High-temperature thermoelectric properties of (1-x)DyBCO – xBNT ceramics

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ABSTRACT
Dysprosium barium copper oxide – bismuth sodium titanate ((1-x)DyBCO–xBNT) ceramics, where x = 0–0.07 mole fraction, were successfully prepared by a solid-state reaction and sintering method. The DyBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7−x} and (Bi\textsubscript{0.5}Na\textsubscript{0.5})TiO\textsubscript{3} powders were separately synthesized by calcining their stoichiometric mixtures at 900°C for 4 h and 800°C for 2 h, respectively. The (1-x)DyBCO–xBNT powders were compounded into pellets and sintered at 930°C for 2 h under normal air atmosphere. Phase identification and morphological analysis of all samples were determined using X-ray diffractometer (XRD). The quantitative phase analysis was analyzed by fitting the XRD pattern using the GSAS-II program. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) was used to study microstructure and chemical composition. In all cases, the result of XRD shows that the DyBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} (Dy-123) was identified as the main crystalline phases, due to the good agreement between the observed and calculated patterns after Rietveld refinement. All BNT-doped DyBCO ceramics showed slightly higher density values than the undoped sample, suggesting that BNT helped improve the densification process. The sign of the Seebeck coefficient (S) was positive for all samples at all measured temperatures, confirming a p-type conduction mechanism. Low BNT doping improved the overall thermoelectric properties of DyBCO ceramics by affecting electrical conductivity (\sigma), Seebeck coefficient (S), and thermal conductivity (\kappa). The dimensionless figure of merit (ZT = S^2\sigma T/k\sigma) of all samples increased with increasing temperature. The highest ZT value of 5.67 \times 10^{-2} was observed for the 0.97DyBCO–0.03BNT sample at 863 K.

1. Introduction
Renewable energy technologies are especially important for the future energy revolution. Thermoelectric (TE) material, which has the ability to directly convert heat to electricity, is one of the potential candidates for future clean energy applications. TE has so far been used mainly in the standalone power-generation technology for biomedical, aerospace, military, and remote power applications [1,2]. The efficiency of TE material is evaluated by the dimensionless figure of merit, ZT = \sigma S^2 T/k\sigma, where \sigma, S, T, and k\sigma are the electrical conductivity, Seebeck coefficient, absolute temperature and total thermal conductivity, respectively [1,2]. Therefore, high \sigma, large S, and low k\sigma are required for a good TE material. Nowadays, the renewable energy technologies for power harvesting from automobile and industrial waste heat may require oxide materials because of their potential advantages over intermetallic alloys in terms of thermal and chemical stability at high temperature. For examples, SrTiO\textsubscript{3}, ZnO, LaCoO\textsubscript{3}, Na\textsubscript{2}Co\textsubscript{3}O\textsubscript{5}, Ca\textsubscript{2}Co\textsubscript{3}O\textsubscript{6.5}, and Bi\textsubscript{2}Sr\textsubscript{2}Co\textsubscript{3}O\textsubscript{6} have been widely studied [3–8]. Misfit-layered cobalt-based oxide semiconductors were reported to exhibit large S and considered to be good candidates for thermoelectric materials [5–8]. Because of the strong electron–electron correlation in these layered Co oxides, there is a possibility for obtaining good thermoelectric properties in these compounds by optimizing the electrical properties and reducing the thermal conductivity. Layered YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7−δ} (YBCO or Y-123) material, which is another typical strong electron correlation layered oxide, have been known as a high-T\textsubscript{c} superconductor. In addition, Y-123 is considered a potential oxide thermoelectric material due to its high \sigma, moderately high S and low k\sigma [9–13]. The maximum ZT of YBCO was reported to be around 0.3–0.7 [9–13] and its electrical and thermal transport properties was significantly related to oxygen deficiency (\delta) in the lattice. It is well known that Y-123 is an oxide compound whose crystal structure is composed of rocksalt and perovskite units. In these materials, the free charge carriers are confined to the planar Cu–O sheets that are separated by insulating layers. The interaction of the special crystal structure leads to the strong anisotropy of electrical conduction which makes these compounds very interesting for thermoelectric properties investigation. REBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7−δ} (RE = Nd, Sm, Eu, Gd, Dy, etc.) have better applicability compared to Y-123 system [14–18]. They show a higher

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metallic-superconducting transition temperature, better surface morphology and also better performance under external magnetic field.

At 300 K, the $\sigma$ of the pure Dy-123 sample ($6.45 \times 10^4 \ \Omega^{-1}\text{m}^{-1}$) was higher than that of pure Y-123 sample ($4.00 \times 10^4 \ \Omega^{-1}\text{m}^{-1}$) at 300 K [18,19]. In terms of thermoelectric properties, the $\sigma$, $S$, and $\kappa_T$ of the Dy-123 ceramic were around $-5 \times 10^4$–$6 \times 10^4 \ \Omega^{-1}\text{m}^{-1}$, $\sim 2$–$5 \ \mu\text{W/K}$, and $\sim 2.7$–$4 \ \text{W/m-K}$, respectively [20,21]. The ZT of the Dy-123 compound exhibited $\sim 10^{-4}$ near room temperature. Nevertheless, there is no known ZT of this compound at high temperature. Hence, some modifications of this compound are of interest so as to optimize and investigate its high-temperature thermoelectric properties.

It is well known that the combination of glass-like thermal conductivity and crystal-like electronic properties (i.e. phonon-glass electron-crystal or PGEC) is required for good thermoelectric materials [22]. This approach is most achievable in materials with complex crystal structure, where vacancies and heavy element atoms would act as effective phonon scattering center and reduce the lattice thermal conductivity ($\kappa_l$). The combination of two or more compounds in the form of nano-composite or solid solution [23] is one method that seems to support the PGEC concept and provide enhancement in performance of thermoelectric materials.

Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) is a non-conducting oxide which is a lead-free perovskite ferroelectric material with reported high $S$ (+375 $\mu\text{W/K}$) but with very low $\sigma$, leading to very low ZT [24]. It is interesting that the BNT contains heavy element atoms which would act as phonon scattering centers, leading to low $\kappa_T$. Recent research suggests that the $\kappa_T$ of the NCO and YBCO compounds could be reduced by the BNT additions due to more efficient phonon scattering [7,24]. In addition, small amount of BNT was found to enhance the $S$ values of YBCO but larger amount caused the major carrier transport mechanism to transform from $p$-type to $n$-type [12]. Due to the high $\sigma$ of DyBa$_2$Cu$_3$O$_{7-\delta}$ (Dy-123 or DyBCO) and high $S$ of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) compound, it might be expected that the combination of Dy-123 and BNT at certain composition could lead to thermoelectric efficiency improvement. Therefore, the aim of this study is to fabricate and characterize (1-x) DyBCO–xBNT ceramics. By employing quantitative phase analysis, the relation of phase formation with crystal-structure and microstructural change, composition, density and thermoelectric properties at high temperature were investigated and discussed in details.

