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ABSTRACT

Single phase materials with both spontaneous electric polarization and magnetization are rare, despite remarkable efforts in developing magnetoelectric multiferroics. In this work, a single-phase polycrystalline GdFe\(_{0.5}\)Cr\(_{0.5}\)O\(_3\) (GFCO) thin film was spin-coated onto a platinized silicon substrate. X-ray diffraction data suggest that the film exhibits an orthorhombic perovskite structure with a \(Pbnm\) space group. No other impurity phases were detected. Magnetization measurements reveal the Néel temperature of the GFCO film to be \(\sim 220\) K and illustrate a weak ferromagnetic component at 5 K, which could be due to spin canting. Frequency dependent ferroelectric–paraelectric transition was observed around \(480\) K, indicating the diffuse relaxor-like behavior. The electric field dependent polarization measurements show a lossy behavior below \(200\) K. The electric field dependent dielectric constant (tunability) measured at \(1\) MHz in a wide temperature range reveals that the tunability maximizes near the observed dielectric maxima, which further confirms the ferroelectric to paraelectric transition in the present film.

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I. INTRODUCTION

Multiferroic materials are the ones that possess two or three ferroic properties: ferroelectricity, ferromagnetism, and ferroelasticity.\(^1\) However, this original definition was later broadened to include antiferroic orders.\(^1\) Such materials have been of great interest over the past fifteen years as they provide a platform to not only study the fundamental physics but also show great potential for technological applications.\(^7\) Magnetoelectric multiferroics (ME MFs), in particular, have drawn interest as they show a cross coupling between the magnetic and electric orders in the same phase that enables mutual control of magnetism and ferroelectricity,\(^ -7\) which is crucial for multifunctional device applications, such as spintronics, magnetoelectric memories, filters, attenuators, and transducers.\(^ -6\)

Room temperature ME MFs are crucial for devices to be operated at room temperature.\(^ -5\) At present, finding new single phase ME MF materials and/or improving (ferroelectric polarization, transition temperatures close to room temperature, and stronger ME coupling) already known materials constitutes an important research direction in materials physics. The perovskite BiFeO\(_3\) is a widely studied single phase ME MF material at room temperature with ferroelectric (due to the A-site lone pair) and antiferromagnetic (B-site cation) transition temperatures at \(T_C \sim 1103\) K and \(T_N \sim 643\) K, respectively.\(^7,8\) The magnetically induced electric polarization or improper ferroelectricity has been observed in RMnO\(_3\) (\(R = \text{Tb, Dy}\)) at low temperatures.\(^9\) Different mechanisms of ferroelectricity, such as inverse Dzyaloshinskii–Moriya (DM) interaction, exchange striction, and spin-dependent p–d hybridization,\(^ -10,11\) have been proposed in these types of ME MFs.\(^ -12,13\)

Recently, orthochromites (RCrO\(_3\)) and orthoferrites (RFeO\(_3\)) have been predicted to be promising candidates as single phase ME MF materials since the incommensurate lattice modulation induced by the special spin arrangement in these materials may lead to improper ferroelectricity.\(^ -12,13\) Both these families of compounds mostly crystallize in the orthorhombically distorted perovskite structure with the \(Pbnm\) space group.\(^ -14\) It is promising that the antiferromagnetic transition temperature of orthochromites, i.e., \(T_N^a\), is lower than room temperature, but way higher than...
those observed in some of their manganite counterparts mentioned above.\textsuperscript{12} Nevertheless, the large ME coupling effect could possibly be achieved by tuning the antiferromagnetic ordering temperature toward room temperature by partial substitution of Cr\textsuperscript{3+} with Fe\textsuperscript{3+}. Such efforts have been reported in half doped orthochromite, i.e., RFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} (R = Y, Dy, Sm, and Nd), systems.\textsuperscript{18,20} For example, ME coupling was reported at the magnetic ordering temperature (\(T_N = 261\) K) in DyFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3}.\textsuperscript{17}

