Vacancy-Induced Temperature-Dependent Thermal and Magnetic Properties of Holmium-Substituted Bismuth Ferrite Nanoparticle Compacts

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1. INTRODUCTION

Multiferroic BiFeO₃ (BFO) is a potential candidate for a plethora of modern applications such as in spintronics, ferroelectric random access memory (F-RAM), transistors, photodetectors, capacitors, data storage devices, and multifunctional sensors.1−5 Although the electrical, optical, and magnetic properties of the multiferroic oxide have been the center of active research in recent years,6−12 the study of the thermal properties and the role of defects in modulating the thermal transport phenomena are commensurately engaging. The ordered structure depends on defects and temperature, and therefore, disordered transitions that usually occur at high temperatures could limit the use of multiferroics for different applications. In addition, the operational stability and performance of F-RAMs, transistors, or multifunctional devices are strongly influenced by their thermal transport properties due to a thermal gradient established within the systems, resulting from the heat absorption of ferroelectrics.13,14 For the dynamic operation of these devices, assessment of thermal diffusivity and heat capacity along with thermal conductivity measurements is becoming a common practice.15 Hence, several studies on the thermal properties of bulk and thin-film BFO have been conducted.16−19 In those studies, the effects of strain fields, domain walls, and grain boundaries on the phonon transport mechanism have been reported. A significant change in thermal conductivity was observed with the substantial structural modification of BFO. Nevertheless, the role of dopants and associated point defects such as oxygen vacancy cannot entirely be decoupled as the effect of fabrication factors such as porosity in polycrystalline ferroelectric materials complicates the analysis. Manipulating the structural parameters such as point defects through processing could increase or decrease thermal transport in BFO. Perovskite-type structures such as DyFeO₃,20 metal-halide perovskites,15 and YFeO₃21 with appropriate thermal, magnetic, and electrical properties bear significant importance in device applications. DyFeO₃, crystals having ultrafast non-thermal control of magnetization...
open the window for applications of ultrafast lasers in magnetic devices.\textsuperscript{20} Metal halides with a large Seebeck coefficient, high electrical conductivity, and low thermal conductivity have become attractive functional materials in thermoelectric applications.\textsuperscript{15} In recent times, holmium (Ho) has stood out as a promising substitution for Bi in BFO as Ho has improved its magnetic and electrical properties by a big margin.\textsuperscript{22}−\textsuperscript{25} Therefore, Ho-substituted BFO deserves an elaborate thermal study to open another potential window for multiferroics in thermal applications.

Herein, motivated by the above concern, the heat capacity and the thermal conductivity of pure and Ho-substituted BFO powders and compacts have been reported to comprehend the role of the defect and nanostructure scattering on the thermal properties of BFO. To the best of the authors’ knowledge, the thermal properties of pure and/or substituted BFO nanoparticles have not been previously explored. To complement the thermal properties, the electrical and magnetic properties of BFO are also reported. The transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) analyses were performed to fathom the role of oxygen vacancies in modifying the electrical properties. The magnetic properties were analyzed in detail over a broad temperature range from 300 to 950 K. The experimental results suggest that the structural modifications brought by Ho substitution in BFO have played an important role in the property enhancement. The measured thermal conductivity of the BFO nanoparticle compacts is reduced significantly due to porosity and defects, which are known as phonon scattering centers. The results of this study provide an insight into tailoring the magnetic and thermal properties of multiferroics, which is beneficial to thermomagnetic applications.

2. EXPERIMENTAL SECTION

2.1. Synthesis of BHFO Nanoparticles. BFO, BHFO-5, BHFO-10, and BHFO-15 nanoparticles were synthesized using a modified sol−gel method.\textsuperscript{22} To synthesize BFO and BHFO nanoparticles, the stoichiometric proportion of bismuth nitrate pentahydrate [Bi(NO$_3$)$_3$·5H$_2$O], iron nitrate nonahydrate [Fe(NO$_3$)$_3$·9H$_2$O], holmium nitrate pentahydrate [Ho(NO$_3$)$_3$·5H$_2$O], citric acid (C$_6$H$_8$O$_7$), and ethylene glycol (C$_2$H$_6$O$_2$) were dissolved in deionized water. Then, the solution was heated with continuous stirring at 75−85 °C for 4 h to form a gel. The gel was dried at 100 °C for 24 h in a drier to obtain precursor xerogel. The ground precursor xerogel powders were annealed at 600 °C for 2 h with a heating rate of 3 °C/min to obtain nanoparticles. To measure the electrical properties and thermal conductivity, BFO and BHFO nanostructured sintered pellets (thickness ∼0.11 cm and diameter ∼1.3 cm) were prepared by mixing precursor xerogel powders with polyvinyl alcohol binder followed by pressing and annealing at 600 °C for 2 h with a heating rate of 3 °C/min.

