Investigation of the Influence of Singly and Dually Doping Effect on Scattering Mechanisms and Thermoelectric Properties of Perovskite-Type STO

Trinh Quang Thong\textsuperscript{1,*}, Le Thi Thu Huong\textsuperscript{2} and Nguyen Trong Tinh\textsuperscript{2}

\textsuperscript{1}Hanoi University of Science and Technology, Hanoi box 10000, Vietnam
\textsuperscript{2}Institute of Applied Physics and Scientific Instruments, Vietnam Academy of Science and Technology, Hanoi box 10000, Vietnam

This paper presents a systematic investigation of typical characterizations of Sr\textsubscript{(1-1.5x0.5)}Dy\textsubscript{x}Ti\textsubscript{1-y}Nb\textsubscript{y}O\textsubscript{3} composition based on single Nb- and Dy-doped as well as Nb/Dy co-doped SrTiO\textsubscript{3}. Nb concentration of 10, 13, 17, 20 and 24 at\% and Dy concentration of 4, 8, 10, and 13 at\% were used for different doping compounds. XRD data was used to calculate the lattice constants. The limit of solubility of doped element in host lattice was determined based on the graph showing the dependence of lattice parameters on doping concentration. The thermoelectric properties were investigated from 20 to 1000°C or 293 to 1273 K. The electrical conductivity increases below 600 K but decreases above 600 K with increasing doping content for all cases. This characterization reached about 900 S/cm at 570 K with 4\% dysprosium and 20\% niobium doped in STO. Both the electrical and thermal conductivity of single Nb-doped samples increase with increasing Nb content. In contrast, the thermal conductivity of single Dy doping decreases with increasing Dy content and consequently best absolute values of Seebeck coefficient. Generally, increasing doping content provides larger magnitude of Seebeck coefficient for all cases of doping. The best magnitude of the figure of merit reaches approximately 0.17 at 1273 K. The optimized composition should comprise quadrinary compounds of which is Sr\textsubscript{9.84}Dy\textsubscript{0.04}Ti\textsubscript{10.96}Nb\textsubscript{0.3}O\textsubscript{3}, especially for fast cooling regime. [doi:10.2320/matertrans.MA201512]

\textbf{Keywords: SrTiO\textsubscript{3} (STO), thermoelectric, Seebeck coefficient, figure of merit}

1. Introduction

In recent years, the oxide compounds used for thermoelectric applications have stimulated a great interest of the researchers in the field of material science because they are stable at high temperatures or under oxidizing conditions and environmental friendly that is opposed to most of the traditional thermoelectric materials.\textsuperscript{1-6} In this circumstance, the compounds having general formula ABO\textsubscript{3} with perovskite structures are also considered as the potential thermoelectric materials which consist of SrTiO\textsubscript{3} (denoted as STO). In fact, ABO\textsubscript{3} perovskite oxides in general and STO in particular are not good at electrical function for such applications because of their low electrical conductivity. However, this property can be improved via doping process that allows introducing the electrically active dopants into the host lattice to increase the free carrier concentration.\textsuperscript{5} It means that the amount of charge carriers and thus the electrical conductivity and thermoelectric properties in this system can be tuned by using suitable substitution elements. Dopants with a higher or lower oxidation level than the host ion will act as donors (n-type) or acceptors (p-type). In the case of STO, the possible donors may be trivalent ions on Sr\textsuperscript{2+} sites or pentavalent ions on Ti\textsuperscript{3+} sites. In addition, the most important principle for a possible substitution of Sr or Ti site ions by dopants is a comparable ionic radius of the corresponding species.

During the past time, many studies on STO doped with rare earth elements like La, Nb, and Dy have been separately reported showing the advanced results of thermoelectric properties of the compounds.\textsuperscript{7-18} In this work, a systematic study of the influence of single and dual doping STO using Nb and Dy based oxides has been implemented. The influence of doping concentration on the electron and phonon scattering as well as thermoelectric properties was considered and discussed to get the optimum composition in suitable processing condition.

2. Experimental Procedure

In our study, the material compound with chemical formula as Sr\textsubscript{(1-1.5x0.5)}Dy\textsubscript{x}Ti\textsubscript{1-y}Nb\textsubscript{y}O\textsubscript{3} was synthesized by the mixed oxide route using the stoichiometric composition of highly pure SrCO\textsubscript{3} (99.8\%), TiO\textsubscript{2} (99.8\%), Nb\textsubscript{2}O\textsubscript{5} (99.999\%), and Dy\textsubscript{2}O\textsubscript{3} (99.99\%). Nb was doped corresponding to different Nb/Ti ratio of 10, 13, 17, 20 and 24 at\% and Dy was doped with Dy/Sr ratio of 4, 8, 10, and 13 at\%, respectively. Beside single Nb- and Dy-doped samples, Nb-Dy co-doped ones were also prepared by keeping constant Dy concentration of 4 at\% but varied Nb concentration of 17, 20, 25, and 30 at\%. The mixed powders were calcined at 1100°C under air for 1 hour and sintering process for Nb-and Dy-doped as well as Nb/Dy co-doped samples were carried out at 1450°C in the forming gas (95\%Ar+5\%H\textsubscript{2}) for 4 h. In order to study the influence of sintering atmosphere on the thermoelectric properties some samples were also sintered at 1400°C in air. The effect of cooling rate to the thermal conductivity as result of boundary scattering after the crystal formation for samples doped with 4\% Dy and 20\% Nb were also examined by performing both regimes of slow and fast cooling.

