Effect of Quantum Confinement on Optical and Magnetic Properties of Pr–Cr-Codoped Bismuth Ferrite Nanowires

Rajasree Das,†,⊥ Gobinda Gopal Khan,*,‡,⊥ Shikha Varma,§ Goutam Dev Mukherjee,∥ and Kalyan Mandal†

†Department of Condensed Matter Physics and Material Sciences, S. N. Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700 098, India
‡Centre for Research in Nanoscience and Nanotechnology, University of Calcutta, Technology Campus, Block JD-2, Sector III, Salt Lake, Kolkata 700 098, India
§Institute of Physics, Bhubaneswar 751 005, India
∥Department of Physical Sciences, Indian Institute of Science Education and Research, Kolkata, Mohanpur Campus, PO BCKV Campus Main Office, Nadia 741 252, India

ABSTRACT: We report the effect of the variation of diameter on the optical, magnetic, and magnetodielectric properties of the Pr–Cr-codoped BiFeO₃ (BFO) nanowires (NWs). Pr–Cr-codoped BFO NWs with different diameters (18, 35, 55, 100, 150, and 250 nm) have been fabricated by employing a simple wet chemical template-assisted route. The effect of quantum confinement has been found to have a significant influence on the room-temperature photoluminescence and Raman spectra of the NWs. An interesting blue shift in the band gap emission is observed in the photoluminescence spectra of the NWs as a result of quantum confinement. The position and the intensity of the Raman peaks are found to change significantly depending on the variation in the NW diameter. The room-temperature ferromagnetism of the codoped BFO NWs increases consistently with the decrease in the diameter of the NWs because of the suppression of the spiral spin structure and the increase in the number of uncompensated for spins at the NW surface (as the surface to volume ratio increases with the decrease in the NW diameter). Strong magnetoelectric coupling is evidenced in the codoped BFO NWs with the decrease in the NW diameter. The tuning of the optical, magnetic, and magnetodielectric properties of the doped BFO NWs appears to be very promising for achieving multifunctionality in a single material.

1. INTRODUCTION

Multiferroic BiFeO₃ (BFO) has attracted ever-increasing amounts of attention because of its well-known coexistence of ferroelectric and antiferromagnetic orders at room temperature suitable for magnetoelectric device fabrication. Considering the wide-spectrum potential applications of BFO in data storage, ferroelectric random access memory, sensors, filters, attenuators, solar energy, and spintronics devices¹–³ because of its high ferroelectric Curie temperature (Tᵥ = 1123 K) and antiferromagnetic Néel temperature (Tᵥ = 647 K),² several research studies have been focused on improving the multifunctional performance of BFO. It has been demonstrated that suitable dopant ion substitution engineering⁴,⁵ film thickness variation⁶,⁷ and even the use of an oxide buffer layer⁸ can significantly enhance the magnetic, electric and magnetoelectric properties of BFO. Recently, it was found that the size effect has a very strong influence on the magnetic behavior of BFO, which exhibits weak room-temperature ferromagnetism (RTFM) on nanometer-scale dimensions.⁹,¹⁰ The improvement in the ferroelectric and magnetoelectric
properties is reported in various BFO nanostructures. In our previous work, we reported the enhanced multiferroic performance of the Pr–Cr-codoped BFO nanotubes (NTs), where a significant improvement in the RTFM has also been observed. Furthermore, we also have evidenced a substantial visible-light photovoltaic effect in BFO NTs. Bulk BFO is a semiconductor ferroelectric material with a direct band gap energy of 2.7 eV exhibiting diodelike characteristics. Therefore, considering the multifunctionality in semiconductor ferroelectric BFO, great interest has been focused on the fabrication of BFO-based novel optoelectronic devices having good carrier transport and a large absorption of visible light. Recently, optical properties of the BFO thin films have been studied, although the optical properties of BFO nanostructures/nanowires (NWs) have not been investigated in detail. Furthermore, the tuning of the RTFM in BFO nanostructures seems to be very exciting as well as challenging for their successful application in magnetoelectric devices.