2.2. Instrumentation and Characterization. The high resolution X-ray diffraction (HR-XRD) technique was employed using a PANalytical Empyrean X-ray diffractometer system with a Cu K$_\alpha$ radiation source (K$_\alpha1$ = 1.540598 Å and K$_\alpha2$ = 1.544426 Å) to analyze the phases of the nanoparticles. Surface morphology and microstructure were investigated using the probe-corrected field emission transmission electron microscope (Titan Themis, FEI, operated at 200 kV) and field emission scanning electron microscope (JEOL, JSM, 7600F). Energy-dispersive X-ray spectroscopy (EDS) was used to obtain the elemental composition of nanoparticles. High-resolution TEM (HRTEM) images and selected area diffraction patterns (SAED) were obtained from TEM. XPS measurements were carried out with the PHI Quantera II spectrometer, and peak fitting was performed in origin. The electrical properties of the sintered pellets coated with silver paste were measured using the precision materials analyzer (Radiant Technologies, Inc.: Premier II, PMF0215-377) connected to a 10 KV HVI-SC interface and a signal amplifier.

![Figure 1. XRD results for BFO, BHFO-5, BHFO-10, and BHFO-15 show the observed (black line), calculated (red dot), and difference (blue line) patterns obtained from Rietveld refinement. Rows of ticks represent Bragg positions of different phases.](image-url)
3. RESULTS AND DISCUSSION

To this end, a series of Ho-substituted BFO were investigated. For that purpose, the following nanoparticle-based samples were synthesized by a modified sol–gel route: BFO, 5 mol % Ho-substituted BFO (BHFO-5), 10 mol % Ho-substituted BFO (BHFO-10), and 15 mol % Ho-substituted BFO (BHFO-15). For crystal structure and phase identifications of nanoparticles, Rietveld refinement of HR-XRD data was performed using HighScore Plus software. Figure 1 shows the observed, calculated, and difference patterns for our samples along with the Bragg positions of the phases used. It was observed that BFO nanoparticles crystallize into a rhombohedral distorted perovskite structure (space group R3c) with two secondary phases. While several previous studies report the formation of pure bismuth ferrite through additional chemical treatments, \(^{30,31}\) the appearance of Bi-rich compound (\(\text{Bi}^{5+} \text{Fe}^{3+}_3\text{O}_9\)) and Fe-rich compound (\(\text{Bi}_2\text{Fe}_4\text{O}_9\)) is also common in the process of BFO synthesis. \(^{10,12}\) The second phase formation can be ascribed to the emergence of non-stoichiometry in the system; there is a tendency for Bi-vacancy formation due to the lower bond strength of Bi–O compared to that of Fe–O. The goodness of fit (GOF), as determined by HighScore Plus software, for BFO with R3c space group is ~1.45, demonstrating the reliability of the refinement process (Figure 1).

It is known that the perovskite structure of BFO transforms from rhombohedral (R3c) to its orthorhombic (Pnma), tetragonal (P4mm), or cubic (Pm3m) polymorph depending on the nature of the substituents. \(^{10,11}\) Looking at the magnified portions of XRD patterns, as shown in Figure S2, within a 2° range of 31–33°, it can be appreciated that considerable structural modification has occurred in the Ho-substituted BFO compounds, especially in BHFO-10 and BHFO-15. The refinement process substantiates that BHFO-5 with R3c symmetry has a lesser amount of secondary phases compared to BFO. Here, the proposition is that the perovskite structure shows higher stability if the A-site dopant atom has greater bond energy with oxygen compared to Bi, and, hence, the tendency for it to decompose into other phases is reduced. \(^{11}\) The bond dissociation energy of Ho–O (606 kJ/mol) is higher than that of Bi–O (343 kJ/mol), \(^{32}\) and so, Bi substitution with Ho restricts the formation of oxygen vacancies and preserves the perovskite structure. Indeed, no secondary phase could be found for 10 and 15 mol % Ho substitution (Figure 1). Figure S2 also depicts that there is a partial merging of (110)/(104) peaks for BHFO-10, implying
a possible structural transition in the synthesized BHFO-10 nanoparticles with the parent $R_3c$ phase remaining. According to our previous work and earlier report on similar systems, this emanant phase can have orthorhombic $Pnma$ symmetry. Thus, a combination of $R_3c$ and $Pnma$ space groups has been found to provide the best match for BHFO-10 with a GOF $\sim 1.16$. On the other hand, along with (104)/(110) peaks, several peaks split at higher $2\theta$ angles in BHFO-15 nanoparticles, as shown in Figure 1, suggesting the presence of multiple perovskite phases. Since there are different peaks in the XRD pattern of BHFO-15 and the composition of BHFO-10 already exhibited two different polymorphs of the perovskite phase, the Rietveld refinement of BHFO-15 was carried out with all possible combinations of perovskite symmetries. All peaks of the sample were well matched with a mixture of orthorhombic ($Pnma$), rhombohedral ($R_3c$), and monoclinic ($C2/m$) phases (Figure 1).

The substitution of Bi$^{3+}$ (1.03 Å) with relatively smaller Ho$^{3+}$ (0.901 Å) leads to a distortion in oxygen octahedral ($FeO_6$) and changes in bond angles and lengths, as shown in Figure 2c,f, where it shows that with increasing Ho$^{3+}$ substitution up to 10 mol %, the Fe–O–Fe bond angle increases, and the Fe–O bond length decreases compared to those of BFO for the $R_3c$ phase. This indicates a substantial distortion in the crystal structure of BHFO (Figure 2e). In contrast, the Fe–O–Fe bond angle decreases, and the Fe–O bond length increases for the $R_3c$ phase in BHFO-15 (Table S1). The aberrant trend of these parameters could be due to a higher $Pnma$ percentage, prevailing in BHFO-15 compared to $R_3c$, and in fact, the bond angle of the $Pnma$ phase increases, and its bond length decreases. The alteration of these crystallographic parameters is expected to have a profound influence on the electrical, magnetic, and thermal properties of BFO and BHFO.