The crystal structure of all samples was analyzed by XRD method and XRD data was used to calculate the lattice parameters. The electrical conductivity and Seebeck coefficient were measured simultaneously as a function of temperature from 20 to 1000°C or 293 to 1273 K in various
atmospheres. Pt wire (0.2 mm) was used as potential probes together for electrical connection. Two Pt-Pt13%Rh thermocouples were used for measuring the temperature difference. The Pt paste was used for the contacts and cured in situ under forming gas for 30 min at 1000°C. All samples of the same composition were used for thermal conductivity measurements using ULVAC TC-7000 laser flash equipment in vacuum.

3. Results and Discussions

In general, XRD patterns of all samples indicated that all diffraction peaks can be assigned to the typical single phase of perovskite structure. Relying on the XRD data of structure analysis, the lattice parameter was calculated using the Bragg’s equation. Figure 1 is a plot showing the change in lattice parameter with respect to dopant concentration. It can be seen that for the singly Nb- and Nb/Dy dually doped samples the measurements showed Vegard’s law which holds a linear relation between the crystal lattice parameter and the concentrations of the constituent elements at constant temperature. It is a lattice distortion caused by substitution of Nb$^{5+}$ with larger ionic radius (0.64 Å and 0.67 Å) than Ti$^{4+}$ ions (0.605 Å) leading to an expanse of lattice. Inversely, the lattice parameters show the decrease when increasing the doping concentration for singly Dy-doped samples. It is because the ionic radius of Dy$^{3+}$ (1.08 Å) is smaller than that of Sr$^{2+}$ (1.32 Å). In addition, such a rapid decrease in the unit cell parameter with dopant concentration may be related to the presence of native defects like oxygen vacancies that contribute both the electrostatic and thermodynamic factors to this change.\(^{19,20}\) As a result, the STO lattice doped with Dy atoms may shrink and also become distorted. It is well-known that the heat transfer in solids is governed by the lattice contribution (phonon vibrations) and the electronic component corresponding to the electron motions. For oxides, the phonon contribution remains the predominant component of the total thermal conductivity. In this circumstance, the distorted lattice enhances the phonon scattering. Furthermore, one can see that for single Nb- and Dy-doped samples, the lattice distortion tends keeping constant corresponding to a certain dopant concentration. Namely, this phenomenon occurs corresponding to the Nb concentration of 20 at% and especially obvious for Dy concentration of 8 at%. It discloses the penetration’s limitation of extrinsic atoms when introduced into a host lattice that can be thought as optimum doping concentration. Accordingly, that is reason why measured results of singly doped samples with the Dy concentration of 8 at% and dual ones using the Dy concentration of 4 at% were used for comparison together with single Nb and dual Nb/Dy doping in the electrical and thermoelectric properties.

The materials characterizations of electrical and thermoelectric properties of single Nb-and Dy doping as well as dual Nb/Dy doping samples are shown in Fig. 2, 3, 4, and 5. It can be seen that for the those measurement results, the fast cooling dually doped samples with 4% dysprosium and 20% niobium always provide the best characterizations. It may be because the heat treatment regime demonstrates the effect of preventing the grains of solid solution from growing too large that results in reducing the boundary scattering at interfaces and consequently reducing the thermal conductivity but increasing electrical conductivity.