Out of various RCrO\textsubscript{3}, GdCrO\textsubscript{3} has \(T_N\) of \(\sim 170\) K, and it shows various novel magnetic features, such as temperature-induced magnetization reversal, temperature-induced magnetization jump, spin reorientation, and giant magnetocalmic effect. Recently, Gd substituted RCrO\textsubscript{3} (R = Ho or Er) was found to exhibit improved magnetocaloric properties, and GdCrO\textsubscript{3} bulk materials displayed the highest relative cooling power, a figure of merit for their applications in magnetic refrigeration.\textsuperscript{13} Thus, it was of great interest to study the half Fe substituted GdCrO\textsubscript{3} (i.e., GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3}) system. Both end members, GdFeO\textsubscript{3} (\(T_N \sim 657\) K) and GdCrO\textsubscript{3}, possess not only a canted antiferromagnetic behavior (with weak ferromagnetic signal) but also a ferroelectric ground state.\textsuperscript{14,15} With increasing iron substitution, \(T_N\) of GdFe\textsubscript{0.5}Cr\textsubscript{1−x}O\textsubscript{3} was found to increase.\textsuperscript{13} For GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3}, the antiferromagnetic ordering occurs \(\sim 250\) K. Dielectric properties of some half doped RFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} materials were studied but only up to room temperature.\textsuperscript{12,20} Moreover, all the studies have so far focused on the bulk RFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} and no investigations have been reported on the GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} thin film. Thin films not only stabilize non-equilibrium phases of materials but also allow strain engineering. From the point of view of applications, thin film offers the possibility to integrate GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} with a variety of devices.\textsuperscript{21} Thus, it is of great interest to investigate not only the magnetic but also dielectric and ferroelectric properties in the thin film of GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} in a wide temperature range. This study aims to synthesize the polycrystalline GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} film and explore its magnetic and dielectric properties in a broad temperature range.

II. EXPERIMENTAL

Polycrystalline GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} (GFCO) thin film was fabricated on Pt (111)/TiO\textsubscript{2}/SiO\textsubscript{2}/Si (100) (from now on written as Pt/Si) by a chemical solution deposition method. Stoichiometric ratios of high purity Gd (NO\textsubscript{3})\textsubscript{3}, Fe (NO\textsubscript{3})\textsubscript{3}, and CrCl\textsubscript{3} precursors were dissolved in acetic acid and used as coating solution. This solution was spin-coated onto the Pt/Si substrate, followed by pyrolysis at 600 °C for 5 min. This process of film coating and pyrolysis was repeated eight times. After the final layer, the sample was obtained by annealing at 700 °C in oxygen atmosphere for 2 h. The film structure was determined by using an x-ray powder diffractometer (XRD, Bruker D2 Phaser) with Cu Ka radiation (\(\lambda = 1.54\) Å). The surface morphology of the film was examined using a field-emission scanning electron microscope (FESEM, JEOL JSM-6335F). The phonon modes of the film were investigated by Raman spectroscopy at room temperature using the Renishaw system 2000 and the 514 nm Ar-ion laser. Dielectric properties were measured using an LCR meter (Agilent E4980A) and a cryostat (from MMR tech) to control the temperature. The electric field dependent polarization was measured utilizing the radiant ferroelectric tester (RT66B). The magnetic behavior of the film was examined using the vibrating sample magnetometer connected to the Evercool Physical Property Measurement System (PPMS) from Quantum Design.