Figure 3 shows the TEM micrographs of BFO and BHFO nanoparticles annealed at 600 °C. It can be noticed from the figures that the nanoparticles are agglomerated appreciably. The field emission scanning electron microscopy (FESEM) study shows the surface morphologies and size distribution of BHFO nanoparticles. The observed nano-
particles of BFO are nearly irregular in shape with an average diameter of $\sim 125$ nm, as depicted in the inset of Figure 3a. On the other hand, the Ho substitution has modified the shape and average size of nanoparticles (the insets of Figure 3b,c). The shape of BHFO-(5, 10, and 15) nanoparticles is almost spherical, and their average size is $\sim 116$, 98, and 101 nm, respectively (Figure S4), manifesting that Ho incorporation up to 10 mol % inhibits the particle growth to some extent. The microstructural characteristics of nanoparticles were further analyzed with the help of HR-TEM and SAED patterns. Figure 3d depicts that the interplanar spacing is about 0.27 nm, which corresponds to the (012) crystallographic plane of BFO with $R_{3c}$ symmetry. Similarly, for BHFO-10, the interplanar spacing of (233) and (110) planes is about 0.58 and 0.60 nm, respectively (Figure 3f), which is as per the $R_{3c}$ phase of the sample and also supports the Rietveld refinement data. Besides, Figure 3g–i depicts the SAED patterns of BFO and BHFO, which corroborate the formation of nanoparticles in the crystalline form.

The HR-TEM images also indicate the variation in the domain structure of the samples with Ho contents. Figure 3d shows that the domain structure of BFO is disordered (D), which appears due to its structural inhomogeneities. On the contrary, there appears an ordered domain structure ($O_d$) in BHFO-5 nanoparticles (Figure 3e), with both the $O_d$ and D regions coexisting together. Moreover, BHFO-5 exhibits superlattice reflection (Figure 3h) unlike the BFO sample, pointing out the presence of an ordered structure in the nanoparticles. With the increase in the Ho concentration, the $O_d$ regions are enlarged for BHFO-10 and BHFO-15 (Figures 3f and S3c), implying that Ho addition brings homogeneity in their structures by reducing the aforementioned defects. EDS analysis (Figure S6) also confirms that the oxygen content increases with increasing Ho concentrations. It is also noticeable from Figures 3hi and S3d that SAED patterns of BHFO-(5, 10, and 15) are different from each other—the superlattice spots observed in BHFO-5 appear to disappear in BHFO-10 and BHFO-15. This phenomenon could be attributed to the modulation of lattice parameters and also confirmed by XRD analysis. The domain structure controls the cycloidal spin structure and polarization phenomenon of BFO and BHFO, which in turn should also determine their magnetic, electrical, and thermal properties.

Figure 4 displays the XPS analysis of BHFO-10, which further validates XRD and HR-TEM findings; it affirms the presence of oxygen vacancies. Deconvoluted XPS spectrum of the O 1s core level (Figure 4a) into two symmetric Gaussian peaks at $\sim 529.4$ and 531 eV corresponds to the $-2$ oxidation state of oxygen and the oxygen vacant sites, respectively. The formation of the off-stoichiometric oxygen vacancies in the crystal lattice could be associated with the essential requirement of maintaining the charge neutrality condition on the occasion of volatilization of Bi and the thermodynamically generated oxygen vacancies during sintering within the material leading to a fluctuation in the oxidation state of Fe ($Fe^{2+/3+}$). The vacancy formation can be presented as follows.
where \( \text{Bi}^\text{+++} \) and \( \text{V}_\text{O}^- \) indicate charged bismuth and oxygen vacancies, respectively, and \( \text{Fe}^{2+} \) represents Fe\(^{2+}\) ion. According to our previous studies, the dopant decreased the oxygen vacancies in the BFO lattice.\(^\text{10}\)

The Ho substitution should have reduced the number of oxygen vacancies in the BFO lattice. Indeed, EDS analysis (Figure S6) indicated that the oxygen content in BFO increased with increasing Ho concentrations. XPS analysis, as depicted in Figure 4b, also affirmed the existence of mixed oxidation states of Fe ions. Here, the XPS spectrum of Fe 2p exhibits two intense peaks of Fe 2p\(_{3/2}\) (at \(\sim 710.4\) eV) and Fe 2p\(_{1/2}\) (at \(\sim 724\) eV).\(^\text{10,22}\) Deconvoluted XPS spectrum of Fe 2p\(_{3/2}\) into two peaks at \(\sim 709.8\) and \(711.6\) eV corresponds to Fe\(^{2+}\) and Fe\(^{3+}\) ions, respectively.\(^\text{10}\)