In this work, we have investigated the diameter-dependent optical, magnetic, and magnetodielectric properties of the Pr–Cr-codoped BFO NWs grown via a wet chemical template-assisted route. The effect of quantum confinement on the optical, magnetic, and magnetodielectric properties of the codoped BFO NWs has been demonstrated in which the codoped BFO NWs are found to exhibit enhanced multiferroic functionality. The 1D nanostructures have large surface to volume ratios that are morphologically more advantageous to obtain long-range magnetic ordering, and it is also interesting to consider their optical properties. The blue shift of the band edge emission is observed in the Pr–Cr-codoped BFO NWs as a result of the quantum confinement effect. A giant increase in magnetization is demonstrated for the codoped BFO NWs by modifying the diameter of the NWs.

2. EXPERIMENTAL METHODS

2.1. Synthesis of Pr–Cr-Codoped BFO NWs. Arrays of single-phase polycrystalline Pr–Cr-codoped BFO NWs with different diameters have been fabricated by a facile wet chemical template-assisted liquid-phase deposition route employing self-ordered nanoporous anodic aluminum oxide (AAO) as the host. Templates with pore diameters of 18, 35, 55, 100, 150, and 250 nm have been used to fabricate the NWs. Here, we have used both the commercially available template and the templates fabricated in our laboratory by means of chemical template-assisted liquid-phase deposition route. The e

2.1. Characterization of the NWs. The crystal structure of the codoped BFO NWs was examined by X-ray diffraction (XRD, X′Pert Pro, Panalytical) with Cu Kα radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM, FEI Quanta 200 MK II) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai TF20 ST) were used to study the morphology of the NWs after dissolving the template in 2 M NaOH solution. The chemical composition and the valence state of the different dopant ions in BFO have been estimated by X-ray photoelectron spectroscopy (XPS, VG Microtech ESCA-2000 Multilab apparatus) measurement using the Mg Kα source and energy-dispersive X-ray spectroscopy (EDAX) attached to the SEM. Room-temperature (RT) photoluminescence (PL) measurements of the NWs have been conducted by using a spectrophotometer (Horiba Jobin Yvon, Fluorolog-3) having a Xe lamp source with an excitation wavelength of 350 nm. A room-temperature (RT) UV–vis investigation of the NWs has been carried out by using a spectrophotometer (Perkin-Elmer, LAMDA 950 UV/vis/NIR spectrophotometer). Raman spectroscopy measurements were carried out in the range of 50–1000 cm−1 using a micro-Raman spectrometer (LABRAM HR from Horiba Jobin Yvon). The magnetic properties of the aligned arrays of template-embedded codoped NWs were measured using a vibrating sample magnetometer (VSM, Lakeshore, model 7144) up to a maximum field of 16 kOe at RT. An impedance analyzer (Agilent 4294A) has been used to measure the dielectric and magnetoelectric properties of the NWs within the frequency range of 40 to 107 Hz at an applied ac voltage of 500 mV at RT.

3. RESULTS AND DISCUSSION

3.1. Morphology, Crystallography, and Chemical Composition. Figure 1a,b presents the TEM image of single

Figure 1. (a–c) TEM micrographs of the different diameter Pr–Cr-codoped BFO NWs. (d) HRTEM image and (e) SAED pattern of the Pr–Cr-codoped BFO NWs.

Pr0.1Cr0.1BFO NWs with diameters of 100 and 18 nm, respectively. Figure 1c shows the TEM image of several NWs (diameter 55 nm) with a uniform outer surface. The HRTEM image (Figure 1d) shows that the d spacing of 0.279 nm is consistent with the d values of (110) lattice planes of BFO. Major bright diffraction rings in the selective area electron diffraction (SAED) pattern (Figure 1e) corresponds to the (012), (110), and (202) crystallographic planes of the codoped BFO NWs with d spacings of 2.81, 2.79, and 1.98 Å. All of these
observations confirm that the codoped BFO NWs are well crystallized with a single-phase rhombohedral perovskite structure with a R3m space group. The SEM micrograph and the XRD pattern of the as-grown codoped BFO NWs are provided in the Supporting Information (Figures S1 and S2).