2. Experimental

The samples of (1-x)DyBa$_2$Cu$_3$O$_{7-\delta}$–xBi$_{0.5}$Na$_{0.5}$TiO$_3$ or (1-x)DyBCO–xBNT ceramics were successfully prepared by a solid-state reaction and sintering method. First, the DyBCO powder was prepared by mixing an appropriate amount of Dy$_2$O$_3$ (99.9%, Sigma-Aldrich), BaCO$_3$ ($\geq$ 99%, Sigma-Aldrich) and CuO (98%, Sigma-Aldrich) starting powders. These powders were mixed in a stoichiometric ratio of DyBa$_2$Cu = 1:2:3 and ball milled for 24 h in polyethylene jar with zirconia ball as milling media. The mixed powders were dried and calcined in an opened alumina crucible at 900°C for 4 h under normal atmosphere. Second, the BNT powder was synthesized by mixing the starting compounds of Bi$_2$O$_3$ (99.9%, Aldrich), Na$_2$CO$_3$ (95.5%, Carlo Erba), and TiO$_2$ (>99%, Sigma-Aldrich) powders in the appropriate ratio and ball milled for 24 h in polyethylene jar with zirconia ball as milling media. The mixed powders were dried and calcined in an alumina crucible at 800°C for 2 h. The powder X-ray diffraction patterns of calcined DyBCO and BNT powder showed single phase with the corresponding orthorhombic and rhombohedral structure, respectively. Finally, the mixed (1-x)DyBCO–xBNT powders, where $x = 0, 0.01$, 0.03, 0.05, and 0.07 mole fraction, were compacted into disc-shaped pellets and sintered at 930°C for 2 h under normal air atmosphere. The apparent density of the ceramics was measured by the Archimedes method using xylene as the liquid medium. Phase formation of the ceramics was investigated by an X-ray diffractometer (XRD) (Phillips Xpert pro Diffractometer). The relative weight fraction of phases present in DyBCO ceramics was also calculated by using quantitative analysis based on experimental XRD patterns and GSAS-II program [25]. The microstructure was observed in backscattered electron mode using a scanning electron microscope (JSM-5910/Jeol-JIT300) and chemical composition identification was carried out using energy dispersive X-ray spectroscopy analysis (SEM-EDS). The variation of electrical conductivity and Seebeck coefficient measurement with temperature of bar-shaped (3 mm x 3 mm x 15 mm) ceramic was measured by the Seebeck Coefficient/Electric Resistance measuring system (ZEM-3, ULVAC-RIKO) from 400–900 K. The variation of thermal conductivity with temperature of disc-shaped pellets (10 mm in diameter and 1 mm in thickness) was observed by a laser flash TC-7000 system (ULVAC SINKU-RIKO) from room temperature to 1000 K.

3. Result and discussion

3.1. Phase formation

Figure 1 shows the XRD patterns of the (1-x)DyBCO–xBNT ceramics. In all cases, the DyBa$_2$Cu$_3$O$_{7-\delta}$ was identified as the main crystalline phase. The XRD pattern of the undoped DyBCO corresponded well with the DyBa$_2$Cu$_3$O$_{7-\delta}$ (Dy-123) phase (JCPDS standard file No. 01-079-0047) indicating the orthorhombic
perovskite structure in Pmmm space group as shown in Figure 2. With BNT addition (JCPDS file No. 36-0340), a small amount of non-conducting Dy$_2$BaCuO$_5$ (Dy-211) secondary phase (JCPDS file No. 00-039-1479) having an orthorhombic structure was present. The result of XRD showed that the diffraction peaks shifted slightly to lower angle when the BNT mole fraction increased as presented in Figure 1. For example, the ceramic with $x = 0.01$ showed the diffraction peak shift of (112), (005), and (113) reflections from 2θ = 32.71° to 32.43°, 38.56° to 38.39°, and 40.28° to 40.11°, respectively. The change in the unit cell parameters was mainly due to the substitution of Dy-123. There has been some reports suggesting that Cu$^{2+}$ ($r_{\text{Cu}^{2+}} = 0.73$ Å) site could be substituted by Ti$^{4+}$ ($r_{\text{Ti}^{4+}} = 0.605$ Å) ions [26–28], which produced excess electrons or cation vacancies. The substitution at the Cu site by Ti$^{4+}$ was consequently producing free CuO [29]. On the other hand, the ionic radius of Na$^+$ ($r_{\text{Na}^+} = 0.95$ Å) is comparable to that of Dy$^{3+}$ ($r_{\text{Dy}^{3+}} = 1.07$ Å) or Ba$^{2+}$ ($r_{\text{Ba}^{2+}} = 1.35$ Å). A number of researchers reported that Na$^+$ could occupy both RE$^{3+}$ (RE$^{3+} = \gamma^{3+}$, Dy$^{3+}$) and Ba$^{2+}$ [30–32] sites, producing hole carriers or anion (i.e. oxygen) vacancies. The effective ionic radius of Bi$^{3+}$ (CN = 8) was 1.17 Å as reported by R. Shannon [33]. If Ba$^{2+}$ was substituted by Bi$^{3+}$, excess electrons or cation vacancies could also be produced, which would not agree with the increase in electrical conductivity observed. Since the ionic radii and valency of Bi$^{3+}$ and Dy$^{3+}$ are similar, there was a possibility that Dy$^{3+}$ would be replaced by Bi$^{3+}$. The substitution at the RE$^{3+}$ ion of RE-123 mostly created the RE-211 and BaCuO$_2$ phase [34–36].

Rietveld refinement of the XRD patterns for all ceramic samples was performed using the structural model (COD database) of all possible occurring secondary phases as Dy-123 (Pmmm), Dy-211 (Pnma), CuO (C2/c), BaCuO$_2$ (Im-3 m), and BNT (R3c). To evaluate quantitatively the best fit of the data, the most accepted factor is the weighted residual minimized in Rietveld refinements ($R_w$) with the 0% value of $R_w$ represents an ideal fit and 10% is acceptable for most cases. The ratio between the two $R$ values defines the goodness-of-fit, $\text{GOF} = \chi^2 = R_w^2/R_{\text{exp}}^2$, where $R_{\text{exp}}$ is the expected error [37]. The $\chi$-value of 1.3 or less is empirically considered to be satisfactory. The simulated XRD pattern was obtained using GSAS-II program [25] and the simulated intensity values fit a model to data was presented in Figure 3. The weight fraction of (1-x)DyBCO-xBNT ceramics were summarized in Table 1. The result showed that when the added BNT content increased, the weight fraction of the Dy-123 phase with orthorhombic structure (Pmmm) noticeably decreased while the Dy-211 (Pnma), CuO (C2/c), BaCuO$_2$ (Im-3c) phases occurred. The presence of BNT phase was not detected in XRD patterns due to the low BNT concentration or

Figure 1. XRD patterns of the (1-x)DyBCO-xBNT ceramics sintered at 930°C for 2 h.

![Crystal structure of orthorhombic Dy-123.](image)
the phase already dissolved in the DyBCO matrix. The results showed that the fraction of CuO of the BNT-added YBCO (0.01 ≤ x ≤ 0.07) samples were detected. CuO was reported to have a band gap of 1.2 eV and p-type semiconducting characteristics [38]. The densification of the RE-123 sample was enhanced by the addition of the CuO content during sintering through the presence of the liquid phase [39]. The high relative density values of BNT-doped DyBCO samples are listed in Table 1. The percentage of non-conducting Dy-211 phase increased with the BNT addition particularly with 0.05 ≤ x ≤ 0.07. Besides, the BaCuO₂ phase is another insulating phase which is frequently observed in the process of preparation of RE-123 [40]. However, the amount of BaCuO₂ for all samples was quite small, i.e. around 0.1–0.3 wt%. Hence, the effect of BaCuO₂ on properties was expected to be negligible compared to Dy-211 (Pnma) and CuO (C2/c).

Phases and structural parameters of the (1-x) DyBCO–xBNT ceramics are listed in Table 2. The result showed that the unit cell volume of the Dy-123 phase expanded with the increase of BNT. It was possible that

![Figure 3. Experimental and simulated XRD patterns of the (1-x)DyBCO–xBNT ceramics sintered at 930°C for 2 h.](image-url)
the Dy\(^3+\) (\(r_{\text{Dy}^3} = 1.07\ \text{Å}\)) ion was likely substituted by the Bi\(^3+\) (\(r_{\text{Bi}^3} = 1.17\ \text{Å}\)) ion and Na\(^+\) ion (\(r_{\text{Na}^+} = 0.95\ \text{Å}\)) and then the Dy-211 and BaCuO\(_2\) phases occurred. As can be seen from Table 2, the volume of Dy-123 slightly increased with the increase of BNT addition. It was possible that the Cu\(^{2+}\) ion (\(r_{\text{Cu}^{2+}} = 0.73\ \text{Å}\)) was replaced by Ti\(^4+\) (\(r_{\text{Ti}^{4+}} = 0.605\ \text{Å}\)) and also the Na\(^+\) ion (\(r_{\text{Na}^+} = 0.95\ \text{Å}\)) substituted at Dy\(^3+\)/Ba\(^2+\) (\(r_{\text{Dy}^3}/r_{\text{Ba}^{2+}} = 1.07\ \text{Å}\) and \(r_{\text{Ba}^{2+}} = 1.35\ \text{Å}\)) site. Based on the calculated unit cell volume from Rietveld refinement, the overall effects from BNT addition gave a slight decrease in lattice parameter \(a\) while lattice parameter \(b\) and \(c\) slightly increased, resulting in a small expansion of the unit cell.