Figure 5a exhibits that BHFO-10 has the minimum leakage current among all nanostructured pellet samples; in fact, this sample has a leakage current lower than those of the Ho-substituted BFO reported in other studies.\(^\text{23,32,37}\) The presence of leakage current in BHFO-10 cannot be avoided because of oxygen vacancy formation, leading to the generation of Fe\(^{2+}/\text{Fe}^{3+}\) hopping centers and thus giving rise to leakage current.\(^\text{10}\) The measured current density in BHFO-10 is \(\sim 1.75 \times 10^{-5}\) A/cm\(^2\) at 7.78 kV/cm (Figure 5a), which is approximately 2 orders of magnitude lower than BFO. Indeed, BFO has the highest DC conductivity (Figures 5a and S8), which implies that it has the maximum amount of oxygen vacancies and/or more charge fluctuations in the Fe sites compared to the other three BHFO samples. With the bond dissociation energy of Ho–O (606 kJ/mol) being larger than that of Bi–O (343 kJ/mol), the substitution of Bi sites with Ho restrains the creation of oxygen vacancies and other defects (Figures 3 and S6). However, the current density of BHFO-15 is \(\sim 2.73 \times 10^{-5}\) A/cm\(^2\) at 7.78 kV/cm, which is 2 times higher than that of BHFO-10. Both BHFO-10 and BHFO-15 had less amount of oxygen vacancies compared to BFO (Figure S6). Therefore, the plausible reason for such increased conductivity at 15 mol % Ho concentration could be the modification of Fe\(^{2+}/\text{Fe}^{3+}\) bond angle and Fe–O length, as listed in Table S1, which could enhance the overlap of electronic wave functions, resulting in the smaller band gap. However, in a previous study,\(^\text{22}\) it was reported that Ho substitution can reduce the effective optical band gap energy of BFO, which renders easy electron transition from the valence band to the conduction band (O\(^{2−}\) 2p \(\rightarrow\) Fe\(^{3+}\) 3d) and thus leading to enhanced conductivity.\(^\text{10}\)

Figure 5b delineates that BFO and BHFO samples do not exhibit proper ferroelectric loops. These types of loops are common in BFO-based systems and are identified as lossy dielectrics.\(^\text{10}\) Here, the opening of the loops is ascribed to the presence of finite leakage current in the samples; the loops become narrower when the leakage current is lower. BFO density in BHFO-10 is \(\sim 1.75 \times 10^{-5}\) A/cm\(^2\) at 7.78 kV/cm (Figure 5a), which is approximately 2 orders of magnitude lower than BFO. Indeed, BFO has the highest DC conductivity (Figures 5a and S8), which implies that it has the maximum amount of oxygen vacancies and/or more charge fluctuations in the Fe sites compared to the other three BHFO samples. With the bond dissociation energy of Ho–O (606 kJ/mol) being larger than that of Bi–O (343 kJ/mol), the substitution of Bi sites with Ho restrains the creation of oxygen vacancies and other defects (Figures 3 and S6). However, the current density of BHFO-15 is \(\sim 2.73 \times 10^{-5}\) A/cm\(^2\) at 7.78 kV/cm, which is 2 times higher than that of BHFO-10. Both BHFO-10 and BHFO-15 had less amount of oxygen vacancies compared to BFO (Figure S6). Therefore, the plausible reason for such increased conductivity at 15 mol % Ho concentration could be the modification of Fe\(^{2+}/\text{Fe}^{3+}\) bond angle and Fe–O length, as listed in Table S1, which could enhance the overlap of electronic wave functions, resulting in the smaller band gap. However, in a previous study,\(^\text{22}\) it was reported that Ho substitution can reduce the effective optical band gap energy of BFO, which renders easy electron transition from the valence band to the conduction band (O\(^{2−}\) 2p \(\rightarrow\) Fe\(^{3+}\) 3d) and thus leading to enhanced conductivity.\(^\text{10}\)

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having a non-centrosymmetric R3c space group fails to display any ferroelectric saturation phenomenon (Figure 5b) because of the high leakage density, as depicted in Figure 5a. The large area under the P-E loop of BFO justifies that the sample has incurred a high amount of loss, owing to a large DC-type leakage. Following TEM analysis, as the presence of defects and defect complexes (V_{O}^{-}^{*}, V_{Bi}^{*}, V_{Bi}^{*} - V_{O}^{-}^{*} or Fe_{B}^{+}/Fe_{B}^{-} - V_{O}^{-}^{*}) makes the BFO domain structure disordered (Figure 3d), this also renders the dipoles to become disordered, causing the dipole moments to have a random orientation, and hence, a spontaneous polarization with an applied electric field cannot readily be obtained. In BHFO compositions, the ordered and disordered regions coexist (Figures 3e,f and S3c), and the polarization in the disordered regions shows similar behavior to that of BFO, whereas the O_{2} regions display a uniform orientation of dipole moments due to the ordered structure of dipoles. Consequently, even though BHFO-5 generates some uniform polarization, this is not sufficient enough for the sample to procure ferroelectricity, owing to its appreciable DC conductivity. On the other hand, because of having lower conductivities, the openings of BHFO-10 and BHFO-15 loops become narrower compared to that of BFO and BHFO-5 (Figure 5b). Indeed, BHFO-10 and BHFO-15 exhibit narrower loops compared to several previous studies on Sr, Ba, and Ta and Ti-doped BFO, where loops were wider due to the considerable amount of oxygen vacancy presence. The absence of ferroelectricity in these samples could be ascribed to the emergence of centrosymmetric space groups (Pnma and C2/m) in their crystal structures (Figure 1).