The XPS studies for the pure and doped BFO NWs are conducted to achieve information about the chemical state and elemental composition. Figure 2a shows the representative XPS spectra of the Bi 4f orbital for both pure and doped BFO NWs. The peaks located at binding energies of 159.0 and 164.3 eV correspond to the Bi 4f7/2 and Bi 4f5/2 orbitals, respectively. The doublet peaks of the Bi 4f spectrum clearly suggest the trivalent oxidation state of Bi without the presence of any metallic Bi in the matrix.18,19 The representative high-resolution XPS spectrum of the Fe 2p orbital in the codoped BFO NWs is shown in Figure 2b. The Fe 2p3/2 and Fe 2p1/2 peaks located at 711.2 and 724.7 eV, respectively, and the tiny peak appearing at 719.3 eV corresponds to the Fe3+ oxidation state of iron in BFO.19,20 Here, no apparent Fe2+-related peak (708.2 eV) is observed, hence it is expected that the BFO NWs have a single phase with an Fe3+ valence state of iron.18,21 The chemical state of the dopant elements has also been investigated by XPS. The Cr 2p core-level spectrum is shown in Figure 2c. The doublet peaks for Cr 2p3/2 and Cr 2p1/2 appear at 576.5 and 585.9 eV, respectively, and indicate that the doped Cr ion is in the trivalent oxidation state where no metallic Cr is present in the doped BFO NWs.22,23 This also signifies that the doped Cr ions substitute for the Fe site in the BFO NWs. However, the tiny peak of Cr 2p3/2 appearing at 785.3 eV indicates the presence of Cr in a higher oxidation state (expected to be in the +4 valence state). Figure 2d shows the Pr 3d core-level spectrum, where the doublet peaks for Pr 3d5/2 and Pr 3d3/2 appearing at 933.5 and 954.2 eV, respectively, indicate that the doped Pr ion is in the trivalent oxidation state.24,25 Another Pr 3d3/2 core-level peak appears at 935 eV (Figure 2d), and the Pr 4d5/2 peak appearing at 116 eV (Supporting Information Figure S3) corresponds to the +4 valence state of Pr.25 This additional +4 valence state of both Cr and Pr in BFO indicates the reduction of the oxygen-vacancy-related defects in the codoped NWs. Further information about the presence of oxygen-vacancy-related defects in the BFO NWs can also be obtained from the O 1s core-level spectra of the pure and codoped BFO NWs (Figure 2e,f) situated at around 530 eV. It is worth noticing that for pure BFO NWs the O 1s spectrum is broader compared to that...
of codoped BFO. Hence, the broad O 1s band of the pure BFO NWs can be fitted with two Gaussian peaks centered at 529.7 and 531.5 eV. The lower-binding-energy peak (529.8 eV) is ascribed to the O 1s binding energy of the BFO phase, and the higher-binding-energy peak (531.5 eV) is attributed to the deficiency of oxygen in the BFO NWs. In codoped BFO NWs, the O 1s peak becomes much sharper and intense compared to that of the pure BFO NWs, and this peak can be fitted with two Gaussian peaks at 530.0 and 531.7 eV, where a close examination indicates that the area covered under the higher-binding-energy peak is very small. Hence, it is found that the ratio of the area of the peaks (higher-binding-energy peak/lower-binding-energy peak) decreases in the codoped BFO NWs compared to its value in the pure BFO NWs. This indicates that the concentration of oxygen-vacancy-related defects in the pure BFO NWs is much higher than in the codoped BFO NWs.