3.2. Microstructural analysis

The microstructure of undoped DyBCO ceramic samples showed that the grains presented a typical elongated form with a mean size of 3.74 μm as previously reported [41,42]. When the amount of added BNT increased, the morphology exhibited irregular shape. The measurement of grain size was difficult because the grain boundaries could not be outlined clearly, which partly might be due to the presence of liquid phase (i.e. BaCuO\(_2\) + CuO). The BSE-SEM of fracture surface was presented in Figure 4. From the figure, the porosity and grain boundary were reduced with BNT addition. For RE-123 [39], the CuO phase induced the grain growth and liquid phase sintering. The relative density and shrinkage of samples are listed in Table 1. The results showed that the density of the samples with BNT content were slightly higher than the undoped sample, suggesting that BNT helped improve the densification process. The backscattered electron BSE-SEM images of the polished surface samples are shown in Figure 5. The results showed that the increasing amount of BNT influenced the formation and distribution of Dy-211 phase (white spots) in the Dy-123 matrix (gray regions). As an example, for the sample with \(x = 0.03\), the Dy-123 and Dy-211 phases were obviously confirmed by the BSE-SEM with EDS technique as presented in Figure 6. The evaluated elemental compositions of the ceramics are listed in

### Table 2. Phases and structural parameters of the (1-x)DyBCO – xBNT ceramics.

| Phase (space group) | Parameters | \(x = 0\) | \(x = 0.01\) | \(x = 0.03\) | \(x = 0.05\) | \(x = 0.07\) |
|---------------------|------------|-----------|-------------|-------------|-------------|-------------|
| Dy-123 (Pmnn)       | \(a\) (Å)  | 3.8976(6) | 3.8711      | 3.8660(4)   | 3.8677(4)   | 3.8745(2)   |
|                     | \(b\) (Å)  | 3.8408(6) | 3.8662      | 3.8640(9)   | 3.8594(6)   | 3.8657(1)   |
|                     | \(c\) (Å)  | 11.6866(4)| 11.7564(7) | 11.7786(4) | 11.7589(8) | 11.7616(2) |
|                     | \(V\) (Å\(^3\)) | 174.953  | 175.955     | 175.958     | 175.531     | 176.163     |
| Dy-211 (Pmmm)       | \(a\) (Å)  | 12.1938(9)| 12.2315(8) | 12.1932     | 12.224(6)   |             |
|                     | \(b\) (Å)  | 5.6812(9) | 5.6727(4)  | 5.6760(9)   | 5.6825(4)   |             |
|                     | \(c\) (Å)  | 7.1647    | 7.1471(4)  | 7.1421(9)   | 7.1534(6)   |             |
|                     | \(V\) (Å\(^3\)) | 496.349   | 495.916     | 494.308     | 496.928     |             |
| BaCuO\(_2\) (Im-3m) | \(a\) (Å)  | 18.3202(7)| 18.3642(4) | 18.2895(1)  | 18.3798(8)  |             |
|                     | \(V\) (Å\(^3\)) | 6148.871  | 6193.257    | 6117.956    | 6209.086    |             |
| CuO (C12/c)         | \(a\) (Å)  | 4.6891(5) | 4.6834(6)  | 4.6753(3)   | 4.6661(6)   |             |
|                     | \(b\) (Å)  | 3.4265(8) | 3.4155(7)  | 3.4387(2)   | 3.4415(7)   |             |
|                     | \(c\) (Å)  | 5.0828(2) | 5.1339      | 5.0814(6)   | 5.1101(3)   |             |
|                     | \(V\) (Å\(^3\)) | 80.488    | 81.025      | 80.482      | 80.871      |             |

![Figure 4](image_url) Backscattered electron SEM images of the fracture surface the (1-x)DyBCO–xBNT ceramics sintered at 930°C for 2 h, where (a) \(x = 0\), (b) \(x = 0.01\), (c) \(x = 0.03\), (d) \(x = 0.05\). and (e) \(x = 0.07\) mole fraction.
The approximate stoichiometric compositions of gray areas were DyBa$_{2.26}$Cu$_{3.27}$O$_{3.80}$, DyBi$_{0.15}$Ba$_{2.03}$Cu$_{2.69}$O$_{3.82}$, DyBi$_{0.15}$Ba$_{2.03}$Cu$_{2.64}$O$_{3.87}$, DyBi$_{0.16}$Ba$_{2.02}$Cu$_{2.66}$O$_{3.37}$ and DyBi$_{0.15}$Ba$_{2.04}$Cu$_{2.76}$O$_{3.62}$ for the $x = 0$, 0.01, 0.03, 0.05 and 0.07 samples, respectively. It can be observed that the calculated oxygen content of Dy-123 ceramics was quite low. Using EDS technique, low oxygen content was similarly reported in RE-123 ($RE = Y, Sm$, and Dy) [43–45]. These compositions were different from the superconducting phase Dy-123 partly due to the measurement error. It is observed that the approximate elemental composition was near the stoichiometry of REBa$_2$Cu$_3$O$_{7-δ}$ (RE-123) phase. The approximate stoichiometric composition of white areas were Dy$_2$Bi$_{0.14}$Ba$_{1.09}$Cu$_{1.04}$O$_{3.05}$, Dy$_2$Bi$_{0.14}$Ba$_{1.15}$Cu$_{0.99}$O$_{3.18}$, Dy$_2$Bi$_{0.15}$Ba$_{1.11}$Cu$_{1.04}$O$_{2.85}$ and Dy$_2$Bi$_{0.15}$Ba$_{1.11}$Cu$_{1.01}$O$_{2.62}$ for the $x = 0.01$, 0.03, 0.05 and 0.07 samples, respectively. These approximate stoichiometric compositions were similar to the non-conducting phase of RE-211. However, the EDS measurement from point analysis could not detect Na and Ti possibly because of the dispersion of these elements.

Figure 5. SEM polished surface of the $(1-x)$DyBCO–xBNT ceramics sintered at 930°C for 2 h, where (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.03$, (d) $x = 0.05$, and (e) $x = 0.07$ mole fraction.

Figure 6. Backscattered electron SEM image and EDS where (a, b) gray and (c, d) white areas of the 0.97DyBCO–0.03BNT ceramic samples, respectively.
### 3.3. Electrical transport

The temperature dependence of electrical conductivity ($\sigma$) is shown in Figure 7. At low temperatures, the electrical conductivity of all (1-x)DyBCO-xBNT samples showed an increasing trend with increasing temperature, indicating the semiconducting behavior. At higher temperatures, the $\sigma$ of all samples reached maximum values and then decreased with increasing temperature, suggesting the transition from semiconducting to metallic conduction behavior. As can be seen from Figure 7, the maximum of $\sigma$ values for $x = 0, 0.01, 0.03, 0.05, and 0.07$ samples were found to be $4.08 \times 10^2, 2.8 \times 10^3, 1.42 \times 10^4, 1.32 \times 10^5,$ and $1.50 \times 10^5 \Omega^{-1} \text{m}^{-1}$, respectively. The substitution level has a pronounced effect on $\sigma$. Due to the sign of the $S$ for the Dy-123 sample was positive which confirmed that the conduction mechanism was mainly governed by holes (p-type behavior). For low BNT content doped Dy-123, Bi$^{3+}$, and Na$^{1+}$ (overall effective charge = 2+) went to replace some of Dy$^{3+}$, leading to an enhanced hole carrier concentration in the Dy-123 based compound. Similarly, the behaviors of BNT doped YBCO were previously reported by P. Prayoonphokkharat et al [12]. With increasing BNT, the substitutions of RE$^{3+}$ by Na$^{2+}$/Bi$^{3+}$ also occurred and created hole but the Cu$^{2+}$ site of the Dy-123 phase was substituted by Ti$^{4+}$ with $0.03 < x \leq 0.07$, which had the effect of reducing hole concentration.