This section emphasizes the temperature evolution of magnetization and the heat capacity and thermal conductivity of BHFO ceramics. Figure 6a shows the variations in the magnetic moment (M) for BFO, BHFO-5, BHFO-10, and BHFO-15 nanoparticles measured under a magnetic field (H) of 100 Oe in the temperature (T) range: 300–950 K. BHFO-10 has the highest magnetization among all samples at 300 K due to the change in the bond length and bond angle (Figure 2), which suppress G-type spiral-modulated spin structure. BHFO-10 has the highest magnetization among all samples at 300 K due to the change in the bond length and bond angle (Figure 2), which suppress G-type spiral-modulated spin structure. The enhancement in magnetization is discussed in detail in the Supporting Information. Figure 6a depicts that BFO and BHFO nanoparticles retain their magnetization up to high temperatures (≥700 K), indicating their stability. It also shows that BFO has two magnetic anomalies at ~630 ± 8 K ± 646 K, indicated by the arrows. This anomaly can be determined from the onset of a noticeable change in the slope, as indicated by arrows in dM/dT versus temperature graph (Figure S10). The pronounced anomaly near 646 K appears due to the antiferromagnetic (AFM) ordering of the Fe moments. This is the Néel temperature of BFO and agrees with previous studies. However, this anomaly for BHFO-(5, 10, and 15) shifts to higher temperature (Figure S11), suggesting that Ho doping has changed the AFM transition temperature. Here, temperature-dependent magnetic (M–T) behavior of BHFO-10 was somewhat different from other BHFO samples and also that found in the literature. The AFM temperature shifted to ~710 K for BHFO-10 and has higher magnetism compared to other BHFO and BFO nanoparticles. The shift in AFM temperature could be related to the number of oxygen vacancies in the samples, as discussed in detail in the following section. BHFO-(5, 10, and 15) showed another anomaly near T = 630 ± 8 K, which did not appear in BFO. According to a previous study, the appearance of this extra magnetic transition is associated with structural transformation in BHFO nanoparticles from R3c to Pnma around this temperature. In this study, the peak intensity of 630 ± 8 K transition point for BHFO-10 and BHFO-15 is relatively higher than BHFO-5, which could be due to having a Pnma phase already at room temperature (Figure 1). BHFO-5 did not have a Pnma phase at room temperature, but it could undergo a phase transformation after 610 K since Ho-substituted BFO has a tendency to exhibit structural transformation. However, the contribution from secondary phases to the magnetization could be ruled out because the impurities of BHFO-5 like Bi_{2}O_{3} and Bi_{2}Fe_{4}O_{9} lose their magnetism at room temperature.

In order to understand the temperature effect on thermal properties, specific heat capacities of BFO and BHFO-(5, 10, and 15) nanoparticles were measured from 350 to 850 K, as shown in Figure 6b. The molar specific heat capacity at constant pressure, C_{p}, was obtained from the differential scanning calorimetry (DSC) signal (Figure S12). Three distinct features can be observed in nanoparticles’ heat capacity curves (Figure 6b), namely, (1) the effects of Ho substitution on heat capacity, (2) the temperature shift in AFM peaks, and (3) an increase in heat capacity even above 646 K (Néel temperature). The structural modification brought by Ho substitution increases the heat capacity of BHFO-10 by 30% compared to that of intrinsic BFO up to the AFM transition temperature (Figure 6b). The lattice dilatation (thermal expansion of the lattice) and change in vibrational components as a function of composition could lead to an increase in the heat capacity. The presence of orthorhombic (Pnma) phases apart from the parent rhombohedral (R3c) and the changes in bond lengths (Figure 2) could bring about some modifications in the lattice vibrations and phonon modes and thus can cause an excess lattice dilatation in BHFO nanoparticles. BHFO-10 and BHFO-15 having a Pnma phase show higher heat capacities than that of BFO. Moreover, a sudden increase in the heat capacity of BHFO-5 is observed after 692 K. This is possibly due to the appearance of a dominant Pnma over the R3c phase. Ho-substituted BFO tends to exhibit structural transition phenomena, and thus, BHFO-5 might undergo a phase transformation process from R3c to Pnma at some temperature around 650 K. In fact, BHFO-5 has an extra magnetic anomaly around this temperature (Figure 6a). This observation indirectly corroborates the proposition that the presence of the Pnma phase in BHFO-(5, 10, and 15) increases the heat capacity. In addition, it has also been found that the vibrational component could be correlated to structural changes as a function of composition. The distortion of FeO_{6} octahedron in the BFO crystal lattice increases with Ho substitution, which manifests itself in terms of a change in the bond length (Figure 2). This phenomenon could, particularly, be observed in the case of BHFO-10 nanoparticles, where the Fe–O bond length in the main R3c phase was reduced by the most significant amount and thus possibly inducing further lattice vibrations in BHFO-10 to increase its heat capacity by 30%. However, in the case of BHFO-15, the coexistence of multiple polymorphic phases might have affected simultaneous lattice vibrations and hence lowered heat capacities compared to that of BHFO-10.

