Electronic structure and thermoelectric properties of nanostructured EuTi$_{1-x}$Nb$_x$O$_3$ (x = 0.00; 0.02)

L. Sagarna, A. Shkabko, S. Popoloh, L. Karvonen, and A. Weidenkaff
Swiss Federal Laboratories for Materials Sciences and Technology (Empa), Solid State Chemistry and Catalysis, Überlandstrasse 129, 8600 Dübendorf, Switzerland

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The thermoelectric properties of polycrystalline nanostructured EuTiO$_{1-x}$ samples are improved by a substitution of 2% Nb for Ti. The figure of merit (ZT) was measured to reach ZT(EuTiO$_{0.98}$Nb$_{0.02}$O$_3$) $\approx$ 0.4 at $T$ = 1040 K while ZT(EuTiO$_{1-x}$) $\approx$ 0.3 at the same temperature. X-ray photoelectron spectra reveal that the in-gap states at the Fermi level are more pronounced for the Nb-substituted samples, resulting in an improved power factor. The valence band peak below the Fermi level is sharply shaped, therefore fulfilling the condition for a large Seebeck coefficient. The specific porosity of the samples reduces the lattice thermal conductivity with a minor effect on the electron transport. © 2012 American Institute of Physics.

It is known from theoretical studies that correlation effects in oxides can enhance thermoelectric properties. Predictions about the thermoelectric performance and the Seebeck coefficient of strongly correlated electron systems were presented by Rüegg et al. Among the perovskite-type oxides, SrTiO$_3$ has shown a particularly high thermoelectric figure of merit ($ZT = (S^2T)/\kappa \rho$), where $S$ = Seebeck coefficient, $\rho$ = electrical resistivity, $\kappa$ = thermal conductivity, and $T$ = absolute temperature) in the high-temperature region. In order to enhance $ZT$, $\rho$ and $\kappa$ have to be minimized and $S$ has to be maximized. The lattice thermal conductivity is often decreased by substituting heavy atoms into the crystal structure, which enhance the phonon scattering. A recent approach to decrease the $\kappa$ of Ti containing perovskite systems (ATiO$_3$; where A = rare earth or alkaline earth metal) have focused on substitutions of the A-site cation with heavier elements. A 20% substitution of Sr$^{2+}$ by Eu$^{2+}$ in SrTiO$_3$ was found to effectively reduce the mean free phonon path by 12% at room temperature. Based on this observation and taking into account the similarities between SrTiO$_3$ and EuTiO$_3$, a lower phonon mean free path is expected in EuTiO$_3$ due to the higher atomic mass of Eu as compared with Sr.

EuTiO$_3$ has been widely studied because of its interesting magnetic properties: it is one of the few antiferromagnetic materials with a positive Curie-Weiss constant ($\theta$) and reveals a strong coupling between magnetic ordering and soft phonon modes. Electronic band structure calculations of EuTiO$_3$ by Ranjan et al. have predicted a sharp peak in the density of states (DOS) below the Fermi level ($E_F$), which is beneficial to increase the $S$ ($\propto \partial \ln f(E)/\partial E|_{E=E_F}$). A broad band dispersion near $E_F$ would further enhance the electronic conductivity. The electrical conductivity of EuTiO$_3$ has been studied at low temperatures, and different methods have been applied for its synthesis.

Another approach to reduce the lattice thermal conductivity is based on nanostructuring. When the grain size decreases and approaches a scale comparable to the mean free path, the phonons are scattered by the grain boundaries. Moreover, nanostructuring can enhance the Seebeck coefficient by the quantum confinement, which modifies the DOS, and by the filtering of low energy electrons. The research carried out by Yu et al. proved the reduction of $\kappa$ and preservation of $\rho$ in nanomesh structures by the alteration of the phonon band structure of a semiconductor thin film. Studies on electrical conductivity of metallic foams and nanocomposites proved that porous materials lead to a high electrical resistivity. However, foams have very different effective properties compared to their bulk counterparts. Finding a suitable porous morphology with a better ratio of the electrical to thermal conductivities could result in increasing the $ZT$ values.