The weight percentage of Dy-211 was 1.30%, 0.80%, 6.30%, and 8.60% for $x = 0.01, 0.03, 0.05$, and 0.07, respectively. The weight percentage of BaCuO$_2$ was 0.30%, 0.20%, 0.20%, and 0.30% for $x = 0.01, 0.03, 0.05$, and 0.07, respectively. At temperature $< 300$ K, the $\sigma$ in the molar ratio of Dy-123:Dy-211 = 100:x was reported to be $8.00 \times 10^5, 7.55 \times 10^5, 7.14 \times 10^5,$ and $5.88 \times 10^5 \Omega^{-1} \text{m}^{-1}$ for $x = 5, 10, 20,$ and 40, respectively [46]. In addition, the $\sigma$ in the mass ratio of the Y-123:Y-211 samples was $1.00 \times 10^4, 4.00 \times 10^5, 8.00 \times 10^5,$ and $3.33 \times 10^2 \Omega^{-1} \text{m}^{-1}$ at 300 K for the Y-123/Y-211 = 90:10, 80:10, 70:30, and 50:50, respectively [47]. These results suggested that the $\sigma$ of the RE-123 decreased with the increase of the insulating RE-211 fraction. In addition, the resistance of Y-123:BaCuO$_2$ increased from 0.8 m$\Omega$ for the BaCuO$_2 = 4$ wt.% sample to 0.9 m$\Omega$ for the BaCuO$_2 = 8$ wt.% sample at $< 300$ K [48]. The decrease of $\sigma$ was found to be associated with formation of insulating Dy$_2$BaCuO$_5$ (Dy-211) and BaCuO$_2$ phases for the 0.03 $< x \leq 0.07$ sample (Figure 7). On the other hand, CuO phase is a p-type semiconductor ($E_g = 1.2$ eV). The weight percentage of CuO was 2.70%, 6.70%, 5.50%, and 6.40% for $x = 0.01, 0.03, 0.05$, and 0.07, respectively. The $\sigma$ of the CuO bulk is $\sim 0.5-3.0 \Omega^{-1} \text{m}^{-1}$ at 298 K and $\sigma \leq 3.0 \times 10^{-6} \Omega^{-1} \text{m}^{-1}$ at 1000 K [38]. It is suggested that the substitution of the Dy-123 played the important role in the increase of $\sigma$, comparing to the effect of secondary phases. The mobile holes for the p-type semiconductor are small polaron hopping conduction (SPHC), and the temperature dependence of $\sigma$ can be generally expressed as $\sigma = n e a^2 (A/T) \exp(-E_a/k_B T)$, where $n$, $e$, $a$, $A$, $E_a$, $k_B$, and $T$ are the carrier concentration, electron charge of carrier, inter-site distance of hopping, pre-exponential term related to the scattering mechanism, activation energy, Boltzmann constant and absolute temperature, respectively [49]. The $E_a$ can be obtained from the slopes of the ln(T/ρ) versus 1000/T plots [64,95] as displayed in Figure 8. Below 673 K, it showed that the activation energy ($E_a$) decreased with low BNT addition. The sample with $x = 0.07$ exhibited the lowest $E_a$ (35.24 meV). Even though the activation energy for polaron hopping mechanism was lowest, the electrical conductivity was rather low which was similar to that of $x = 0.05$ sample. We expected that the ionic substitution (e.g. Ti$^{4+}$ substituting Cu$^{2+}$, inducing electrons and reducing mobile holes) and the presence of insulating secondary phases played a role in these two compounds. For the $x = 0.01$ and $x = 0.03$ samples, the effects of hole carrier production due to Bi$^{3+}$ and Na$^{1+}$ substituting Dy$^{3+}$ may dominate the conduction mechanism. As presented in Figure 4, the $0.01 \leq x \leq 0.07$ samples have a larger grain size and lower grain boundary than the sample with $x = 0$. The textures were enhanced, leading to a reduction in the amount of grain boundaries and interfaces, helping to reduce

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**Table 3.** Evaluated elemental composition of the polished (1-x)DyBCO-xBNT ceramics.

| x  | Areas | Dy  | Ba  | Cu  | O   | Bi  |
|----|-------|-----|-----|-----|-----|-----|
| 0  | Gray  | 9.7 | 21.8| 31.7| 36.8|     |
| 0.01| White | 27.3| 14.9| 14.2| 41.7| 1.9 |
| 0.03| White | 26.8| 15.4| 13.3| 42.6| 1.9 |
| 0.05| White | 10.3| 21.3| 27.1| 39.8| 1.6 |
| 0.07| White | 28.0| 15.5| 14.5| 39.9| 2.1 |
|     | Gray  | 10.9| 22.0| 28.8| 36.6| 1.7 |
|     | Gray  | 29.0| 16.1| 14.7| 38.0| 2.2 |
|     | Gray  | 10.5| 21.3| 28.9| 37.8| 1.6 |
$E_g$ [50]. It suggested that the increase of BNT content play a significant role of $E_g$.

At high temperature, the $\sigma$ decreased when the temperature increased due to the release of the weakly bond oxygen according to Kroger-Vink notation [51], $O'_a \rightarrow V_o + 2e^- + (1/2)O_2(g)$, where $O'_a$, $V_o$, and $e^-$ are the O-site substitution with O, oxygen vacancies and electrons, respectively. Due to the fact that the (1-x) DyBCO–xBNT samples exhibited the p-type conduction as will be shown in the next part. Following this behavior, the carrier concentration was decreased by the combination between electron ($e^-$) and hole ($h^+$) to give a low $\sigma$ of the samples at high temperature. Similar behavior has been previously reported in oxide like LnBaCuMeO$_{\delta+}$ ($Ln = La, Pr, Nd, Sm; Me = Fe, Cu$) [52–54], RE-123 (RE = Nd, Sm, Eu, Dy) [55–59], etc. The $\sigma$ of the Dy-123 and Sm-123 turned up due to the orthorhombic-tetragonal (O/T) transition at high temperature when the oxygen partial pressure was below $10^{-2}$ atm and $10^{-3}$ atm, respectively [56,58]. Hence, with 1 atm flowing He gas, the phase transition from orthorhombic to tetragonal occurred around $\sim$700 K for the RE-123 (RE = La, Nd, Eu, Dy, Ho, Er, Tm) [59]. As shown in Figure 7, at a temperature higher than 800 K, the increase of $\sigma$ for all samples increased slightly with increasing temperature which was attributed to the phase transformation from Dy-123 (Pmmm) to Dy-123 (P4/mmm).

