} = 4F_{1u}(x) + 2F_{2u}(-) + 1A_{1g}(x^2 + y^2 + z^2) + E_g(x^2 + y^2 - 2x^2, \sqrt{3}x^2 - \sqrt{3}y^2) + 2F_{2g}(xy, yz, xz).$$

(6)

It seems that only 4 phonons of $F_{1u}$ symmetry should be seen in the FIR spectra and 4 modes ($A_{1g}, E_g$ and $F_{2g}$ symmetries) in Raman spectra. We see 6 modes in Fig. 2. It means that BFCO probably remains in the rhombohedral phase in the whole investigated temperature range up to 900 K and the structural phase transition only occurs, similarly as in BiFeO$_3$, at higher temperatures. The absence of a phase transition from the ferroelectric to paraelectric phase below 900 K is also supported by observed gradual increase of the static permittivity on rising temperature - see inset in Fig. 2. Further investigations, like high-temperature structural or second harmonic generation, are needed for revealing the $T_c$ and symmetry of the high-temperature phase(s).

Let us discuss the magnetic properties of BFCO thin film, which we investigated by means of vibration magnetometry and CEMS Mössbauer spectroscopy. The BFCO film deposited on the LaAlO$_3$ substrate, originally investigated by IR spectroscopy, exhibits a strong diamagnetic signal from the substrate and the magnetic hysteresis loops were only revealed at low temperatures below 20 K (not shown here). It can be explained by a weak B-site order which suppresses the magnetic phase transition temperature. On the other hand, the well-ordered BFCO thin film on the STO:Nb substrate exhibits nice magnetic hysteresis loops not only at RT but also at higher temperatures (see Fig. 2). Negative slope of magnetization at higher magnetic fields seen above 800 K can be explained by a diamagnetic contribution of the STO:Nb substrate, but below 600 K the open hysteresis loop is clearly seen. The value of saturated magnetization is typical for antiferromagnets with weak ferromagnetism induced by a canting spin structure and the value of RT spontaneous magnetization corresponds well to the previously published results\textsuperscript{[5,10]. The low value ($\sim 0.3 \mu_B$/f.u.) of magnetization at saturation of the film regarding the expected theoretical value of $2 \mu_B$/f.u.\textsuperscript{23} could be explained by (i) the Fe-Cr ordering which may be only partial, (ii) the partial chemical disorder that generates an antiferromagnetic antiscissors contribution (Fe-Fe, Cr-Cr), or/and (iii) the partial relaxation of the strain in the film leading to a more distorted structure.

Fig. 4 shows the temperature dependence of the magnetization at various magnetic fields. The magnetic experiments above and below 300 K were performed separately, which is probably the reason of the change of slope seen at 300 K in temperature dependence of mag-
netization measured at 1500 Oe. The magnetization remains nonzero up to 1000 K in the field of 1500 Oe, but the hysteresis loop is very slim at temperatures above 800 K. It is difficult to determine exactly the magnetic phase transition from Fig. [4] and [5] but it seems that it could lie somewhere between 600 and 800 K. It is worth noting that Beattig et al. predicted \( T_N \) in BFCO only near 100 K, which can correspond to recent result of Suchomel et al., who claim, based on transmission Mössbauer spectrum of BFCO ceramics, that \( T_N \) lies below 130 K. Suchomel’s low \( T_N \) can be explained by chemical disorder in the Fe and Cr cations in the [111] direction, while our thin film is at least partially chemically ordered (we observed satellites peaks both in the XRD and in the selected area electron diffraction patterns taken by TEM).

The inset of Fig. 4 shows the room-temperature CEMS Mössbauer spectrum of the BFCO film. Surprisingly, only a doublet is seen, which is typical for the paramagnetic state of Fe\(^{3+}\) ions in the sample, while a sextet is expected in a magnetically ordered state. This is rather puzzling because clear magnetic hysteresis loops are seen in the same sample by vibration magnetometry (Fig. 4). Conversion Electron Mössbauer spectroscopy of \(^{57}\)Fe is based on the detection of electrons with the energy of 7.3 keV which were knocked out of the K shell of the \(^{57}\)Fe atom after re-emission of the gamma quantum originally resonantly absorbed by the \(^{57}\)Fe nucleus. The release is almost instantaneous (within \( 10^{-7} \) s) and has a rather high probability. Most of these electrons are again absorbed in the material, but some of them, depending on the depth, where the electron emission occurs and on the electron work function, reach the surface of the sample and are finally detected. The depth from which the information is collected by the CEMS method is usually \( \sim 200 \) nm depending on the absorption properties of the material, the electrons emitted from deeper regions of the sample do not reach the surface. Our thin film is only 210 nm thick, which means that we should see the CEMS signal from the whole volume of the film. However, the film is not only magnetic but also ferroelectric, and electric field in the ferroelectric domains should substantially influence the work function of the electrons. The ferroelectric domain structure of BFCO is complex and assuming it is similar to that reported for BiFeO\(_3\) the polarization (and related internal electric field) is oriented 41.8° or even 131.8° to the normal surface of (001) oriented thin film. Therefore, the emitted electrons are returned back to the film and most of them lose their energy, are absorbed and do not leave the film. Only electrons emitted from a very thin surface layer (\( \sim 10 \) nm) may reach the surface and are detected in the CEMS experiment. The thin film surface layer is most likely non-magnetic (probably due to chemical disorder of Fe and Cr cations at the surface), therefore only a doublet is observed in our CEMS Mössbauer spectra shown in the inset of Fig. 4 although the volume of the film is magnetically ordered, as seen from the magnetic hysteresis loops measured by vibrating-sample magnetometry.