The AFM phase transition temperature of the heat capacity measurement depends on the number of oxygen vacancies. The oxygen vacancies in the perovskite structures can control the shifting of AFM transition temperature. The hypothesis is that the lower is the number of oxygen vacancies,
the higher is the magnetic ordering temperature of the perovskite.\textsuperscript{43,45} The AFM transition temperature of BFO nanoparticles is \( \sim 669 \text{ K} \), indicated by the arrow (Figure 6b), which is consistent with a previous study.\textsuperscript{17} BHFO-(5, 10, and 15) exhibits two transition peaks: the first transition temperature is \( \sim 637 \text{ K} \), and the second temperature is \( > 700 \text{ K} \). The major transition temperature at 669 K has shifted to higher temperatures with the Ho substitution (Figure S11), indicating that BHFO samples with lower oxygen vacancies (as derived from Figures 3f and S5a) have maximum \( \sim 40 \text{ K} \) higher AFM temperature compared to BFO. Similar characteristics are found in the magnetic behavior of these nanoparticles, where the transition temperature is found to shift by \( \sim 64 \text{ K} \) (Figure 6a). Therefore, a close agreement between the AFM transition temperatures from specific heat capacity measurements and the \( M-T \) curve is observed, suggesting that the transition at higher temperature is indeed induced by a magnetic phase transition, involving heat exchange. There is also a small feature near 637 K in BHFO-(5, 10, and 15) (Figure 6b), which also corresponds to the lower temperature magnetic transition. As already discussed in the magnetic section, this magnetic transition might be due to the presence of \( Pm a m \). Another feature of this transition temperature is the peak broadening observed in BHFO-5 and BHFO-10 samples, which implies a strong coupling between the magnetism and the structural distortion.\textsuperscript{46}

Figure 6b depicts that the heat capacity of the nanoparticles does not show any saturation at higher temperatures. This type of unsaturated heat capacity is not rare in BFO (Figure S13) and other functional material systems.\textsuperscript{48–56} An attempt has been made to explain the unsaturated heat capacity in terms of phonon heat capacity, \( C_p(T) \), and the excess component of the specific heat capacity, \( \Delta C_p(T) \), considering, \( C_p(T) = \Delta C_p(T) + C_0(T) \). Figure 6c shows measured heat capacity along with fitted heat capacity and phonon heat capacity. The phonon heat capacity \( C_0(T) \) is calculated for a composite of \( N \) phases, using the following equation

\[
C_0(T) = \frac{\pi k_B}{3} \sum_{i=1}^{N} \frac{\nu_i \rho_i}{M_i} \left( \frac{T}{T_0} \right)^3 \int_0^{T_{\text{D}}/T} \frac{x^2 e^{-x}}{(e^x - 1)^2} dx
\]

(3)

Here, the contribution of different phases to heat capacity is considered at first, where \( \theta_{\text{D}}, N, \rho, \) and \( \nu \) are the Debye temperature (K), total number of atoms/mole, gram molecular weight (gm/mol), density (gm/cm\(^3\)), and volume fraction, respectively, of the \( i \)th phase. The details of the equation are given in the Supporting Information. Using this eq 3 and the values of Table S3, the phonon heat capacity curves of BFO and BHFO nanoparticles are obtained (Figures 6c and S15). The calculated heat capacity complies with the first principle phonon calculation (Figure 6c).\textsuperscript{46} It can be observed that \( C_0 \) is lower than the measured \( C_p \) implying that phonon heat capacity cannot alone explain the measured heat capacity behavior. Indeed, \( \sim 50\% \) of the measured heat capacity is dominated by excess heat capacity, \( \Delta C_p \) at 800 K (Figures 6c and S14). Previous reports suggest that such excess heat capacity of BFO and rare-earth doped BFO system can be interpreted in terms of Schottky anomaly for three-level energy states,\textsuperscript{17,57} which can be expressed as follows:\textsuperscript{17,58}

\[
\Delta C_p = \frac{\Delta E_1}{k_B T} \frac{\Delta E_2}{k_B T} \left\{ \left[ 1 + D_1 \exp \left( \frac{-\Delta E_1}{k_B T} \right) + D_2 \exp \left( \frac{-\Delta E_2}{k_B T} \right) \right] \right\} \left[ D_1 \exp \left( \frac{-\Delta E_1}{k_B T} \right) + \frac{\Delta E_2}{k_B T} \right] \right\}
\]

(4)

where \( \Delta E_1 \) and \( \Delta E_2 \) are the energy barriers that separate three different occupying energy states, \( k_B \) is the Boltzmann constant, \( \theta_0 \) is the number of moles, \( R \) is the universal gas constant, and \( D_1 \) and \( D_2 \) are the ratios of the degeneracy orders of the levels. The measured heat capacities, as shown in Figures 6c and S15, were fitted using both eqs 3 and 4. The model parameters for the nanoparticles are obtained and listed in Table S4. However, the fitted values of \( D_1 \) are at least 3 orders of magnitude higher than that of previously reported values,\textsuperscript{7,57} which is not physical for the current heat capacity scenario. Therefore, the excess part of the current work cannot be explained in terms of the Schottky anomaly for the three-level energy states of BFO and BHFO. It appears that the excess heat capacity, \( \Delta C_p \), might be dominated by other factors such as anharmonicity, partial densification of nanoparticles, and/or thermal expansion of the lattice. First, anharmonicity due to entropy could lead to an unsaturated heat capacity in the ceramic systems.\textsuperscript{56,59} The existence of cations’ (Bi, Ho, and Fe) disordering in the BFO lattice might increase the entropy of the BFO system. It is indirectly evident from XRD, HR-TEM, and EDS analyses that BFO and BHFO had an appreciable amount of oxygen vacancies, and so, the cations should have disordering even at room temperature. This cation disordering should grow at higher temperatures and increase the entropy and heat capacity of the nanoparticles. Partial densification of nanoparticles at high temperatures could further contribute toward unsaturated heat capacity.\textsuperscript{60} The BFO nanoparticles tend to form necking and hence densify during heating.\textsuperscript{61} Figure 3a–c shows that some nanoparticles have already formed necking and others are in good contact with each other. Therefore, it is not unlikely that due to heating above 400 °C, such neck-formation leading to partial densification reduces the porosity of the powder bed and increases the heat flow with temperature (Figure S12) and hence the heat capacity. Lastly, the thermal expansion of the lattice, which is responsible for unusually high heat capacity,\textsuperscript{56} might influence BFO heat capacity as well. The lattice parameters of BFO and BHFO systems modify as a function of composition (Table S1) and temperature.\textsuperscript{8,62} Thermal expansion associated with an increment in lattice parameters might contribute towards the observed increase in heat capacity.