Seebeck coefficient ($S$) of (1-x)DyBCO–xBNT ceramic samples was measured as shown in Figure 9. The result showed that the $S$ first decreased at low temperature range and then increased continuously at higher temperature. The sign of the $S$ for all samples was positive which confirmed that the conduction mechanism was mainly governed by holes (p-type behavior). The sample which possessed lower $\sigma$ also showed higher values of Seebeck coefficient. At low temperature, the $S$ of all samples decreased with when the temperature rose. At low temperature range, the temperature dependence of the $S$ for hole (p) single-band of the non-degenerate semiconductor [60] is explained by $S = (k_b/e)(E_{fi} - E_{f})/k_BT$ + $S_0$, where $k_b$, $e$, $E_{fi}$, and $S_0$ are the Boltzmann constant, the electronic charge, chemical potential, the valence band and a constant, respectively. In this model, the $Y_{1-x}Pr_x$Ba$_2$Cu$_3$O$_{y-\delta}$ [61], YBa$_2$Cu$_3$O$_{y-\delta}$ [62], YBa$_2$Cu$_3$O$_{y-\delta}$ [63], Sm$_{1-x}$Ba$_2$Cu$_3$O$_{y}$ [64], La$_{1.85}$Sr$_{0.15}$Cu$_{1-x}$Ni$_x$O$_{y+0.6}$ [65] and Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{y+0.6}$ [66] compounds were used to express the decrease of $S$ with the increase of temperature. Above $560 K$, the $S$ of all samples increased when the temperature increased. This behavior was similar to the $S$ of $Y_{1-x}Pr_x$Ba$_2$Cu$_3$O$_{y-\delta}$ [61], YBa$_2$Cu$_3$O$_{y-\delta}$ [67], YBa$_2$Cu$_3$O$_{y-\delta}$ [62], PrBa$_2$Cu$_3$O$_{y}$ [68] etc. The functional dependence of the $S$ on the variable range hopping regime for an energy dependent density of states can be defined as [69]:

$$S = (1/2)k_B^2T^{-1/2}|\ln N/E|_{E_F} = (1/2)k_B^2T^{-1/2}|\ln N/E|_{E_F} = (1/2)k_B^2T^{-1/2}.$$  

The above expression predicts a linear increase in $S$ with the increasing temperature.

As can be seen in Figure 9, the temperature independence of $S$ were observed in the ceramics where $x = 0.01$ and 0.03 samples, indicating that there was narrow valence band around the Fermi energy $E_F$. In this assumption, the temperature independent of $S$ is dominated by the entropy of distribution of the charge carriers among available sites as provided by the

![Figure 8](image1.png)  
**Figure 8.** Linear fit for $\ln(\sigma T)$ versus $1000/T$ plots of (1-x) DyBCO–xBNT ceramics.

![Figure 9](image2.png)  
**Figure 9.** Seebeck coefficient of the (1-x)DyBCO–xBNT ceramics sintered at 930°C for 2 h, where $x = 0, 0.01, 0.03, 0.05$ and 0.07 mole fraction.
modified Heikes formula [70–73]. For the thermal energy $k_B T$ are smaller than the on-site Coulomb repulsion ($U$) as $S = -(k_B/|e|) \ln \left( 1 - (k_B/|e|) \ln((1 - n)/n) \right)$ where $n$ is number of electrons per Cu site, the conduction process involves hopping of d electrons from one Cu$^{2+}$ (d$^9$) ion to a Cu$^{3+}$ (d$^8$) ion, then entropy considerations lead to the above formula with $n$ equal to the ratio of Cu$^{2+}$ ions to the total number of Cu ions. If all copper atoms can be considered equivalent, then $n = 2(1 + \delta)/3$ for RE-123 [61,62,72]. In case of the Coulomb interaction ($U$) are smaller than the thermal energy $k_B T$, the $S$ is defined [62,73,74] as $S = (k_B/|e|) \ln(2 - n)$, where $n$ is the number of electrons (per unit cell) in the top band as $n = 1 + \delta$. Following this model, the $S$ related directly with oxygen deficiency or oxygen content of RE-123. At high temperature, the oxygen content of RE-123 tended to reduce when the temperature increased, and thus the increase of the $S$ were observed as shown in Figure 9, corresponding to the narrow band model. Similar behavior of $S$ has been previously reported in YLa$_x$Ba$_{2-x}$Cu$_2$O$_{7-\delta}$ [62], YBa$_2$Cu$_3$O$_{7-\delta}$ [63,73,75–77], Pr$_x$Y$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ [74,78] at high temperature (300 K ≤ $T$ ≤ 1200 K).

The combined effect of electrical conductivity and Seebeck coefficient on the thermoelectric performance is illustrated by the temperature dependence of power factor (PF) as calculated from $\sigma T^2$ (see Figure 10). The power factor values of the (1-x)DyBCO–xBNT ceramics were found to be weakly dependent on temperature. The maximum power factor values for $x = 0$, 0.01, 0.03, 0.05, and 0.07 samples are 6.30, 20.91, 36.07, 12.01, and 17.18 $\mu$W/mK$^2$, respectively. Despite the relatively small $S$, the power factor of 0.97DyBCO–0.03BNT ceramic showed highest values regardless of temperature which indicated the greater influence of the electrical conductivity upon BNT doping.

The total thermal conductivity ($\kappa_T$) of the ceramics was calculated from the measured thermal diffusivity ($D$), the specific heat capacity ($C_p$) and density ($\rho$) using the relation $\kappa_T = DC_p/\rho$. The values were plotted as a function of temperature from 300 to 1000 K as shown in Figure 11. The results show that low $\kappa_T$ (~2.6–3.8 W/mK) of the ceramics were observed near room temperature. This may be compared to the $\kappa_T$ of pure Dy-123 annealed under flowing oxygen which was previously reported to be about ~4 W/mK at 300 K [20] and ~5 W/mK at 150 K [79]. It is also interesting to note that all ceramic samples without oxygen flowing have a lower $\kappa_T$ at low temperature. The $\kappa_T$ values of all ceramic samples decreased with increasing temperature, indicating that the phonon scattering from lattice vibration became more active. For the ceramic sample with $x = 0.05$, the $\kappa_T$ is ultra-low to 0.32 W/mK at 973 K (thermal diffusivity = 0.00142 cm$^2$/s and heat specific capacity = 0.36 J/gK). It is well known that the thermal conductivity includes two parts: lattice thermal conductivity ($\kappa_l$) and electronic thermal conductivity ($\kappa_e$). The $\kappa_l$ corresponds to the propagation of phonons in the three spatial dimensions through the crystal lattice and is defined as $\kappa_l = (1/3)C_vv_{ph}l_{ph}$, where $C_v$ is the specific heat per unit volume, $v_{ph}$ is the velocity of sound, and $l_{ph}$ is the phonon mean free path. The $\kappa_l$ is governed by the combination of phonon–phonon scattering, point defect scattering or boundary scattering [3], and is expressed as $\kappa_l = \kappa_{l,\text{anisotropic}} + \kappa_{l,\text{boundary}} + \kappa_{l,\text{phonon}}$. Below 573 K, the $\kappa_T$ of the sample with 0.01 ≤ $x$ ≤ 0.07 has higher values than the undoped sample, which was possibly due to the reduction of boundary scattering. If we consider the effect of porosity and use the simplified Maxwell-Eucken model to calculate thermal conductivity of the solid phase (by assuming zero thermal conductivity of pores) according to the equation [80,81], $\kappa_m = \kappa_l(1 - V_p)/(1 + V_p/2)$, where $\kappa_m$, $\kappa_l$, and $V_p$ are the measured thermal conductivity, the thermal conductivity of the solid phase, and the pore volume...
fraction, respectively. It could be shown that a higher pore volume fraction decreased the thermal conductivity of the ceramics. Therefore, the ceramic sample with \( x = 0 \) has the lowest thermal conductivity with the increase of BNT content. Above 573 K, the presence of secondary phase, heavy element and/or point defects which act as scattering canters, would be another factor for the reinforcement of phonon scattering, resulting in the reduction of the thermal conductivity. These thermal conductivity values are among the lowest known for prospective thermoelectric oxides. However, the thermal conductivity of the samples slightly increased with increasing measuring temperature above 873 K (Figure 11), which corresponded to the phase transition, i.e. from RE-123 (Pmmn) to RE\(_{123}\) (P4/mmm) [55–59]. Based on several studies on similar material systems, at room temperature, the thermal conductivity of Sm-123 was 4.50, 4.00 and 3.00 W/mK for 7-\(\delta\) = 6.11, 6.85, and 6.73, respectively [64]. Thermal conductivity of Eu-123 was 4, 3.67, 3.33, and 2.73 W/mK at 300 K for 7-\(\delta\) = 6.45, 6.97, 6.85, and 6.37, respectively [82]. The phase transitions of RE-123 from orthorhombic to tetragonal phase occurred at 7-\(\delta\) = 6.45 and 6.5 for RE = Eu and Sm, respectively [56,57]. It suggested that the thermal conductivity of RE-123 not only depended on temperature and oxygen content, but also on the charge carriers and phonons and their interactions, as well as on the oxygen ordering [82].

