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# Thermoelectric properties of Nb-doped $(Nd_{0.55}Li_{0.36})TiO_3$bulk ceramics with superlattice structure

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ABSTRACT

We report the thermoelectric properties of Nb-doped $(Nd_{0.55}Li_{0.36})TiO_3$ bulk ceramics prepared by the conventional sintering method. Superlattice structure present throughout the crystalline grain was observed and a glass-like thermal conductivity (~2 W/m·K) was obtained. The electrical properties of $(Nd_{0.55}Li_{0.36})TiO_3$ were improved due to the Ti-site-Nb-doping. The low solid solubility of Nb and the distortion of $TiO_6$ octahedron impaired the electrical performance of Nb-doped $(Nd_{0.55}Li_{0.36})TiO_3$. The sample with 5 at%Nb gave the maximum ZT value of 0.05 at 650 K. This work is helpful for the design of novel oxide thermoelectric materials.



## 1. Introduction

Thermoelectric materials can directly interchange electric energy and heat energy, which makes them promising in both the solid state refrigeration and the recovery of electricity from waste heat. Thermoelectric performance of materials is characterized by a dimensionless figure of merit,$ZT=S^2\sigma T/\kappa=S^2\sigma T/(\kappa_e+\kappa_l)$, where$S$,$\sigma$,$\kappa$, $\kappa_e$,$\kappa_l$, and $T$ represent Seebeck coefficient (also called thermopower), electrical conductivity, thermal conductivity, electronic thermal conductivity, lattice thermal conductivity and absolute temperature, respectively [1]. At present, high-performance thermoelectric materials with $ZT$ values exceeding 1.0 are mostly alloy materials, such as $Bi_2Te_3$-based alloys [2,3], PbTe-based alloys [4], $Yb_{14}MnSb_{11}$ [5], etc. But the use of rare or toxic elements will limit their large-scale commercial applications.

Recently, oxide thermoelectric materials have been receiving increased interest because of their non-toxicity, the abundance of source elements, thermal and chemical stability, etc. However, unfortunately, the ZT values of most oxides are still too low to compete with those of alloy thermoelectric materials. Xu et al. [6] reported a maximum ZT value of 0.1 at 1000 K for $NdMo_8O_{14}$ ceramics synthesized via a solid state reaction method followed by the spark plasma sintering. Wang et al. [7] prepared a Ni-substituted $NaCoO_2$ polycrystalline ceramic by the citric acid complex method, and got the highest ZT value of 0.176 at 673 K. Nong et al. [8] obtained ZT = 0.36 at 1073 K for $Ca_{2.8}Lu_{0.2}Co_4O_{9+\delta}$ polycrystalline ceramics fabricated by a solid state reaction and subsequent hot pressing. A maximum $ZT$ value of 0.37 for n-type $SrTiO_3$ ceramics at 1000 K was also reported [9]. Mostly, it is the high lattice thermal conductivity that restricts the thermoelectric performance of oxide materials. For example,$\kappa_l$ is about 12 W/(m·K) for the $SrTiO_3$ bulk crystal at room temperature [10], which is almost an order of magnitude higher than that of typical alloy thermoelectric materials, such as 1–1.5 W/(m·K) for $Bi_2Te_3$ [11]. Therefore, finding effective solutions to reduce the lattice thermal conductivity is important for enhancing the thermoelectric performance of oxides.

Nanostructuring has been proven to be an effective approach to enhance the thermoelectric performance of many materials, and most of the enhancement is attributed to the dramatic reduction of the lattice thermal conductivity because of the increased phonon

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scattering at the low dimensional interfaces [12–18]. Interestingly, $(Nd_{2/3-x}Li_{3x})TiO_3$ ($0.047 < x < 0.151$) bulk ceramics were reported to have the superlattice structure throughout the crystalline grain, and the superlattice structure can be even maintained after the Ti-site-doping using specific compositions and/or appropriate heat treatment [19–25]. Therefore, it seems tempting to investigate the lattice thermal conductivity and thermoelectric performance of $(Nd_{2/3-x}Li_{3x})TiO_3$ ($0.047 < x < 0.151$) bulk ceramics. A low thermal conductivity may be expected due to the strong phonon scattering at the superlattice interfaces, and the improved electrical properties could be anticipated because of the Ti-site-doping. Moreover, $(Nd_{2/3-x}Li_{3x})TiO_3$ contains a high percentage of vacancies and undersized highly mobile cations on the A-site [19]. These 'A-site-deficiencies' might scatter phonons at high frequencies to further decrease the phonon thermal conductivities.