Room temperature and temperature-dependent thermal conductivities of BFO and BHFO nanostructured sintered pellets measured by a hot disk utilizing the transient plane source technique\textsuperscript{26,27} are listed in Table 1 and depicted in Figure 6d. The measured room temperature thermal conductivity of BFO varies from 0.19 ± 0.04 to 0.38 ± 0.06 W m\(^{-1}\) K\(^{-1}\) depending on the density of the sintered pellets, indicating that the measured values are significantly lower compared to the literature values (0.78–3.5 W m\(^{-1}\) K\(^{-1}\)).\textsuperscript{17,19} A detail comparison of room-temperature thermal conductivity for BFO synthesized using different techniques is proved in Table S5. This low thermal conductivity of BFO could be attributed to the presence of porosity in the pellets.\textsuperscript{17,18} To
prove the role of porosity, two sets of sintered pellets at two different (2 and 5 tons) compressive pressures were prepared. The sintered pellets of BFO and BHFO are not fully dense and have a large void fraction (Table 1), possibly because of a low implied hydraulic pressure (2 and 5 tons) during their formation. Thermal conductivity enhances up to ~46% when the formation pressure increases from 2 to 5 tons, implying that thermal conductivity improves with increasing density (Table 1). Here, the amount of porosity within the pellets formed at 5 tons decreased by up to ~42% compared to the pellets of 2 tons. Moreover, the effect of porosity on the thermal conductivity is determined using the effective medium equation outlined by Nan et al.,\textsuperscript{63,64} where the pores are treated as a separate phase, and the samples were modeled as a mixture of two different thermally conductive components (i.e., BFO nanoparticles and pores). The equation is as follows:

\[
\kappa^* = \frac{\kappa_p (1 + 2\alpha) + 2\kappa_m + 2f[\kappa_p (1 - \alpha) - \kappa_m]}{\kappa_p (1 + 2\alpha) + 2\kappa_m - 2f[\kappa_p (1 - \alpha) - \kappa_m]}
\]

Here, \(\kappa^*\) is the effective thermal conductivity of the bulk, \(\kappa_m\) is the calculated thermal conductivity of the solid phase, \(\kappa_p\) is the thermal conductivity of air, \(f\) is the air-filled void fraction in the pellet, and \(\alpha = 2R\kappa_p/d\), where \(d\) is the largest pore diameter within pellet and \(R\) is the thermal boundary resistance. \(R\) can be calculated from the volumetric heat capacities \(C_v\) and group velocities \(v\) following Chen:\textsuperscript{65}

\[
R \approx 4 \left( \frac{C_v v_1^2 + C_{v,2} v_2^2}{C_v v_1 C_{v,2} v_2} \right)
\]

Here, \(C_{v,1}\) is the volumetric heat capacity of air, \(C_{v,2}\) is the volumetric heat capacity of samples, \(v_1\) is the phonon group velocity in air, and \(v_2\) is the phonon group velocity in BFO. Using the measured thermal conductivity of the bulk with porosity (\(\kappa^* = 0.26 \text{ W m}^{-1} \text{ K}^{-1}\)) and thermal conductivity of only solid phase (\(\kappa_m = 1.5 \text{ W m}^{-1} \text{ K}^{-1}\)) for BFO prepared at 5 tons, the void fraction of the pellet \(f\) is found to be 0.69, which is close to our calculated void fraction (Table S6). Since the average particle size of BFO was ~125 nm, the calculation is performed assuming an average pore size of 125 nm.