### 3.2. Optical Properties

#### 3.2.1. Photoluminescence and UV–Vis Spectroscopy

The photoluminescence properties of the different-diameter template-embedded Pr–Cr-codoped BFO NWs are studied in comparison to those of pure BFO NWs. Figure 3a shows the room-temperature PL spectra of the different-diameter Pr–Cr-codoped BFO NW samples with respect to that of pure 18 nm BFO NWs, recorded using an excitation of 350 nm light from a Xe lamp source. In the inset of Figure 3a, the PL spectrum of the template-embedded pure BFO NWs is compared to that of the AAO template. The AAO template exhibits broad blue emission centered at 440 nm due to the presence of some oxygen vacancy defects. Pure BFO NWs provide a strong blue emission peak at 421 nm that is attributed to the band-to-band electronic transition in BFO NWs. The estimated band gap energy (2.9 eV) is in good agreement with the values obtained from the PL absorption spectra of the pure and codoped BFO NWs. All of the NW samples show a sharp absorption edge at ~424 nm corresponding to the band-to-band transition for BFO. The estimated band gap of BFO (2.9 eV) is in good agreement with the values obtained from the PL absorption spectra of the pure and codoped BFO NWs. For all of the doped NWs, there is another absorption edge at 492 nm that is believed to be due to the electronic transitions of Pr3+ ions because for the pure BFO NWs there is no absorption edge around 492 nm.

#### 3.2.2. Raman Spectroscopy

For further insight into the lattice properties and spin-phonon coupling, Raman scattering studies have also been carried out on the codoped BFO NWs. Figure 4a shows the comparison of the Raman spectra of the pure and codoped BFO NWs at RT by parallel polarization using a laser with an excitation wavelength of 488 nm (LABRAM HR). The shift of the Raman peaks in the codoped BFO NWs with respect to the pure BFO NWs is due to the change in the band length between the atoms in the BFO crystal due to doping. Here, both the pure and doped NWs exhibit similar Raman phonon modes, which is quite expected because both the pure and doped BFO NWs have the same crystal structure. Figure 4b shows the Raman spectra of the aligned arrays of the as-prepared codoped BFO NWs with different diameters at RT. Group theoretical analysis predicts that 13 (4 A1 + 9 E phonon modes) Raman phonon modes are associated with pure BFO ceramics. All of the 13 Raman-active phonon modes for bulk BFO ceramics with slight differences in the peak positions due to the changes in oxygen bonding and disorder have also been detected experimentally. Here, the observed natural
frequency (cm⁻¹) of each peak position can be assigned to a different Raman-active mode. Table 1 shows the position of the Raman modes of 200 nm undoped BFO NWs and a comparison with the earlier reported data on BFO single crystal and nanoparticles.

Table 1. Position of the Raman Modes (cm⁻¹) in Our Study on BFO NWs in Comparison to the Reported Values

<table>
<thead>
<tr>
<th>Raman modes</th>
<th>our work</th>
<th>Fukumura et al.³⁴</th>
<th>Jaiswal et al.³²</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁-1</td>
<td>124</td>
<td>147</td>
<td>139</td>
</tr>
<tr>
<td>A₁-2</td>
<td>158</td>
<td>176</td>
<td>169</td>
</tr>
<tr>
<td>A₁-3</td>
<td>223</td>
<td>227</td>
<td>216</td>
</tr>
<tr>
<td>A₁-4</td>
<td>409</td>
<td>490</td>
<td>425</td>
</tr>
<tr>
<td>E</td>
<td>239</td>
<td>265</td>
<td>260</td>
</tr>
<tr>
<td>E</td>
<td>268</td>
<td>279</td>
<td>276</td>
</tr>
<tr>
<td>E</td>
<td>313</td>
<td>351</td>
<td>321</td>
</tr>
<tr>
<td>E</td>
<td>375</td>
<td>348</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>469</td>
<td>437</td>
<td>467</td>
</tr>
<tr>
<td>E</td>
<td>533</td>
<td>473</td>
<td>529</td>
</tr>
<tr>
<td>E</td>
<td>598</td>
<td>525</td>
<td>598</td>
</tr>
<tr>
<td>E</td>
<td>77</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>109</td>
<td>136</td>
<td>98</td>
</tr>
</tbody>
</table>