Nevertheless, we have to stress that we repeated the CEMS Mössbauer experiment also with another BFCO film (thickness 86 nm, STO:Nb substrate), which exhibited strong satellites in the XRD (i.e. a higher Fe and Cr chemical order than in the previous sample), as well as broad magnetic hysteresis loop and still we found only doublet in CEMS spectra typical for the paramagnetic order. Finally, we note that the doublet cannot originate from the substrate, because the Mössbauer spectrum is sensitive only to the Fe cations not present in the STO:Nb substrate.

Parameters of the Mössbauer spectra fit are summarized in Table I. From the Fe isomer shift \( \delta \) the valency of the iron can be clearly estimated. The Fe\(^{3+}\) cations in the oxidic compound have its isomer shift in the range of 0.1-0.5 mm/s while the Fe\(^{2+}\) cations show \( \delta \) in the range of 0.8-1.5 mm/s. Our obtained value \( \delta = 0.39 \) mm/s confirms the absence of Fe\(^{2+}\) states and the presence of only Fe\(^{3+}\) states in the investigated film. Mössbauer spectra also allow determining the site symmetry for Fe\(^{3+}\) cations in the structure. According to Refs. 25, 26, the usual isomer shift values for Fe\(^{3+}\) in the case of the spectra measured at RT are as follows: 0.10-0.30 mm/s for Fe\(^{3+}\) in a tetrahedral site, 0.28-0.50 mm/s for Fe\(^{3+}\) in an octahedral site. When we compare the above-mentioned values with our \( \delta = 0.39 \) mm/s, we can confirm that Fe\(^{3+}\) in BFCO is in the octahedral position.

When we compare our fitting parameters in Table I with the parameters obtained from the Mössbauer spectra (measured in the transmission mode) of disordered ceramics published by Suchomel et al., we can state that both ceramics and surface layer of our thin film have the same or similar non-magnetic structure at RT, although the magnetic measurements by vibrating-sample magnetometry give evidence for a magnetic order in the thin film far above RT.

In the light of our high-temperature magnetic data we can suggest that the phonon anomalies seen near 600 K are due to a magnetic phase transition. Near this temperature a sudden drop of the permittivity is seen, which is typical for spin-phonon coupling. Nevertheless, further magnetic, structural, and dielectric studies are necessary for the confirmation of this suggestion.

| Table I: Comparison of the fit parameters of Mössbauer spectra in Fig. 4 and in Ref. 9. |
|---------------------------------|---------------------|
|                                | Our data | Suchomel et al.  |
|                                | (CEMS)   | (Trans. mode)    |
| Isomer shift \( \delta \)      | 0.39 mm/s| 0.39 mm/s        |
| Quadrupole splitting \( \Delta E_q \) | 0.52 mm/s| 0.48 mm/s        |
| "Peak width"-FWHM (\( \Gamma \)) | 0.39 mm/s| N/A               |
IV. CONCLUSION

The complex dielectric response of a BFCO film was determined by a novel method - IR reflectance of a BFCO thin film deposited on a LaAlO$_3$ substrate. Most of the polar phonons seen in the IR spectra reveal gradual softening on heating from 20 to 900 K, which causes a progressive increase of the static permittivity with increasing temperature. Therefore we speculate that the ferroelectric phase transition lies (similarly to the related BiFeO$_3$) above 900 K, although some phonon anomalies, probably connected with the magnetic phase transition, were observed near 600 K. Magnetic properties of the BFCO thin film were investigated between 6 and 1000 K and revealed that the BFCO film is a good high-temperature multiferroic with a magnetic phase transition that we assumed to take place somewhere between 600 and 800 K. Conversion electron Mössbauer spectrum did not reveal magnetic order in the BFCO thin film in contrast to vibration magnetometry, because the electric field presented in ferroelectric domains extends the track of emitted electrons and prevents their detection from most the volume depth of the thin film. Therefore probably only electrons from the thin skin non-magnetic layer of the film are detected. Further structural, magnetic and dielectric high-temperature studies on a well B-site-ordered samples are in progress.

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