In order to gain a better understanding of the Ho substitution effect, the thermal conductivity of the BFO and BHFO samples prepared under 2 tons of pressure as a function of temperature was measured (Figure 6d). The thermal conductivity of all nanostructured pellets falls in the range of 0.15–0.25 W m\(^{-1}\) K\(^{-1}\) with ±0.06 W m\(^{-1}\) K\(^{-1}\) error limit. The small difference between the average thermal conductivities of the pellets arises from instrumental uncertainty, heat capacity uncertainty, and sensor uncertainty. An uncertainty of 3–6\% assigned to the density measurements was also incorporated into the hot disk measurement uncertainty. Figure 6d also depicts that the thermal conductivity remains more or less constant over the whole temperature range, resembling an amorphous or glass-like behavior.\textsuperscript{66,67} The apparent similarity in thermal conductivity of BFO and BHFO pellets indicates that the impact of Ho substitution on thermal conductivity could not be resolved because of the large number of bulk porosities in nanostructured sintered pellets. Moreover, the linear relationship between thermal conductivity and heat capacity did not hold as the following equation, \(\kappa = 1/3C_p v_0 l\), where \(C_p\) is the specific heat, \(v\) is the speed of sound, and \(l\) is the average phonon mean free path length.\textsuperscript{68} In this study, heat capacity and magnetism of BFO and BHFO nanoparticles increased with increasing Ho concentrations. This is because the physical property measurement system and simultaneous thermal analyzer measured the intrinsic magnetism and heat capacity of these nanoparticles. They are less sensitive to bulk porosities compared to the hot-disk measurement method employed to estimate the thermal conductivities of the nanostructured sintered pellets rich in porosity. The existence of porosities reduces the room-temperature thermal conductivity of BFO and BHFO nanostructured sintered pellets and leads to an amorphous or glass-like behavior as a function of temperature. A temperature-dependent thermal conductivity and magnetic correlation cannot be also established because of this experimental limitation. In addition to the porosity of nanostructured sintered pellets, other factors such as pore boundaries, local charge disorder, configuration disorder, and presence of mixed phases could also play a role in reducing the thermal conductivity as well. The scattering of phonons across the pore boundaries might reduce the thermal conductivity of porous pellets.\textsuperscript{69} Moreover, the contributions of local ionic charge disorder and configuration disorder cannot be ruled out in plummeting the thermal conductivity.\textsuperscript{70} The formation of oxygen and bismuth vacancies could bring local ionic charge disorder and generate random local-stresses throughout the crystal which may, in turn, induce lattice vibrations and thereby lead to the glass-like thermal conductivity in the BFO system. Cahill et al.\textsuperscript{66} and Schelling et al.\textsuperscript{67} also attributed the glass-like thermal conductivity behavior of the oxide systems to the presence of excess oxygen vacancies. In fact, previous studies on BFO\textsuperscript{10,11} report that the depletion of oxygen atoms from the lattice sites has a constraining effect on the lattice, which is supported by Rietveld analysis that shows distortion in FeO\textsubscript{y} octahedron while preserving a long-range crystallographic order (Figures 1 and 2f). The addition of Ho\textsuperscript{3+} (0.901 Å) in the place of Bi\textsuperscript{3+} (1.03 Å) cannot eliminate the local ionic charge disorder completely but reduces the formation of oxygen vacancies. Ho introduces a local configurational disorder such as mass mismatch and atomic radii mismatch. This could result in additional phonon scattering. Moreover, the existence of mixed phases could influence the BFO thermal conductivity. Indeed, the appearance of different phases apart from R3c can reduce the thermal conductivity of BFO.\textsuperscript{71} The presence of mixed phases could change ionic coordination and lead to a much weaker Fe−O or Bi−O bonding along the [001] direction in the primary phase of BFO and BHFO samples.\textsuperscript{19} This weak interlayer coupling could increase anharmonicity and results in scattering. A saturation of phonon scattering from porosity, pore boundaries, local charge

<table>
<thead>
<tr>
<th>sample</th>
<th>theoretical density (g cm(^{-3}))</th>
<th>measured density (g cm(^{-3}))</th>
<th>measured thermal conductivity (W m(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2 tons</td>
<td>5 tons</td>
</tr>
<tr>
<td>BFO</td>
<td>8.13</td>
<td>2.65</td>
<td>4.18</td>
</tr>
<tr>
<td>BHFO-5</td>
<td>8.34</td>
<td>3.2</td>
<td>4.3</td>
</tr>
<tr>
<td>BHFO-10</td>
<td>8.40</td>
<td>2.4</td>
<td>3.23</td>
</tr>
<tr>
<td>BHFO-15</td>
<td>8.64</td>
<td>2.39</td>
<td>3.83</td>
</tr>
</tbody>
</table>

*The pellets were prepared under 2 and 5 tons uniaxial compressive forces.*
disorder, configuration disorder, and mixed phases limits the thermal conductivity reduction achievable with an increasing Ho concentration.

4. CONCLUSIONS

In summary, this work illustrates the correlation between thermal and magnetic properties of Ho-substituted BFO and studies their dependence on oxygen vacancies and structural modifications. Magnetic transitions found in temperature-dependent heat capacity and magnetic behaviors imply a strong coupling between magnetism and heat transfer. The BFO magnetic transition shifts to higher temperatures by ~64 K with Ho addition due to a reduction in oxygen vacancies. The structural modification brought by Ho substitution increases the heat capacity of BHFO-10 by 30% compared to that of intrinsic BFO up to the AFM transition temperature. Saturated heat capacity for BFO and BHFO nanoparticles cannot be achieved, and they retain magnetization even at 850 K. The thermal conductivity of BHFO is strongly affected by the presence of porosities in the nanostructured sintered pellets, demonstrating nearly an order of magnitude reduction in thermal conductivity relative to its pristine counterpart, and a glass-like trend in thermal conductivity over the range of temperature is observed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c02696.

XRD patterns and Rietveld refinement data; HR-TEM image and SAED pattern of BHFO-15; EDS analysis on oxygen contents of BFO and BHFO nanoparticles; room-temperature electrical conductivity and magnetization of samples; temperature coefficient of magnetization as a function of temperature curves to determine magnetic anamoly; heat flow patterns and phonon heat capacity calculation; and room-temperature BFO thermal conductivity comparison (PDF)

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Notes

The authors declare no competing financial interest.

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