For the codoped NWs (Figure 4b), in our experiment, the Raman-active modes are found to be prominent for the larger-diameter (~100–200 nm) NWs. The four peaks at 128, 170, 212, and 426 cm⁻¹ can be assigned as longitudinal-optical (A₁) phonon modes A₁-1, A₁-2, A₁-3, and A₁-4, respectively.³⁵ The broad nature of the A₁-1 peak clearly indicates the presence of the A₁-2 mode at around 170 cm⁻¹ in the spectra. The subsequent six peaks situated at 269, 326, 348, 499, 598, and 90 cm⁻¹ are related to the transverse-optical (E) phonon modes.³⁶ The absence of some of the Raman peaks may be due to the higher local stress in the NWs and the existence of point defects in the codoped NWs.³⁷ Here, the spectra reported are for the parallel polarization configuration because the sample is polycrystalline; therefore, it is expected that the intensity of A₁ modes will not be significantly reduced for the cross-polarization configuration.³⁷ However, the peak positions are found to be diameter-independent. The Bi–O₁ vibrational peak at 130 cm⁻¹ (for 200 nm codoped NW) is responsible for the magnetoelectric coupling in the samples. This Bi–O₁ peak (A₁-1 mode) is found to shift toward lower frequency as the diameter of the NWs increases, which might be due to the change in force constant in the codoped NWs resulting from the microstructural changes related to doping.³⁸ Moreover, the broadening of the peaks is also observed with the decrease in the diameter of the NWs. The peak intensities of 200 and 150 nm NWs are almost equal, but the gradual decreases in the peak intensity with further decreases in the diameter of the NWs are mainly due to the smaller physical dimension of the scattering crystalline NWs. The gradual decrease in the peak intensity (lowest for 18 nm NWs) indicates the suppression of the contribution of the Bi–O₁ vibrational mode that is probably due to the greater lattice distortion or increased coupling between the ferroelectric and magnetic order parameters resulting from the quantum confinement effect.³⁹ The inset of Figure 4b shows the thermal effects on the Raman spectra of 18 nm codoped NWs observed at 10 and 6 mW laser power. The laser heating is expected to increase the width of the Raman modes as observed in this study. Laser heating occurs during the energy transfers from the excited electron to the lattice via electron–phonon scattering, but no signature of bond weakening is observed in our experiment with the application of a high concentration of excited electrons to the codoped NWs. The increase in the intensity of Raman modes with higher laser power is due to more photon flux.

3.3. Magnetic Property. Figure 5a shows the room-temperature (300 K) hysteresis (M–H) loops of the different-diameter codoped BFO NWs. The magnetic signal of the aligned arrays of codoped BFO NWs was obtained after subtracting the diamagnetic response of the AAO template. It is observed that all of the codoped BFO NWs exhibit RTFM. Interestingly, the magnetic response is found to be enhanced by the decrease in the diameter of the BFO NWs. The maximum saturation magnetization (Mₛ) of 0.57 emu/g has been obtained for the 18-nm-diameter codoped BFO NWs. Figure 5b shows the M–H loops for the undoped and codoped 18-nm-diameter BFO NWs for comparison. A significant enhancement of the magnetic signal of the doped NWs is evident in Figure 5b. Between 200 to 55 nm diameter, the magnetization increasers very insignificantly with the decrease in the NW diameter. The variation of Mₛ with the diameter of the NWs is shown in the inset of Figure 5a, which demonstrates the effect of quantum confinement on magnetization. The diameter-dependent variation of the magnetization, coercive field, and remanence in codoped BFO NWs is summarized in Table 2.