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Mesoporous samples have been prepared by different methods like Chirnic douce synthesis or citric acid-assisted soft chemistry synthesis. In this work, a nanostructuring approach producing porous samples has been applied on EuTi$_{1-x}$Nb$_x$O$_3$ ($x = 0.00; 0.02$) samples were prepared in two steps. First, a stoichiometric mixture of Eu$_2$O$_3$, Ti$_2$O$_3$, and Nb$_2$O$_5$ powder was ball-milled and reacted in air for 10 h at 1273 K, resulting in a pyrochlore-type phase (A$_2$B$_2$O$_7$). Then, the powder was reground and pressed into bars (10 $\times$ 2 x 2 mm$^3$) using 2 $\times$ 10$^6$ Pa uniaxial pressure. In order to perform thermal diffusivity measurements at high temperature, another set of samples was pressed into 10 mm diameter and 1.5 mm thick disk shaped pellets. Finally, all the samples were sintered for further 10 h at 1273 K under reducing atmosphere (flowing mixture of 5% $\text{H}_2$ in Ar). The resulting phase is a cubic-perovskite Pm$\bar{3}$m with $a = 3.905$ Å for EuTi$_{1-x}$Nb$_x$O$_3$ ($x = 0.00$) and $a > 3.905$ Å for $x = 0.02$ samples. The grains form porous sintered bodies with well interconnected crystallites of 150 nm size (Fig. 1(a)). The relative densities of the sintered bars were 54% and 49% for $x = 0.00$ and $x = 0.02$, respectively, and 42% ($x = 0.00$) and 45% ($x = 0.02$) for the disk shaped pellets. In order to investigate the influence of the density on the thermoelectric properties, a 100% dense sample of EuTiO$_3$ was produced by floating zone technique.

The electrical resistivities of the samples as a function of temperature are shown in Figure 2. The decrease of $\rho$ with $T$ is observed for both samples, reaching $\rho(x=0.00) = 1.2 \times 10^{-3}$ $\Omega$ m (Fig. 2(a)) and $\rho(x=0.02) = 6.7 \times 10^{-4}$ $\Omega$ m (Fig. 2(b)) at...
The transport behavior would predict a value of the total thermal conductivity ($k_T$) and, therefore, not recorded. The activation energy of the $x = 0.00$ sample up to 65 K can be fitted with the Efros-Shklovskii (ES) variable-range hopping (VRH) [Eq. (2)], where the responsible conduction mechanism is the Coulomb interaction in the hopping regime which produces a gap in the density of states:

$$
\rho = \rho_0 \exp(T_0/T)^{1/2},
$$

where $\rho_0$ and $T_0$ are material parameters (see inset Fig. 2(b)). At $T = 65$ K, the electronic transport turns into metallic conduction within $65 \text{ K} < T < 120 \text{ K}$. This is understood as a transition from localized electronic states to nonlocalized states. When the energy of the electrons increases, the “electronic droplets” merge reaching the percolation level and the electrons can move through the entire system. The difference in electronic transport properties compared to the $x = 0.00$ sample is due to higher concentration of “electronic droplets” caused by charge-carrier doping, which reduces the hopping lengths. The activation energy calculated for the $x = 0.02$ sample is 0.24 eV above 343 K.

The porous structure, formed by well-fused particles, provides the low overall densities of the samples. The high porosity has a significant effect on the thermal conductivity. Figures 3(a) and 3(b) show the total thermal conductivity ($\kappa$) of the $x = 0.00$ and $x = 0.02$ porous sample pellets. Thermal conductivity values of $\kappa_{x=0.00} = 2.5 \text{ W K}^{-1} \text{ m}^{-1}$ and $\kappa_{x=0.02} = 2.2 \text{ W K}^{-1} \text{ m}^{-1}$ are reached at $T = 330 \text{ K}$. The values are significantly lower than the $\kappa = 7 \text{ W K}^{-1} \text{ m}^{-1}$ measured for the 100% dense EuTiO$_3$ sample, indicating the influence of the porosity. The lowered crystallite size also affects $\kappa$ since the theoretical calculation of the thermal conductivity with Maxwell formula would predict a value of $\kappa = 5.7 \text{ K}^{-1} \text{ m}^{-1}$ for the 100% dense sample. In this case, the change in $\kappa$ is a decrease by 56% from the dense sample to the porous one.