The lattice thermal conductivity is calculated by subtracting the electrical thermal conductivity from the total thermal conductivity (\(\kappa_e = \kappa_T - \kappa_l\)) as shown in Figure 12(c). Usually, the \(\kappa_e\) is calculated from the Wiedemann–Franz law i.e. \(\kappa_e = \sigma L T\) where Lorenz number (\(L\)) is \(2.45 \times 10^{-8}\) WΩK\(^2\), \(\sigma\) is the electrical conductivity, and \(T\) is the absolute temperature. For all the samples, the \(\kappa_e\) increases with increasing temperature, as shown in Figure 12(a), and the \(\kappa_e\) of the 0.01 ≤ \(x\) ≤ 0.07 samples are higher than the un-doped sample. However, it could be noticed that the estimated \(\kappa_e\) values for all samples were less than 20% of the \(\kappa_T\) except the sample with \(x = 0.03\). This shows that the total thermal conductivity value came mainly from the lattice vibrations as seen from Figure 12(d). The highest \(\kappa_e\) value was observed for the sample with \(x = 0.03\) due to its highest \(\sigma\) at 765 K, as shown in Figure 12(b), the \(\kappa_e/\kappa_T\) was about ~80% at 765 K. This showed the effect of \(\kappa_e\) behavior of this sample. Similar phenomena have been reported for thermoelectric material due to its complex structure and/or multiphase [83,84].

The combination of electrical and thermal transport properties allows to estimate the figure of merit, 
\[ ZT = (\sigma S^2 / K)T, \]

as a function of temperature in the (1-x) DyBCO→xBNT ceramics (Figure 13). The \(ZT\) value tended to increase with increasing temperature within the measured temperature range. The addition of BNT was found to improve \(ZT\) in DyBCO system. For comparison, the highest \(ZT\) values (~5.63 x 10\(^{-2}\) at 866 K) was observed

Figure 12. Thermal conductivity dependence \(x\) of of the (1-x)DyBCO→xBNT ceramics where (a) electronic thermal conductivity (\(\kappa_e\)), (b) the percentage (%) of \(\kappa_e/\kappa_T\), (c) lattice thermal conductivity \(\kappa_l\) and the percentage (%) of \(\kappa_l/\kappa_T\).
in the 0.97DyBCO−0.03BNT sample, which was about 4.12 times greater than the ZT value of \(1.38 \times 10^{-2}\) for DyBCO at the same temperature range. Comparing to other RE-123 compound, this study was comparable to the previously reported results of PrBCO (ZT = 0.03) and YBCO (ZT = 0.008) at 773 K [80]. It can be obviously seen that the ZT of 0.97DyBCO−0.03BNT sample was found to be higher than the un-dope RE-123 (RE = Y, Pr and Dy) compounds. However, this compound may not be a suitable candidate for use as thermoelectric material due to their low electrical conductivity and Seebeck coefficient. In order to improve ZT, changing stoichiometry and/or doping [9–13] in order to optimize the carrier concentration may be a viable solution. Following by this process, the thermoelectric properties of Dy-123 compounds would be improved in the future. Compositional and band structure engineering by a more appropriate dopant type and concentration may need to be further explored for the DyBCO compound considering its advantage of very low thermal conductivity at high temperature.

4. Conclusions

Dysprosium barium copper oxide–bismuth sodium titanate ((1-x)DyBCO–xBNT) ceramics, where \(x = 0, 0.01, 0.03, 0.05, \) and 0.07 mole fraction, were successfully synthesized by a solid-state reaction and sintering method. In all cases, the Dy-123 ceramics were identified as the main crystalline phases. The samples with \(0.01 \leq x \leq 0.07\) showed slightly higher density values than the undoped sample, suggesting that BNT helped improve the densification process. Also, the BSE-SEM images of ceramics exhibited the distribution of Dy-211 phase on the Dy-123 matrix due to the BNT doping. The electrical conductivity of the Dy-123 samples was enhanced by the amount BNT content with \(0.01 \leq x \leq 0.03\), and the maximum electrical conductivity (14,200 \(\Omega^{-1}\) m\(^{-1}\)) was obtained for the 0.97DyBCO-0.03BNT sample. The values of Seebeck coefficient are positive for all samples, showing that they are p-type conductors. Due to its highest power factor with a low thermal conductivity, the highest figure of merit (ZT) of the sample with \(x = 0.03\) was found to be \(5.63 \times 10^{-2}\) at 866 K. The ZT was comparatively small for the practical application as the high temperature thermoelectric materials. However, due to its attractively low thermal conductivity, this material can still be further optimized in terms of the power factor by doping and/or changing the stoichiometry.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Twaha S, Zhu J, Yan Y, et al. A comprehensive review of thermoelectric technology: materials, applications, modelling and performance improvement. Renew Sustain Energy Rev. 2016;65:698–726.
[2] Snyder GJ, Toberer ES. Complex thermoelectric materials. Nat Mater. 2008;7:105–114.
[3] Ren G, Lan J, Zeng C, et al. High performance oxides-based thermoelectric materials. JOM. 2015;67:211–221.
[4] Berardan, Byl C, Dragoe N. Influence of the preparative conditions on the thermoelectric properties of Al-doped ZnO. J Am Ceram Soc. 2010;93:2352–2358.

[5] Li F, Li JF. Effect of Ni Substitution on electrical and thermoelectric properties of LaCoO$_3$ ceramics. Ceram Int. 2011;37:105–110.

[6] Zhang FP, Zhang X, Lu QM, et al. Effects of Pr doping on thermoelectric transport properties of Ca$_{3-x}$Pr$_x$Co$_4$O$_9$. Solid State Sci. 2011;13:1443–1447.

[7] Buntham S, Keawprak N, Watcharapason A. Thermoelectric and magnetic properties of Bi$_2$)$_3$Na$_{0.5}$TiO$_3$-doped Na$_2$CoO$_2$ ceramics. J Nanosci Nanotechnol. 2017;17:3439–3442.

[8] Diez JC, Rasekh S, Constantinescu G, et al. Effect of annealing on the thermoelectric properties of directionally grown Bi$_2$Sr$_2$Co$_3$O$_6$. Ceram Int. 2012;38:5419–5424.

[9] Rodríguez J. Ag-YBCO compounds as thermoelectric material. Phys Status Solidi. 2008;205:1173–1176.

[10] Rodríguez JE. YBCO samples as a possible thermoelectric material. Phys Status Solidi. 2005;2:3605–3608.

[11] Rodríguez JE, López J. Thermoelectric figure of merit of oxygen-deficient YBCO perovskites. Phys B. 2007;387:143–146.

[12] Prayoonphokharat P, Watcharapason A. Transport properties and thermoelectric figure of merit of YBa$_2$Cu$_{3−x}$O$_{6−y}$ ceramics. Sci Adv Mater. 2017;9:1872–1875.

[13] Wannasut P, Prayoonphokharat P, Jaiban P, et al. Thermoelectric properties of YBa$_2$Cu$_3$O$_{6−x}$-Na$_2$CoO$_2$ doped oxide ceramics. Mater Lett. 2019;236:378–382.