Figure 5. (a) Diameter-dependent variation of the hysteresis loops of the codoped BFO NWs measured at 300 K. The inset of panel a shows the change in the values of the saturation magnetization of the codoped BFO NWs as a function of 1/d (surface to volume ratio). (b) Hysteresis loops of the 18-nm-diameter undoped and codoped BFO NWs measured at 300 K.
The origin of the enhanced ferromagnetic signal from the Pr–Cr-codoped BFO NWs could be demonstrated on the basis of the following discussions. Here, replacing Bi with a Pr ion and Fe with a Cr ion changes the canting angle and increases the degree of the distortion, resulting in a smaller bond angle of the antiferromagnetic Fe–O–Fe chain of spins leading to enhanced magnetization, might be one of the significant reasons behind the strong ferromagnetic property in the codoped NWs compared to the pure BFO samples. Doping the Pr ion in BFO is found to increase its magnetization. Furthermore, the 3d3+ for Cr3+ ions with $S = \frac{3}{2}$ present in the doped BFO NWs (as indicated by XPS study) can also introduce an effective magnetic moment of $\sim 3.87 \, \mu B$, which can introduce local FM ordering at the dopant ion site and introduce a net moment through superexchange. It is known that the increase in the FM in BFO-based materials is sometimes attributed to the existence of the double exchange interaction between Fe3+ and Fe4+ ions through oxygen. However, in our experiment the XPS study indicates that only the Fe3+ ion is present in the samples, hence the contribution of the Fe3+ ions to FM could be neglected here. In BFO, magnetic ions are coupled ferromagnetically within the (111) planes and antiferromagnetically between adjacent planes. Nanostructures of antiferromagnetic BFO show magnetic moments that are mainly due to the incomplete magnetic compensations between these planes. This incomplete magnetic ordering in nanostructures occurs as the long-range antiferromagnetic order is frequently interrupted at the grain surfaces. Hence, the weak FM order in the codoped BFO NWs has been ascribed to the size effect. This work presents direct evidence of the size effect on the magnetic order, which is antiferromagnetic in bulk BFO, due to the complicated spiral spin structure of wavelength 62 nm. Here, the increase in the magnetic signature in the NWs with the decrease of the diameter agrees well with the reports on the thickness-dependence magnetization in BFO thin films and size-dependent magnetization of BFO nanoparticles. With decreasing diameter in the NWs, the surface-to-volume ratio increases, which enhances the effect of the antiferromagnetic-order interruption at the grain surfaces, and thus the magnetization increases remarkably. It is believed that the uncompensated ferromagnetic surface spins of the NWs increases with the increase in their surface to volume ratio, leading to enhanced FM in the quantum confined structures. According to the Neel model, in the case of single-domain antiferromagnetic particles the susceptibility is expected to scale as $\sim \frac{1}{d}$ (surface to volume ratio). The inset of Figure 5a shows a plot of the magnetization as a function of $\frac{1}{d}$ at an applied field of 15 kOe. The magnetization of NWs with diameters of 35 to 200 nm shows linear behavior, with $\frac{1}{d}$ indicating that the Neel model is applicable here. Therefore, except for the NWs with 18 nm diameter others can be modeled as the superposition of the ferromagnetic surface/shell and an antiferromagnetic core. However, the enhanced magnetization in 18-nm-diameter NWs cannot be explained with this model. The large magnetization in the NWs of 18 nm diameter might be a combination of structural distortion, a large surface-to-volume ratio, higher magnetic anisotropy due to strain, and a strong interaction between lattices and spin. Furthermore, in such a quantum confined structure there is a possibility of the appearance of the Fe3+ ions in the NWs during the high-temperature annealing, leading to a huge increase in saturation magnetization.