The total thermal conductivity $\kappa$ consists of the electronic ($\kappa_{el}$) and the lattice ($\kappa_{lat}$) contributions. The electronic contribution can be approximated using the Wiedemann-Franz law: $\kappa_{el} = L_0 T/\rho$, where $L_0 = 2.443 \times 10^{-8} \text{ W S}^{-1} \text{ K}^{-2}$ is the Lorenz number for the free electron gas. Using this approximation, it is possible to reveal that $\kappa$ is strongly dominated by the lattice contribution, presenting more than 95% of the total thermal conductivity. Therefore, the results of $\kappa$ measurements are highly affected by the relative densities of the samples, and the effect of 2% Nb-substitution on $\kappa$ can be considered negligible.
At low temperatures, $\kappa_{\text{lat}}$ is limited by scattering processes induced by the lattice defects and grain boundaries. The small peaks at $T_{(x=0.00)} = 268$ K and $T_{(x=0.02)} = 273$ K can be related to the specific heat anomaly caused by a structural phase transition predicted by Bussmann-Holder et al.\(^\text{29}\) At higher temperatures, the mean free path of the phonons becomes shorter, as the Umklapp processes turn out to be the dominating scattering scheme over the lattice-defect related scattering. At high temperature range, $\kappa_{\text{lat}}$ decreases proportional to $1/T$, reflecting the increasing amount of phonons available to participate in the Umklapp scattering. In our case, the calculated 56% decrease of $\kappa$—compared to 100% dense unsubstituted sample—by the enhanced porosity outweighs the simultaneous decrease of 41% in $\rho$, which is considered beneficial for the ZT value in line with the results of Ref.\(^\text{22}\).

The Seebeck coefficient ($S$) of both samples (Fig. 4) is negative over the whole temperature range confirming n-type conductivity. Large negative values of $S_{(x=0.00), T=268 \text{K}} = -1084 \mu$V K$^{-1}$ and $S_{(x=0.02), T=691 \text{K}} = -421 \mu$V K$^{-1}$ are reached. The origin of the pronounced peak in the $S$ values of EuTiO$_{3-x}$ can be associated with a phonon drag effect,\(^\text{30}\) taking place in the low-temperature regime where phonon-electron interactions dominate. In such a condition, the phonons tend to deflect the electrons towards one end of the material, giving rise to an enhanced $|S|$.\(^\text{31}\) This peak can also be related to the structural transition reported in Ref.\(^\text{29}\), since the maximum in the $S_{(x=0.00)}$ occurs at the same temperature ($T = 268$ K) as the small change in thermal conductivity (Fig. 3). A structural transition influences the DOS near the Fermi level ($E_F$) and thus the Seebeck coefficient.

At high temperature, the $S(T)$ values of both samples converge, reaching $S_{(x=0.00)} = -389 \mu$V K$^{-1}$ and $S_{(x=0.02)} = -360 \mu$V K$^{-1}$ by 1040 K. The behavior of the Seebeck coefficient at the high temperatures limit, where the kinetic terms of $S$ can be neglected, can be described by Heikes formula.\(^\text{32}\) In the case of highly correlated electron system with large electron-electron repulsion ($U$) and forbidden double occupancy (as it is assumed in this system\(^\text{29}\)), the following modified Heikes formula can be considered to estimate the expected $S$:\(^\text{34}\)

$$S(T \to \infty) = -(k_B/e)\ln[(2 - 2n)/n],$$

where $n$ = charge carrier concentration per unit cell. The calculated value for EuTiO$_{0.98}$Nb$_{0.02}$O$_{3-x}$ is $S_{(T \to \infty)} = -395 \mu$V/K (with $n = 0.02$) and has a small deviation from the measured value. However, we cannot apply the formula for the unsubstituted sample since an appropriate value of $n$ for EuTiO$_{3-x}$ ($n \sim 10^{-5}$) would give a $|S|$ value above 1000 $\mu$V/K, which is in disagreement with the measurement. The measured $S$ of both samples tends to similar values at high temperature. This behavior could be explained by Heikes formula if we consider that the extra electrons induced by oxygen vacancies in the $x = 0.00$ sample raise the charge carrier density to $n \approx 0.02$. Another possible explanation is given by Kobayashi,\(^\text{35}\) who postulates that the electric conduction occurs in a highly localized way and the exchange of entropy and charge occurs via the neighboring Ti$^{3+}$ and Ti$^{4+}$ ions.