[14] Jia QX, Maiorov B, Wang H, et al. Comparative study of REBa$_2$Cu$_3$O$_7$ films for coated conductors. IEEE Trans Appl Supercond. 2005;15:2723–2726.

[15] MacManus-Driscoll JL, Foltyn SR, Jia QX, et al. Systematic enhancement of In-field critical current density with rare-earth ion size variance in superconducting rare-earth barium cuprate films. Appl Phys Lett. 2004;84:5329–5331.

[16] MacManus-Driscoll JL, Foltyn SR, Maiorov B, et al. Rare earth ion size effects and enhanced critical current densities in Y$_2$Sm$_{y}$Ba$_2$Cu$_3$O$_{6−x}$ co- doped conductors. Appl Phys Lett. 2005;86:032505.

[17] Civaile L, Maiorov B, Servais A, et al. Angular-dependent vortex pinning mechanisms in YBa$_2$Cu$_3$O$_7$ coated conductors and thin films. Appl Phys Lett. 2004;84:2121.

[18] Datta A, Srivastava CM, Venkataramani N. Normal state DC electrical resistivity in RE-123 superconductors. Physica C. 1993;210:408–412.

[19] Tarascon JM, McKinnon WR, Greene LH, et al. Oxygen and rare-earth doping of the 90-K superconducting perovskite YBa$_2$Cu$_3$O$_y$. Phys Rev B. 1987;36:226–234.

[20] Geetha M, Rao A, Thukaram M, et al. Electrical and thermal transport properties of Dy$_{1−x}$Pr$_x$Ba$_2$Cu$_3$O$_y$ with (M=Fe, Co, Ni and Zn) bulk superconductors. Solid State Commun. 2014;187:38–42.

[21] Huang JZ, Lin JG, Lin JJ, et al. Thermoelectric power and superconducting transition in high-temperature superconductors Dy$_{1−x}$Pr$_x$Ba$_2$Cu$_3$O$_y$. Physica C. 1996;260:220–224.

[22] Slack GA. CRC handbook of thermoelectrics: new materials and performance limits for thermoelectric cooling. United States: CRC Press; 1995.

[23] Han C, Li Z, Dou S. Recent progress in thermoelectric materials. Chin Sci Bull. 2014;59:2073–2091.

[24] Yi JY, Lee JK, Hong KS. Dependence of the microstructure and the electrical properties of Lanthanum-substituted (Na$_x$)$_3$Bi$_{12}$TiO$_{33}$ on sintering conditions. J Am Ceram Soc. 2002;85:3004–3010.

[25] Toby BH, Von Dreiele RB. GSAS-II: the genesis of a modern open-source all purpose crystallography software package. J Appl Cryst. 2013;46:544–549.

[26] Sahoo M, Behera D. Effect of Ti doping on structural and superconducting properties of YBa$_2$Cu$_3$O$_{7−Y}$ high T$_c$ superconductor. J Supercond Nov Magn. 2014;27:83–93.

[27] Bals S, Rijnders G, Blank DHA, et al. TEM of ultra-thin DyBa$_2$Cu$_3$O$_{7−x}$ films deposited on TiO$_2$ terminated SrTiO$_3$. Physica C. 2001;355:225–230.

[28] Rijnders G, Blank DH. Frontiers in Superconducting Materials: high T$_c$ cuprates-thin film processing, atomic layer controlled deposition. Berlin Heidelberg: Berlin: Springer-Verlag; 2005.

[29] Hanic F, Ciç[i]n A, Briančin J, et al. Substitution of Ti$^{4+}$ for Cu$^{2+}$ in YBa$_2$Cu$_3$O$_{7−x}$ T$_c$. Solid State Phenom. 2003;90:91;297–302.

[30] Yang WM, Tang YL, Li GZ, et al. Effect of Na-dopant on the levitation force of single domain YBCO bulk superconductors fabricated by TSMTG process. J Supercond Nov Magn. 2011;24:2211–2214.

[31] Chen H, Kumar B. Structural and thermal properties of (YBa$_2$Cu$_{3}$)$_{1−x}$Na$_{2}$O$_{7−x}$ materials. Appl Phys Lett. 1993;63:3074–3072.

[32] Orlova TS, Laval JY. Microstructure and superconducting properties of the DyBaCuO ceramic doped with Na$_2$CO$_3$, NaCl and KClO$_3$. Phys Solid State. 2007;49:1964–1970.

[33] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. 1976;32:751–767.

[34] Sumadiyasa M, Adnyana I, Wendri N, et al. Synthesis and characterization of GLBCO-123 phase: gd$_{1}$−$_{y}$Ba$_2$Cu$_3$O$_{7−x}$ ($x=0.0-0.5$). J Chem Eng Mater Sci. 2017;5:49–57.

[35] Kita R, Yokoyama K. Substitution effect of RE elements on formation of (Yb,RE)Ba$_2$Cu$_3$O$_7$. Physica C. 2003;392-396:488-492.

[36] Pęczkowski P, Zachariasz P, Jastrzębski C, et al. On the superconductivity suppression in Eu$_{1−x}$Sr$_x$Ba$_2$Cu$_3$O$_{7−x}$. Vol. 14, Materials (Basel Switzerland); MDPI. 2021. 3503.

[37] Toby BH. R factors in rietveld analysis: how good is good enough? Powder Diff. 2006;21:67–70.

[38] Jeong YK, Choi GM. Nonstoichiometry and electrical conduction of CuO. J Phys Chem Solids. 1996;57:81–84.

[39] Shin MW, Kiong AI, Hare TM, et al. The effects of excess CuO on the grain growth kinetics, sintering and microstructure of the YBa$_2$Cu$_3$O$_{7−x}$ superconductor. Mater Lett. 1992;15:13–18.

[40] Paulus EF, Miege G, Fues H, et al. The crystal structure of BaCuO$_2$. J Solid State Chem. 1991;90:17–26.

[41] Boonsong P, Wannasut P, Buntham S, et al. Electrical and thermal transport properties of dysprosium barium copper oxide ceramic. Chiang Mai J Sci. 2018;45:2809–2816.

[42] Yoon S, Kwon OJ, Ahn S, et al. The effect of grain size and density on the thermoelectric properties of Bi$_2$Te$_3$PbTe compounds. J Electron Mater. 2013;42:3390–3396.

[43] Prayoonphokharat P, Jiansirisomboon S, Watcharapason A. Fabrication and properties of YBa$_2$Cu$_3$O$_{7−x}$ ceramics (YBa$_2$Cu$_3$O$_{7−x}$) at different sintering temperatures. Electron Mater Lett. 2013;9:413–416.

[44] Boonsong P, Wannasut P, Rachakom A, et al. Quantitative phase analysis and crystal structure of DyBCO ceramics prepared at different sintering conditions. Chiang Mai J Sci. 2018;45:1835–1842.
[45] Boonsong P, Wannasut P, Sriprachuabwong C, et al. Synthesis and characterization of SmBa$_2$Cu$_3$O$_y$ powder prepared by solid-state reaction. Sci Adv Mater. 2020;12:180–185.

[46] Fujishiro H, Nariki S, Murakami M. Thermal conductivity and thermoelectric power of DyBaCuO bulk superconductors. Supercond Sci Technol. 2006;19:S447–S450.

[47] Win W, Wali M, Obien JM, et al. Electrical and magnetic studies of YBa$_2$Cu$_3$O$_y$;Y$_2$BaCuO$_4$ composites. Physica C. 1990;172:217–228.

[48] Kruaehong T. Electrical properties and crystal structure of Y123, Y358 and Y257/Y211 composite bulk superconductors. Int J Phys Sci. 2014;9:360–367.

[49] Bosman AJ, VanDael HJ. Small-polaron versus band conduction in some transition-metal oxides. Adv Phys. 1970;19:1–117.