III. RESULTS AND DISCUSSIONS

The structure and morphology of the as prepared sample were characterized by XRD, Raman, and FESEM. Figure 1(a) shows the room temperature XRD patterns of the GFCO thin film deposited on the Pt/Si substrate and of the bare Pt/Si substrate. All peaks in the XRD pattern of the film indicate that the film has crystallized in the orthorhombic perovskite GFCO phase with space group \(Pbnm\), except some peaks, which were assigned to the substrate (marked by asterisks in the graph). No other secondary phase/impurity peaks were detected, which indicates the successful formation of the polycrystalline single-phase GFCO thin film. The lattice parameter was found to slightly increase as compared to pure GdCrO\textsubscript{3} studied before due to the large ionic radii of Fe\textsuperscript{3+} (0.645 Å) compared to Cr\textsuperscript{3+} (0.615 Å). The cross section FESEM images of the GFCO thin film deposited on the Pt/Si substrate (near the film/substrate interface) are depicted in Figs. 1(c) and 1(d). The film is found to be dense and seems to adhere well to the substrate. The thickness of the GFCO thin film is estimated to be \(\sim 445\) nm as indicated by the arrow in the FESEM image [Fig. 1(d)]. Room temperature Raman spectra of the GFCO film and the bare Pt/Si substrate are shown in
Fig. 1(b). The orthorhombic \(Pbnm\) structure is different from the ideal cubic perovskite structure due to two structural distortions, namely, rotation of \(\text{CrO}_6\) octahedra around [101] and [010] as well as displacement of the rare-earth ion. Thus, the symmetry is lowered and according to the group theory, the orthorhombic \(Pbnm\) structure with four formula units per unit cell could give rise to 24 Raman active modes; \(7A_2 + 5B_{1g} + 7B_{2g} + 5B_{3g}\). The present GFCO film exhibited six prominent Raman modes out of 24 in the measurement range that can be distributed into three regions: (i) region I (below 200 cm\(^{-1}\)), (ii) region II (200–380 cm\(^{-1}\)), and (iii) region III (380–500 cm\(^{-1}\)). Region I was characterized by two sharp peaks (~139 cm\(^{-1}\) and ~158 cm\(^{-1}\)) corresponding to the stretching vibrations induced by displacements of the Gd ions. Bands in mid-spectral region II are sensitive to the orthorhombic distortion of the lattice (hence, more important here) and largely related to Fe/CrO\(_6\) octahedral tilting and were assigned to \(B_{2g}\) and \(A_g\) modes at 250 cm\(^{-1}\), \(B_{2g}\) at 283 cm\(^{-1}\), and \(A_g\) at 324 cm\(^{-1}\). Peaks in region III are mainly due to the motion of oxygen ions or vibrations of Cr/FeO\(_6\) octahedra. The band at around 472 cm\(^{-1}\) could be assigned to \(B_{2g}\) and \(A_g\) that are associated with out of phase bending and octahedral bending of Fe/CrO\(_6\), respectively. In GdCrO\(_3\), the \(\text{CrO}_6\)–Cr (out of plane) bond angle is 145.36° and the \(\text{Cr}–\text{O}\) bond length is 2.0218 Å. In GdFeO\(_3\), the \(\text{Fe}–\text{O}\)–Fe (out of plane) bond angle is 145.07° and the \(\text{Fe}–\text{O}\) bond length is 2.038 Å. Thus, it can be inferred that GdFeO\(_3\) is more distorted than GdCrO\(_3\) and consequently GdFeO\(_5\)Cr$_2$O$_3$ in the present case is expected to have more orthorhombic distortion than in GdCrO\(_3\). In GdFeO\(_3\), the \(\text{FeO}_6\) octahedra around \([101]\) and \([010]\) as well as displacement of the rare-earth ion. Thus, the symmetry is lowered and according to the group theory, the orthorhombic \(Pbnm\) structure with four formula units per unit cell could give rise to 24 Raman active modes; \(7A_2 + 5B_{1g} + 7B_{2g} + 5B_{3g}\).

Figure 2(a) shows the temperature dependent magnetization (\(M\)) of the GFCO film recorded under zero field cooling (ZFC) and field cooling (FC) modes at 1000 Oe, in the temperature range of 5–300 K. It should be mentioned that the sample was also measured at 50 Oe magnetic field. Negative magnetization was not observed in the entire measured temperature range as has been reported for GdCrO\(_3\) material. However, the ZFC data measured at 50 Oe were noisy for temperatures >120 K due to resolution limit of the VSM system. In single crystal GdCrO\(_3\), with decreasing temperature, paramagnetic to antiferromagnetic (G-type) transition (\(T_{N2}^{\text{G}}\)) was reported at ~170 K along with spin reversal at 7 K and Gd ordering at 2.3 K. The spin reversal observed in the parent compound (GdCrO\(_3\)) was not found in the present GFCO film and believed to be suppressed with Fe substitution. In Fig. 2(a), the ZFC and FC magnetization curves slightly bifurcate at about 270 K. The \(dT\/dT\) vs temperature (\(T\)) graph as shown in the inset may indicate the Néel temperature (\(T_N\)) of the GFCO film at ~ 220 K. However, the data were noisy in the 150–300 K range. \(T_N\) for hydrothermally synthesized powder of GFCO was reported to be 258 K (with 1000 Oe), which was determined by a change of slope in the \(1/\chi\) vs \(T\) plot. For the GFCO powder prepared by the sol-gel method, \(T_N\) was reported at ~250 K with 2000 Oe. Thin films, in general, could show a slightly different transition temperature as compared to the bulk material. \(T_N\) in the present film is still close to those stated earlier, and no impurity phase was detected through XRD or Raman measurements; we believe the shift in \(T_N\) is entirely due to structural distortion in GdCrO\(_3\) due to Fe substitution. The temperature dependence of inverse susceptibility of the present GFCO film in the paramagnetic region was fitted by the Curie–Weiss (CW) law, \(\chi = C/(T - \theta)\), where \(C\) is the Curie constant and \(\theta\) is the Weiss constant. The Curie–Weiss fitting represented by the red line in Fig. 2(b) yielded \(\theta = -297.50\) K, indicating the dominant antiferromagnetic (AFM) exchange interaction in the film. Below 20 K, a rapid increase in the magnetization is observed in both the ZFC and FC, which is believed to be due to the strong paramagnetic contribution of the Gd\(^{3+}\) ions (\(T_{N2}^{\text{G}}\) ~ 2.3 K) compared to the relatively weak AFM interactions between Fe\(^{3+}\)–O–Fe\(^{3+}\), Cr\(^{3+}\)–O–Cr\(^{3+}\), and Fe\(^{3+}\)–O–Cr\(^{3+}\) below \(T_N\).