The electrical conductivity depending on temperature of all samples is demonstrated in Fig. 2. There is a semiconductor-metal transition around 500 K between 450 and 550 K observed for all cases. Below this temperature range,
the electrical conductivity of both single and dualNb and Dy-doped samples firstly increases with increasing temperature showing the semiconductor behavior of the material. Namely, the electrical conductivity reaches the maximum values of 500 to 700 Scm$^{-1}$ for single Nb doping, 175 to 375 Scm$^{-1}$ for single Dy doping, and 500 to 900 Scm$^{-1}$ for dual Dy/Nbdoping. As a semiconductor, increase of temperature provides heating energy to promote some electrons across the band gap leading to the increase of electrical conductivity. In addition, it is also seen that the increase in dysprosium content decreases the electrical conductivity while the increase in Niobium content increases this property. The obtained result may be affected by the scattering effects. For doped STO, the carrier concentration is intrinsic then the mobility is dominated by lattice scattering. According to result shown in Fig. 1, the doping with Dy atoms shrinks the STO lattice and the second phase leading to the reduction of the carrier mobility then more doping concentration lower the electrical conductivity is. Once again the effect of doping limitation can be examined with this measurement result. Inversely, doping with Nb atoms expands the STO lattice leads to the increase of the carrier mobility and consequently the increase of the electrical conductivity with higher Nb concentrations. The dually doped samples using Dy/Nb ratio of 4/17 and 4/20 demonstrated the higher values of electrical conductivity compared to that of 4/25 and 4/30. Obviously, Nb concentration of 20 at% should be considered as saturation degree for this type of doping element. Above that temperature range, the electrical conductivity is decreased with the increase of temperature up to 1100 K showing
clearly a metallic behavior. The reason may come from the scattering of phonon and charge carriers that there is an exchange of energy and momentum between them. Higher temperature more scattering is and it causes the obstruction of the motion of charge carriers resulting in the decrease of electrical conductivity. When the temperature is higher than 1100 K, the electrical conductivity tends not to change with a slope decreasing towards zero. This behavior may be due to the existence of a narrow conduction band around the Fermi energy $E_F$, according to the Heikes theory.\(^{21}\)

The Seebeck coefficient is determined by measuring the change in voltage at two temperatures which are hot and cold one. The plots of Seebeck coefficient versus temperature are shown in Fig. 3. The Seebeck coefficient of all samples is negative and increases with increasing temperature and also doping content. It proved that electron carriers are introduced by Nb and Dy substitution in doping process. The temperature dependence of this characterization differs from the electrical conductivity. Basically, the Seebeck coefficient represents the average balancing act between the thermally driven diffusion and electrical forces. For almost all typical thermoelectric semiconductors the carrier concentration is increased together with temperature making the increase of electrical conductivity but the decrease of Seebeck coefficient.\(^{22,23}\) However, our measurement results show that Seebeck coefficient of all samples increase while their electrical conductivity increases. This tendency may be attributed by the increase of lattice scattering when temperature is increased because there were more thermal diffusions happening. In this case, it can be said that the lattice scattering mechanism of oxide materials dominates the thermoelectric properties instead of the influence of the electronic structure as shown in some previous reports for other oxide compounds.\(^{23,24}\) One can also see that the Seebeck coefficient seemed not to change when Dy content in STO varied. The reason comes from the limitation of Dy concentration when the Dy atoms penetrate into a host lattice as discussed at the beginning of this section.

The characterization of thermal conductivity was measured using both un-doped and highly doped samples for comparison as indicated in Fig. 4. The total thermal conductivity ($\kappa$) is the sum of the lattice contribution ($\kappa_L$) and electronic contribution ($\kappa_e$). Then, we have $\kappa_L = \kappa - \kappa_e$. Below 750K, the lattice thermal conductivity monotonically decreases mainly resulting from the lattice vibrations, or phonons and at higher temperatures when electronic thermal conductivity is reduced this characterization remains constant. The lattice thermal conductivity of samples with Dy concentration of 8 at% is relatively low compared to that of single Nb doping and Nb/Dy co-doping (Fig. 4(b)) because the electric thermal conductivity is significantly decreased due to more appearance of scattering centers. At 750 K the lattice thermal conductivity was reduced by only 1 W/mK between different doping samples.

Once the electrical conductivity ($\sigma$), Seebeck coefficient ($S$), and thermal conductance ($\kappa$) are known, the materials figure of merit can be determined as $ZT = \sigma \cdot S^2 / \kappa$. The temperature dependence of dimensionless figure of merit is plotted in Fig. 5. Here, it should be noted that this dependence is not linear although it seems that when observed. The best magnitude of this parameter reaches approximately 0.17 at 1273 K for the samples with 4% Dy and 20% Nb doped in STO. In this case, the obtained measurement result of Seebeck coefficient played the main role to make the trend of the graphs for ZT because of the relationship with ZT as mentioned in the expression to define this parameter.

4. Conclusion

The Nb and Dy-doped STO compounds were prepared by the reduced solid-state reaction method, and their electric properties were investigated from 293 to 1273 K. The limit of solubility of doped element in host lattice was determined using the XRD examination. Generally, there is a semiconductor-metal transition around 500 K in the characteristics of electrical conductivity of all samples. Higher doping concentration better the electrical conductivity is observed for all doped samples. The thermoelectric data obtained follow the same trend even show a little bit better value compared to that of published works. Single Nb-doped samples increase the electrical conductivity but also the thermal conductivity compared to those of singly Dy-doped ones. The better characterizations were obtained with dually Nb/Dy samples. Increasing doping concentration provides larger value of electrical conductivity and Seebeck coefficient for all cases of doping. The comparison of each sample group of doping retrieved that co-doping can minimize the phonon and also grain-boundary scattering due to the different size of the grains providing a quaternary compounds considered to be optimum option for oxide based thermoelectric materials.

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