[50] Sun T, Hng HH, Yan QY, et al. Enhanced high temperature thermoelectric properties of Bi-doped Ca$_2$O$_y$ thin films by pulsed laser deposition. J Appl Phys. 2010;108:8.

[51] Kroger FA. The chemistry of imperfections. New York (NY): Interscience Publishers; 1974.

[52] Klynyuk AI, Chizhova EA. Effect of heterovalent substitutions in the Cu and Fe sites on the thermal expansion and electrical properties of the layered ferrocuprate LaBaCuFe$_2$O$_6$. Inorg Mater. 2004;44:762–765.

[53] Klynyuk A, Chizhova YA, Sazanovich NV, et al. Thermoelectric properties of some perovskite oxides. J Thermoelectric. 2009;3:73–80.

[54] Zeng C, Liu Y, Lan J, et al. Thermoelectric properties of Sm$_{1-x}$La$_x$Ba$_2$Cu$_3$O$_y$ ceramics. Mater Res Bull. 2015;69:46–50.

[55] Flor G, Chiodelli G, Spinolo G, et al. Nd$_2$Ba$_2$Cu$_3$O$_{y+6}$(Nd-123) low- and high-temperature conductivity. Physica C. 1999;316:13–20.

[56] Chiodelli G, Wenneker I, Ghigina P, et al. Oxygen non-stoichiometry and high temperature DC conductivity of SmBa$_2$Cu$_3$O$_y$. Physica C. 1998;308:257–263.

[57] Ghigina P, Spinolo G, Malavasi L, et al. The Eu$_1-x$Ba$_2$x Cu$_3$O$_y$ system: oxygen content, phase transitions, point defect equilibria and charge carriers. Phys Chem Phys. 2001;3:606–612.

[58] Ishizuka H, Idemoto Y, Fueki K. Oxygen nonstoichiometry and high-temperature conductivity of DyBa$_2$Cu$_3$O$_y$. Physica C. 1992;195:145–156.

[59] Yang HC, Hisieh MH, Sung HH, et al. High-temperature resistivity of RBa$_2$Cu$_3$O$_{7-\gamma}$, where R = La,Pr,Nd,Sm,Eu, Dy, Ho, Er, and Tm. Phys Rev B. 1989;39:9203.

[60] Shldosvki BL, Efros AL. Electronic properties of doped semiconductors. Berlin Heidelberg: Berlin: Springer-Verlag; 1984.

[61] Goncalves AP, Santos IC, Lopes EB, et al. Transport properties of the oxides Y$_{1-x}$Pr$_x$Ba$_2$Cu$_3$O$_{7-\gamma}$ (0<\<1): effects of band filling and lattice distortion on superconductivity. Phys Rev B. 1988;37:7476–7481.

[62] Ponnambalam V, Varadaraju UV. Observation of variable-range hopping up to 900 K on the YLa$_2$Ba$_2$Cu$_3$O$_{7-\gamma}$ system. Phys Rev B. 1995;52:16213–16216.

[63] Gerdanian P, Picard C. Seebeck coefficient and electrical-resistivity measurements for semiconducting antiferromagnetic YBa$_2$Cu$_3$O$_y$ up to 1000 K evidence for phonon drag and strong electron-phonon coupling. Physica C. 1995;246:145–155.

[64] Plackowski T, Jeżowski A, Sulkowski C, et al. Thermal transport in Sm$_{1-x}$Ba$_2$xCu$_3$O$_y$ solid solution. Physica C. 1998;306:58–66.

[65] Zhiqiang M, Gaojie X, Hongjie Y, et al. Transport mechanism in La$_{1+5}$Sr$_{1.5}$Cu$_3$-xNi$_x$O$_{7-\gamma}$ (0<\<x<1). Phys Rev B. 1998;58:15116–15119.

[66] Gaojie X, Qirong P, Zejun D, et al. Microstructure, localized Cu$^{2+}$ spins, and transport properties of Bi$_2$ Sr$_2$Ca$_1$Y$_1$Cu$_2$O$_{6.8}$. Phys Rev B. 2000;62:9712–9718.

[67] Budhani RC, Tzeng SMH, Bunshah RF. Metal-insulator transition and superconductivity in Y$_2$Ba$_2$Cu$_{3-x}$O$_y$. Phys Rev B. 1987;36:8873–8876.

[68] Fisher B, Genossar J, Patlagan L, et al. Hopping conductivity in fully oxygenated PrBa$_2$Cu$_3$O$_y$ and PrBa$_2$Cu$_3$O$_{y+6}$. Phys Rev B. 1994;50:4118–4124.

[69] Mott NF, Davis EA. Electronic processes in non-crystalline materials: theory of electrons in a non-crystalline medium. New York (NY): Oxford University Press; 1979.

[70] Anderson PW. The resonating valence bond state in La$_2$CuO$_4$ and superconductivity. Science. 1987;235:1196–1198.

[71] Kwak JF, Beni G, Chaikin PM. Thermoelectric power in hubbard-model systems with different densities: n-methylphenazinium-tetracyanoverdioxide (NMP-TCNQ) and quinolinium ditetrayanoquinoxaline. Phys Rev B. 1976;13:64:1.

[72] Bhattacharyya AK, Pan R, Naugle DG, et al. Thermopower of Rb$_2$Cu$_2$O$_{6.8}$(R=Y,Er). Phys Rev B. 1990;41:4002.

[73] Fisher B, Genossar J, Lelong IO. Thermoelectric power measurements of YBa$_2$Cu$_{3-x}$O$_y$ up to 950°C and their application to test the band structure near Er. J Supercond. 1988;1:53–61.

[74] Fisher B, Genossar J, Patlagan L, et al. Resistivity and thermoelectric-power measurements of Pr$_2$Y$_{1-x}$Ba$_2$Cu$_3$O$_{6.8}$ up to 1200 K and an electronic-structure analysis. Phys Rev B. 1991;43:2821–2827.

[75] Genossar J, Fisher B, Lelong IO, et al. On the Normal state resistivity and thermoelectric power of YBa$_2$Cu$_3$O$_y$ experiments and interpretation. Physica C. 1989;157:320–324.

[76] Ramasesha SK, Mathews T, Jacob KT. High temperature seebeck measurements on YBa$_2$Cu$_3$O$_{7-\gamma}$. Mater Res Bull. 1990;25:149–155.

[77] Ohtani T, Okuhara K. High temperature thermopower measurements in impurity-substituted YBa$_2$Cu$_3$O$_{7-\gamma}$ Solid State Commun. 1989;72:767–770.

[78] Prayoonphokkharat P, Amonpattaratik P, Kosuga A, et al. Thermoelectric properties of Pr-substituted YBCO ceramics. J Alloys Compd. 2021;871:159552.

[79] Ikebe M, Fujishiro H, Nakasato K, et al. Thermal conductivity of REBa$_2$Cu$_3$O$_y$ (RE = Y, Dy, Sm, Nd) superconducting oxides. Physica C. 1996;263:309–312.

[80] Levy FL. A modified Maxwell-Eucken equation for calculating the thermal conductivity of two-component solutions or mixtures. Int J Refrig. 1981;4:223–225.

[81] Zhang Z, Wu S, Niu Y, et al. Thermoelectric properties of multi-wall carbon nanotube-embedded Cu$_2$S thermoelectric materials. J Mater Sci Mater Electron. 2019;30:5177–5184.

[82] González G, Rodríguez-Mijangos R, Galván D. Oxygen doping dependence of thermal conductivity measurements in EuBa$_2$Cu$_3$O$_{6+\delta}$. Phys Stat Sol (A). 2001;184:303–308.

[83] Tanya B, Fu C, Auffermann G, et al. Enhancing thermoelectric performance of TiNiSn Half-Heusler compound via modulation doping. Chem Mater. 2017;29:7042–7048.

[84] Joseph E, Amoury Y. Towards a predictive route for selection of doping elements for the thermoelectric compound PbTe from first-principles. J Appl Phys. 2015;117:175102.