Figure 2(c) depicts the magnetic field (\(H\)) dependent magnetization (\(M\)) of the GFCO thin film at low temperatures (5–15 K). The present GFCO film exhibits a slight non-linearity (measured at 5 K, 10 K, and 15 K) due to a weak ferromagnetic contribution superimpose on the otherwise antiferromagnetic behavior well below \(T_N\). The presence of two magnetic components can be represented as \(M = \chi_{\text{AFM}}H + \sigma\), where the first term is the contribution of the AFM phase and the second term is the saturation magnetization of the weak ferromagnetic phase. A weak ferromagnetic contribution was expected at low temperatures due to the canted
antiferromagnetic structure of the ions at the Cr/Fe-site as observed in RCr\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{3}.\textsuperscript{17} However, magnetic coercivity is smaller when compared to the hysteresis of bulk pure GdCrO\textsubscript{3} at 5 K stated in other reports, indicative of the weakening of ferromagnetic component due to the canting of the Cr\textsuperscript{3+} magnetic moment with iron doping.\textsuperscript{17} This could possibly be explained by the formation of considerable concentration of Fe\textsuperscript{3+}\textsuperscript{−}O\textsuperscript{2−}\textsuperscript{−}Fe\textsuperscript{3+} networks when Cr\textsuperscript{3+}/Fe\textsuperscript{3+} = 1 in the present film, which will not only promote the collinear AFM but also reduce the spin-canted structure (weakly ferromagnetic) of the Cr\textsuperscript{3+} sublattice.\textsuperscript{20} This leads to the appearance of almost linear behavior.

In order to establish the multiferroicity in this compound, the dielectric characteristics of the GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} thin film were investigated in a wide temperature range of 100–635 K at different frequencies from 1 kHz to 2 MHz. For these measurements, a small ac-voltage of 500 mV was also applied. The temperature dependent dielectric constant (\(\varepsilon\)) and dielectric loss (\(\tan \delta\)) at three selected frequencies are depicted in Figs. 3(a) and 3(b), respectively. \(\varepsilon\) at temperatures in the 100–200 K range is found to be low and independent of temperature and measurement frequency. This could be attributed to the freezing of polaron hopping. The dielectric constant value increases with an increase in temperature due to electron hopping stimulated by lattice vibration.\textsuperscript{23,29} However, at \(T > 200\) K, dielectric data of the GFCO film here show an anomaly that is believed to be due to the ferroelectric to paraelectric (FE-PE) transition, which is frequency dependent indicating a diffuse transition or relaxor-like behavior. It should be noted here that \(\varepsilon\) (\(T\)) data in other reports on Fe substituted RCrO\textsubscript{3} investigated earlier were mostly presented only up to 150 K or 300 K.\textsuperscript{17,20,21} In the present work, two anomalies were observed in the \(\varepsilon\) (\(T\)) data of the GFCO film as presented in Fig. 3(a). One anomaly is at \(\sim 600\) K, which seems to be frequency independent. This anomaly could be possibly identified as the Burns temperature, below which the polar nanoregions start to grow in the present GFCO film.\textsuperscript{37} All the four contributions to the total polarization (ionic, electronic, dipolar, and space charge) dominate significantly at the low frequency region that could result in the high dielectric constant values observed at low frequencies in the present case as well. The temperature dependence of dielectric loss in Fig. 3(b) exhibits relaxation peaks, which shifted from 200 K to 350 K with increasing frequency indicative of relaxations not revealed in \(\varepsilon\) (\(T\)) measurement. In Fig. 3, it can be seen that the temperature of anomaly in the \(\tan \delta\) plot (200–350 K range), which could be due to different hopping process of charge carriers.\textsuperscript{17} The exponential enhancement in \(\tan \delta\) at higher temperature could either be ascribed to scattering of thermally activated charge carriers\textsuperscript{17} or mostly due to the electrical conduction.