### 3.4. Magnetodielectric Properties

Figure 6a shows the variation of the dielectric constant ($\varepsilon$) of the codoped BFO NWs grown in the AAO template, measured in the $10^2$–$10^6$ Hz frequency range at RT. In the case of NWs with 35–200-nm-diameter ranges, $\varepsilon$ decreases with the decrease in the diameter, which is also observed in the case of thin films. Here, the 18-nm-diameter NWs exhibit a maximum $\varepsilon$ value compared to others. It can be explained from the grain or grain boundary phase-induced polarization that occurs as a result of the obstruction of charge carriers at the grain boundaries. It is observed that when the diameter of the NWs decreases below a critical value there is a possibility of the appearance of mixed phases or the phase transition can take place, which leads to a

### Table 2. Diameter-Dependent Variation of the Magnetization, Coercive Field, and Remanence in Codoped BFO NWs

<table>
<thead>
<tr>
<th>NW samples (nm)</th>
<th>remanant magnetisation (memu/g)</th>
<th>coercive field (Oe)</th>
<th>maximum magnetisation (at 15 kOe) (memu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>19.2</td>
<td>50</td>
<td>570</td>
</tr>
<tr>
<td>35</td>
<td>20.1</td>
<td>200</td>
<td>410</td>
</tr>
<tr>
<td>55</td>
<td>4.5</td>
<td>45</td>
<td>180</td>
</tr>
<tr>
<td>100</td>
<td>3.2</td>
<td>160</td>
<td>127</td>
</tr>
<tr>
<td>150</td>
<td>4.0</td>
<td>240</td>
<td>89</td>
</tr>
<tr>
<td>200</td>
<td>15</td>
<td>330</td>
<td>59</td>
</tr>
</tbody>
</table>

Figure 6. (a) Frequency dependence of the dielectric constant and (b) resistivity of the different-diameter codoped BFO NWs. (c) Magnetic field-induced change in the dielectric constant in the different-diameter codoped BFO NWs measured at a frequency of 1 kHz at room temperature.
buildup of charges at the interface, resulting in strong polarization and subsequently a high dielectric constant. The resistivity plot (Figure 6b) of the NW samples indicates that the resistivity of the NWs increases with the decrease in the diameter. High resistivity and the grain boundary scattering effect in the NWs give rise to the high magnetodielectric effect, expressed by $\frac{[\varepsilon_r(H) - \varepsilon_r(0)]}{\varepsilon_r(0)}$. Figure 6c shows the RT magnetic field dependence of the magnetodielectric (MD) effect at a frequency ($f$) of 1 kHz for all of the NWs. Here, the 18-nm-diameter NW shows maximum magnetoelectric coupling. The NWs with diameter between 35 to 200 nm exhibit enhanced magnetoelectric coupling with the decrease in the diameter of the NWs.

4. CONCLUSIONS

Different-diameter Pr–Cr-codoped BFO NWs have been fabricated successfully by template-assisted wet chemical route. The XPS investigations confirm that oxygen-vacancy-related defects in BFO NWs are reduced significantly by Pr–Cr ion codoping. All of the NWs exhibit intense blue band edge light emission, where an interesting blue shift of the band gap emission is observed because of the quantum confinement effects in the nanoscale dimension. The blue emission (around 490 nm) of the codoped BFO NWs is ascribed to the electronic transitions of Pr$^{3+}$ ions, implying that the quantum confinement effect in large-diameter NWs may originated from the polycrystalline NWs, where the dimensions of some of the crystals are much smaller than the diameter of the NWs. The room-temperature ferromagnetic signature of the NWs is found to improve with the decrease in the diameter of the NWs, which indicates that the quantum confinement effect (increase of the surface-to-volume ratio with the decrease in the NW diameter) has a significant influence on their magnetic properties. The magnetoelectric coupling in the NWs is found to increase with the decrease in the diameter.

REFERENCES

(38) Wu, J.; Wang, J. Effects of SrRuO3 buffer layer thickness on multiferroic (Bi0.9La0.1)(Fe0.9Mn0.05)O3 thin films. J. Appl. Phys. 2009, 106, 054115.