In this paper, thermoelectric properties of Nb-doped $(Nd_{0.55}Li_{0.36})TiO_3$ bulk ceramics with a superlattice structure were investigated. The $Nb^{5+}$-doping at the $Ti^{4+}$-sites in a perovskite-type titanate brings extra electrons into the system which would finally enter the Ti-3d conduction bands to take part in the electrical conduction at elevated temperatures. This doping process is thermodynamically facilitated in a reducing atmosphere, as can be explained by the Kroeger-Vink notations as follows:

$$2AO + Nb_2O_5 \rightarrow 2Nb_{Ti}^{'} + 2A_A^X + 2e^{'} + 6O_O^X + (1/2)O_2\uparrow$$

where A represents the atom at A-site of $ATiO_3$ perovskite. The extra electrons (e') would occupy the empty states in Ti-3*d* bands, leading to the formation of $Ti^{3+}$ essentially [15,26].

To explain the distinctive thermoelectric properties of Nb-doped $(Nd_{0.55}Li_{0.36})TiO_3$ bulk ceramics, data for $SrO(SrTiO_3)_n$ [27] were presented as reference. Layered perovskite-type $SrO(SrTiO_3)n$ (n = integer) is termed as Ruddlesden–Popper(RP) phase [28,29], which has a layered structure composed of alternate stacks of rock salt SrO layer and perovskite $(SrTiO_3)_n$ block layer along the c-axis. Low thermal conductivities were reported due to the phonon scattering at the interfaces between SrO layers and $(SrTiO_3)_n$ block layers [27].

## 2. Experimental procedure

$(Nd_{0.55}Li_{0.36})(Ti_{1-y}Nb_y)O_3$ ($0 \le y \le 0.10$) powder was prepared by the solid state reaction approach. First, the homogeneously mixed powder of stoichiometric $Nd_2O_3$, $Li_2CO_3$, $TiO_2$ and $Nb_2O_5$ was put into an alumina crucible and calcined at 1100 °C for 12 h in air to decarbonate and react. Then, the powder was put into a graphite crucible and calcined at 1430 °C under an argon atmosphere for 3 h.

The powder was pelletized under an isostatic pressure of 450 MPa.The pellets were sintered in a graphite crucible under an argon atmosphere by the conventional sintering method. First, the sintering was carried out at 1250 °C for 12 h. After that, the temperature was decreased to 650 °C with a cooling rate of 150 °C/h. Finally, the pellets were cooled inside the furnace to room temperature. During the sintering process, all the pellets were embedded in the powder with the same composition to avoid evaporative loss of lithium.

The structural analysis was conducted by the powder X-ray diffraction using a diffractometer with Cu *Kα* radiation (XRD, RINT-2001, Rigaku Corporation). The microstructure of the specimens was observed by a high resolution transmission electron microscope (HR-TEM, EM-002B, Topcon Corporation). The electrical properties, that is, the Seebeck coefficient and electrical conductivity, were measured from room temperature to 650 K in an argon atmosphere using an automatic thermoelectric measuring apparatus (RZ-2001K, Ozawa Scientific Corporation). The thermal conductivity was calculated using the relationship $\kappa = \rho \cdot C_V \cdot \alpha$, where $\rho$, $C_V$, $\alpha$ are the density measured by Archimedes method, the volumetric specific heat capacity measured with a differential scanning calorimeter (DSC-2910, TA Instruments Corporation) and the thermal diffusivity measured by a laser flash method (TC-9000V, ULVAC-RIKO Corporation), respectively.