The relaxor ferroelectrics can be described by the modified Curie–Weiss (C–W) law,

\[
\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^{\gamma}}{C},
\]

where \(\varepsilon_m\) is the peak dielectric constant that occurs at temperature \(T_m\), \(\varepsilon\) is the dielectric constant at temperature \(T\), \(C\) is the Curie constant, and \(\gamma\) is a diffusion exponent.\textsuperscript{36} Fitting with the modified C–W law yielded \(\gamma = 1.87\), as shown in Fig. 4(a). It should be noted that \(\gamma\) ranges from 1 (for a normal ferroelectric) to 2 (for an ideal relaxor ferroelectric) and the value in between 1 and 2 indicates diffuse ferroelectric characteristics.\textsuperscript{37} Thus, the value of \(\gamma(=1.87)\) in the present GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} film indicates relaxor-like behavior that can probably be induced either by the randomly distributed Cr and Fe ions at the B-site or due to their multiple valence state (Cr\textsuperscript{4+}/Cr\textsuperscript{3+}, Fe\textsuperscript{3+}/Fe\textsuperscript{2+}) caused by oxygen vacancies.\textsuperscript{17} It should be noted that the bulk sample prepared by drying the same coating solution and
annealed even up to 900 °C does not show the presence of other oxidation state of Cr (other than Cr²⁺).

In relaxor ferroelectrics, polar nanoregions form around the Burns temperature and interact with neighboring polar nanoregions via dipoles and dipole-induced dipole-exchange. This kind of behavior cannot be described by the Arrhenius law, which is used to describe the Debye relaxation process. Here, the analysis of the relaxation process was performed by fitting the cooling data of \( \tau \) to the empirical Vogel–Fulcher (VF) law, which includes the interaction between random local relaxation processes and is a modified Arrhenius expression,

\[
\tau = \tau_0 \exp \left[ \frac{E_a}{k_B (T_m - T_{VF})} \right],
\]

where \( \tau \) is the inverse of the ac field frequency \( f \), \( \tau_0 \) is the inverse of the fundamental attempt frequency of the dipoles, \( E_a \) is the activation energy of local polarization, \( k_B \) is Boltzmann’s constant, \( T_m \) is the temperature corresponding to the maximum dielectric constant at frequency \( f \), and \( T_{VF} \) is the static freezing temperature. By plotting the natural logarithm of \( \tau \) against the temperature of the dielectric maximum during cooling process, as shown in Fig. 4(b), the fitting parameters could be obtained as \( \tau_0 \sim 0.14 \) ns, \( E_a \sim 0.11 \) eV, and \( T_{VF} \sim 398.7 \) K. The close agreement of the data with the VF fitting suggests the relaxor behavior with polarization fluctuations above a freezing temperature at 398.7 K, which corresponds to the phase transition from the ergodic polar to nonergodic relaxor phase.  

Patri et al. analyzed the dielectric properties of the bulk Yb(Fe₃O₄)₃O sample by VF fitting and found the parameters as below: \( \tau_0 \sim 112.36 \) ns, \( E_a \sim 0.04 \) eV, and \( T_{VF} \sim 462 \) K. The fitting parameters have substantial differences with our sample, which is partly due to the VF fitting and is sensitive to the choice of data, type, and microstructure (grain size and grain boundary) of the sample. However, the activation energy of 0.11 eV is comparable to those polarization fluctuation induced by charge carrier hopping, such as 0.16–0.22 eV for TbMnO₃ and La₂NiMnO₄, 0.2–0.33 eV for iron based oxides (BiFeO₃, LaFeO₃, and LuFeO₃), 0.11 eV for disordered perovskite KTa₋₃₋ₓNbₓO₄:Ca, 0.18–0.26 eV for perovskite-type chromites Yₓ₋₃₋ₓMₓCrO₃ (M = Mg, Ca, Sr, Ba).  