Ti$^{4+}$ is the predominating oxidation state of titanium in both samples, as demonstrated in Figure 5(a) with the Ti 2p x-ray photoelectron spectra (XPS) of the $x = 0.02$ sample. The most intense peak is centered at $E_b = 459.24$ eV, similarly to SrTiO$_3$ perovskite phases, indicating Ti$^{4+}$ species.\(^\text{36}\) The small low-energy shoulder can be explained by a less intensive feature centred at $E_b = 456.4$ eV, indicating

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FIG. 3. Temperature dependence of the total thermal conductivity ($\kappa$) at low and high temperatures ranges for (a) EuTiO$_{3-x}$ and (b) EuTi$_{0.98}$Nb$_{0.02}$O$_{3-x}$ (error bars according to Populoh et al.\(^\text{38}\)).

FIG. 4. Temperature dependence of the Seebeck coefficient ($S$) of the samples.
The small hump at around 143 eV (indicated with the asterisks.

The spectrum of Eu\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7} was recorded for comparison (Fig. 5(b)) has two main peaks at 129.72 eV and 134.97 eV, which belong to the multiplet structure resulting from the 5\textit{d}^64\textit{f}\textsuperscript{2} ground-state configuration of Eu\textsuperscript{2+}, as was recently found.\textsuperscript{37} The small hump at around 143 eV (indicated with an arrow) can be associated to additional Eu\textsuperscript{3+}. For comparison, the Eu 4\textit{d} spectrum of Eu\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} was also recorded and the two peaks corresponding to Eu\textsuperscript{3+} where found at 136.51 eV and 142.51 eV (Fig. 5(b)).

The valence band (VB) spectra of the samples plotted in Figure 6 show a narrow peak centred at 2.50 eV below the \( E\textsubscript{F} \), as theoretically predicted for EuTiO\textsubscript{3}.\textsuperscript{12} The spectrum of Eu\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} was recorded for comparison (Fig. 6): the peak related to Eu\textsuperscript{2+} 4\textit{f} states appears at a similar energy but with a lower intensity. It is, indeed, expected a higher intensity of this peak for the perovskite EuTiO\textsubscript{3} phase than for the pyrochlore Eu\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} phase. The three additional features below \( E\textsubscript{F} \) in the data sets of Figure 6 correspond to O 2\textit{p} (5.5 eV), indicated with the arrows, and Eu\textsuperscript{3+} (8 eV and 12 eV),\textsuperscript{37} marked with the asterisks. However, the high spectral intensity from 4 eV up to 14 eV is characteristic only for the Eu\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} phase, due to the higher oxygen and Eu\textsuperscript{3+} contents.

It is known from theory,\textsuperscript{13} that a sharp DOS near the Fermi level results in a high Seebeck coefficient. In Figure 6, the VB spectra of EuTiO\textsubscript{3} and EuTi\textsubscript{0.98}Nb\textsubscript{0.02}O\textsubscript{3} are compared. Both samples show a high and narrow peak below \( E\textsubscript{F} \), which reflects the large of \( S \) values of the samples at room temperature. Besides, tailing of the band-edges towards and beyond the zero-point energy manifests additional in-gap states at \( E\textsubscript{F} \) affecting the electronic transport. The comparison of the VB spectra of both materials shows that the density of the in-gap states is higher in the Nb-substituted \( x = 0.02 \) sample than in the unsubstituted \( x = 0.00 \) sample, leading to a lower electrical resistivity by substitutions.

Structural, thermo-electrical, and x-ray photoemission characterization was carried out on porous polycrystalline samples of Eu\textsubscript{3}Ti\textsubscript{1−\textit{x}}Nb\textsubscript{\textit{x}}O\textsubscript{3} (\( x = 0.00; 0.02 \)). The porosity decreased the thermal conductivity by 56% compared with the dense sample, while the electrical conductivity was lowered by only 41%. The VB spectra revealed a sharp DOS near the Fermi level due to Eu 4\textit{f} electrons in both samples. This caused the measured high Seebeck coefficient,\textsuperscript{13} which reached \( S_{\text{x=0.00}} = -1053 \mu \text{V/K} \) and \( S_{\text{x=0.02}} = -267 \mu \text{V/K} \) at room temperature. The additional in-gap states observed in the VB spectra justified the high electronic conductivity, especially in the case of the Nb-substituted samples. The \( ZT \) values obtained at 1040 K, \( ZT_{\text{\textit{x=0.00}}} \sim 0.3 \) and \( ZT_{\text{\textit{x=0.02}}} \sim 0.4 \), are among the highest within the family of thermo-electric oxides.

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