## 3. Results and discussion

Fig. 1 presents the X-Ray Diffraction patterns of the samples with various Nb doping content ($0 \le y \le 0.10$). The samples indexed to JCPDS File 46–0464 in all cases. Here, in addition to the underlying parent cubic perovskite reflections, (0 0 1/2) peaks reveal the c-parameter doubling often seen in the A-site ordering of $(Ln_{2/3-x}Li_{3x}TiO_3)$ [19]. Peak for an unidentified phase at about 25.5° appeared for the 10 at%Nb-doped sample, suggesting a much lower solid solubility of Nb in $(Nd_{0.55}Li_{0.36})TiO_3$ compared with that in other titanates, for example, over 20 at% in $SrTiO_3$ [9], and in Ruddlesden-Popper phase $SrO(SrTiO_3)_n$ [27].

Fig. 2 reveals the microstructure of non-doped and Nb-doped samples. Obviously, Superlattice structure of the non-doped sample is preserved after the Nb doping.

The satellite points in the [001] zone electron diffraction pattern indicate a modulation of the crystal structure on the nanometer scale [19,21], which is in accord with the diamond-like pattern. Additionally, compared with the strong spot satellite diffraction for the non-doped sample (inset in Fig. 2(a), the spot satellite diffraction for the Nb-doped sample (inset in Fig. 2(b)) is weak, which indicates a diffuse scattering around the main Bragg reflections. The fading of the spot satellite diffraction after the Nb doping is due to the weakened periodicity of the microstructure as shown by the HR-TEM image in Fig. 2(b). This phenomenon was also found after the Ti-site-Mn-doping [21]. Anyway, the preservation of the superlattice structure after the Nb-doping is important for the thermoelectric properties of $(Nd_{0.55}Li_{0.36})(Ti_{1-y}Nb_y)O_3$, because it will provide plenty of interfaces to scatter phonons to effectively reduce the lattice thermal conductivity. Meanwhile, electron carriers will be generated through the substitution of Ti by Nb.

Fig. 3 shows the temperature dependence of the thermal conductivity of $(Nd_{0.55}Li_{0.36})(Ti_{1-y}Nb_y)O_3$ ($0 \le y \le 0.10$). The dependence for $SrO(SrTiO_3)_n$ ($n = 1, 2$) is also shown for comparison [27].

The samples of $(Nd_{0.55}Li_{0.36})(Ti_{1-y}Nb_y)O_3$ with various doping contents have close relative densities of ~90%. Thermal conduction in solids is usually contributed by phonons and carriers. Here, because the electronic thermal conductivity calculated by Wiedeman-Franz law is as small as ~0.1 W/(m·K), the thermal conduction should be mainly contributed by phonon propagation. Moreover, in comparison with $SrO(SrTiO_3)_n$ ($n = 1, 2$), $(Nd_{0.55}Li_{0.36})(Ti_{1-y}Nb_y)O_3$ ($0 \le y \le 0.10$) shows a glass-like thermal conductivity. This possibly means that the scattering of phonons at the superlattice interfaces is higher than that at the $SrO/(SrTiO_3)_n$ interfaces. Furthermore, compared with RP phase $SrO(SrTiO_3)_n$ ($n = 1, 2$), the high percentage of A-site deficiencies including vacancies and high mobile lithium ions could scatter phonons with high frequencies, which also contributes to the low thermal conductivity of $(Nd_{0.55}Li_{0.36})(Ti_{1-y}Nb_y)O_3$ ($0 \le y \le 0.10$). Thermal conductivity is as low as ~2 W/(m·K), which is unusual for oxides, especially for titanates.

Fig. 4 shows the temperature dependence of the electrical properties of $(Nd_{0.55}Li_{0.36})(Ti_{1-y}Nb_y)O_3$ ($0 < y \le 0.10$). That for SrO $[Sr(Ti_{1-z}Nb_z)O_3]_n$ ($n = 1, 2$; $z = 0.05, 0.10$) is also shown for comparison [27]. Fig. 4 (a) presents the dependence of the electrical conductivity on temperature. For $(Nd_{0.55}Li_{0.36})(Ti_{1-y}Nb_y)O_3$ ($0 < y \le 0.10$), it shows a semiconducting behavior. The electrical