The relaxation in our sample is less likely due to the diffusion of oxygen vacancies, considering the typical activation energy of thermal motion of oxygen vacancies in various perovskite-type oxides is in the range of 1–2 eV. Ke et al. investigated dielectric relaxation of the Bi₂₋₁₄₋ₓLaₓ₋₄₋ₓFeₓ₋₄₋ₓMg₀.₂ₓO₃ thin film and found the activation energy for hopping electrons along the Fe³⁺−V₀−Fe⁵⁺ (V₀: single charged oxygen vacancies) chain to be 0.136 eV. Thus, the most probable fluctuation mechanism for the dielectric relaxation peak in our sample is hopping electrons along the single-charged oxygen vacancy chain.

In order to do the electrical measurements, the GFCO film was sputter coated with Pt top electrodes using a shadow mask to create a Pt/GFCO/Pt/Si capacitor. To examine the ferroelectric properties of the GFCO film, the electric field dependent polarization (P-E) measurements were taken at 100 Hz. Figure 4(c) exhibits the P-E loops of the sample measured at 100 K, 150 K, and 200 K. All the P-E loops show little tendency of saturation at given electric field and look more like those of leaky dielectrics. This phenomenon of non-saturation in the P-E loop is common in polycrystalline FE oxide films due to high electrical leakage. The lossy nature of the film may originates from space-charge carriers or oxygen vacancies that could mask the intrinsic ferroelectricity here. The magnitude of the electric polarization cannot be truly estimated from the current P-E measurement because of some overlapping effects due to rather lossy nature of the film. The polarization value of similar family of materials has been summarized in Table I. It is clear that there is a strong controversy in the transition temperature and the polarization values even among reports of similar materials. For example, the polarization and FE-PE transition temperature (\( T_C \)) of DyFe₀.₅Cr₀.₅O₃ was reported to be 0.059 \( \mu \)C/cm² and 261 K, respectively, by Yin et al. However, Sharma et al. estimated a different \( T_C \) (130 K) and a polarization value of 0.0050 \( \mu \)C/cm² for the same material. The controversial results arise due to experimental limitations and significant leakage in the RCrO₃ material system. More work is needed to reduce the extrinsic effects in order to study the true magnitude of the dielectric constant, dielectric losses, and electric polarization of this material. Ferroelectric properties could also be explored with a high driving frequency to reduce the influence of leakage current on ferroelectric hysteresis loops. It should be noted that the initial pyroelectric current data of the film (not shown

| Sample               | \( T_N \) (K) | \( T_C \) (K) | \( P \) (\( \mu \)C/cm²) | References |
|----------------------|--------------|--------------|--------------------------|------------|
| GdCrO₃ (poly)        | 167          | 167          | 0.70                     | 52         |
| GdFeO₃ (sc)          | 661          | 2.5          | 0.12                     | 53         |
| DyFeO₃ (sc)          | 645          | 4            | 0.20                     | 54         |
| DyFeO₃ (poly)        | 645          | 645          | 0.16                     | 50         |
| DyCrO₃ (poly)        | Not identified | 578          | 19                       | 51         |
| DyFe₀.₅Cr₀.₅O₃ (poly)| 261          | 261          | 0.059                    | 16         |
| DyFe₀.₅Cr₀.₅O₃ (poly)| 261          | ~130         | 0.0050                   | 31         |
| YFe₀.₅Cr₀.₅O₃ (poly) | 260          | 260          | 0.70                     | 55         |
| Dy₀.₅Gd₀.₅Fe₀.₅Cr₀.₅O₃| Not identified | ~150        | 0.0068                   | 31         |
| GdFe₀.₅Cr₀.₅O₃ (poly)| 220          | 475          | Not identified           | This work  |
here) was measured by poling the sample with 0.5 V and measuring current continuously while increasing the temperature with the rate of 5 K/min. The data indicate the pyroelectric nature of the film and the pyroelectric current maximizes near 540 K. However, the result needs to be further optimized and analyzed. Apparently, some reports have indicated that bulk of rare-earth chromites can show similar behavior.\textsuperscript{37,51}

Figures 5(a) and 5(b) show the temperature dependence of tunability of the GFCO film measured at 10 kHz and 1 MHz with 500 mV oscillation and a given dc electric field of 22.5 kV/cm and 44.9 kV/cm during cooling. The dielectric tunability of the GFCO film is determined from the following equation:

\[
\text{Tunability (\%)} = \left( \frac{\varepsilon_{\text{E0}} - \varepsilon_{\text{E}}} {\varepsilon_{\text{E0}}} \right) \times 100, \quad (3)
\]

where \(\varepsilon_{\text{E0}}\) and \(\varepsilon_{\text{E}}\) are the dielectric constant under zero electric field and a given electric field, respectively. Due to the asymmetry of dielectric constant-bias field curve, the tunability is larger on the positive biased region. This can be attributed to the non-equivalent Pt/GFCO (top electrodes) and GFCO/Pt (bottom electrodes) interfaces. Some researchers proposed that a built-in electric field could be formed at the film/electrode interfaces which may be caused by trapped oxygen vacancies at the interfaces, and the built-in fields on top and bottom interfaces cannot counteract completely. Moreover, different thermal histories and deposition sequence between the top and bottom electrodes can also change the Schottky barrier over, different thermal histories and deposition sequence between on top and bottom interfaces cannot counteract completely. More trapped oxygen vacancies at the interfaces, and the built-in fields.

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The dielectric tunability of the GFCO film is determined from the following equation:

\[
\varepsilon_{\text{E}} = \frac{\varepsilon_{\text{E0}}}{(1 + a E_0^2 \varepsilon_{\text{E0}}^2 E^2)^{1/2}} + \frac{P_0 \chi_3}{\varepsilon_0} \left[ \cosh (\chi E) \right]^{-2}, \quad (4)
\]

where \(\varepsilon_{\text{E0}}\) and \(\varepsilon_{\text{E}}\) are the dielectric constant under zero dc electric field and a given dc bias electric field, \(a\) is the anharmonic coefficient, \(E_0\) is the vacuum permittivity, \(E\) is the external dc bias electric field, \(\chi = P_0 V/k_B T\), \(P_0\) is the polarization of a nanodomain, \(V\) is its volume, \(k_B\) is Boltzmann’s constant, and \(T\) is the temperature.\textsuperscript{37,59,60} The first term of the equation (Johnson term) represents single polarization contribution from ferroelectric system, while the second term (Langevin term) represents extrinsic reorientational polarization.\textsuperscript{37,59,60} Figure 5(c) shows the dielectric constant under different bias field measured at 500 K where the tunability maximizes. The data were well fitted by Eq. (4) with a coefficient of determination (R\textsuperscript{2}) of 0.9993. Different contribution to the tunability could be identified by the multiple polarization model as shown in Fig. 5(c). It is obvious that the extrinsic contribution, such as reorientation of polar nanoregions, is important at low electric fields. However, the intrinsic contribution becomes dominant at moderate or high fields, which represents the field induced ferroelectric polarization response. According to the fitting, the contribution of extrinsic mechanism to the total dielectric constant was ~10% at 22.5 kV/cm, which is more likely due to the nanoregions with local polarization.\textsuperscript{37} The intrinsic mechanism (ferroelectric Johnson contribution) accounts for the remaining ~90% of the total dielectric constant.\textsuperscript{37}

IV. CONCLUSION

In summary, the polycrystalline GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} film was successfully synthesized by using a layer-by-layer spin coating approach. The single phase GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} film with orthorhombic \textit{Pbnm} symmetry was confirmed by the XRD pattern. Temperature dependent magnetization measurement in the paramagnetic phase was fitted with the Curie–Weiss law, revealing the \textit{Néel} temperature to be ~220 K, which can be attributed to the Fe\textsuperscript{3+}–O–Cr\textsuperscript{3+} interaction of antiferromagnetic ordering. The dielectric studies exhibit a diffuse relaxor-type dielectric transition close to ~480 K, which is related to the multipole valence and random distribution of Cr\textsuperscript{3+} and Fe\textsuperscript{3+} ions at the B site. Open and unsaturated polarization-electric field hysteresis loops due to leakage currents were observed at a series of temperatures. The film exhibits a tunability of 46.8% at 44.9 kV/cm and 1 MHz, in which the extrinsic polarization accounts for 1.0% of the dielectric constant according to the multipolarization mechanism model. Further investigations are required to better reveal the ferroelectric nature of the GdFe\textsubscript{0.5}Cr\textsubscript{0.5}O\textsubscript{3} film. The iron doped orthochromites may provide an alternative approach to room temperature single phase multiferroics.

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