



Glass-like thermal conductivity of $\text{Nd}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ bulk ceramics with nano-chessboard superlattice structure

Yaoshuai Ba^{a,b}, Chunlei Wan^{b,c}, Yifeng Wang^b, Wataru Norimatsu^c, Michiko Kusunoki^c, Kunihiro Koumoto^{b,c,*}

^a School of Mechanical Engineering and Automation, Northeastern University, Shenyang 110004, China

^b Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

^c CREST, Japan Science and Technology Agency, Tokyo 102-0075, Japan

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ABSTRACT

We report the thermal conductivity of bulk $\text{Nd}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ ($0.047 < x < 0.151$) ceramics, prepared by a conventional solid-state reaction method. These materials possess a nano-chessboard superlattice structure present in every crystallite, with a superperiodicity of ~ 4 nm along the [110] orientation. A glass-like low thermal conductivity ($1\text{--}2$ W/(mK)) was shown in the $\text{Nd}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ system and it was almost temperature independent. Moreover, a shorter periodic length of the superlattice structure caused a lower thermal conductivity due to the increased interface phonon scattering. The low thermal conductivity is not always seen in oxide materials. In combination with the tunability of the electrical properties and the maintainability of the microstructure, we believe that this work provides an insight into the nanostructure design for the development of novel oxide thermoelectric materials.

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1. Introduction

Over the past two decades, oxide materials have received much attention from researchers in thermoelectrics due to their advantages over traditional alloy thermoelectric materials, such as low cost, nontoxicity, thermal and chemical stability. The performance of thermoelectric materials is usually characterized by dimensionless figure of merit $ZT = S^2\sigma T / (\kappa_e + \kappa_l)$, where S , σ , κ_e , κ_l and T represent the Seebeck coefficient, electrical conductivity, electronic thermal conductivity, lattice thermal conductivity and absolute temperature, respectively. Usually, a ZT value equal to or higher than unity is needed for practical applications of thermoelectric materials. Although some obvious progress has been made in oxide thermoelectric materials, for example, $ZT=0.37$ for n-type SrTiO_3 at 1000 K [1, 2], high lattice thermal conductivity prevents the advancement of thermoelectric performance of oxides. For instance, κ_l is about 11 W/(mK) for SrTiO_3 at room temperature, which is much higher than that of the state-of-the-art alloy thermoelectric materials, such as 2–3 W/(mK) for Bi_2Te_3 [3]. Therefore, arriving at effective solutions to reduce the lattice thermal conductivity is very important to improve the thermoelectric performance of oxides. Nanostructuring is

recognized as being such one and is being widely applied [4]. In this letter, we report a glass-like thermal conductivity shown by bulk $\text{Nd}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ ceramics whose lattice thermal conductivity is dramatically suppressed by the superlattice structure present in every crystallite.

2. Experimental details

Two compositions ($x=0.05$, $x=0.12$) were studied in our experiment. The $\text{Nd}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ powder was prepared by a solid-state reaction of Nd_2O_3 , Li_2CO_3 and TiO_2 powders at 1100 °C for 12 h. The powders were pelletized and sintered at 1250 °C for 12 h, cooled to 600 °C with a cooling rate of 150 °C/h, and then naturally cooled down. During the sintering process, the pellet was embedded in the powder with the same composition to avoid evaporative loss of lithium. The crystalline structures were determined by powder X-ray diffraction (XRD) ($\text{CuK}\alpha$). The morphologies of the specimens were observed by a field-emission scanning electron microscope (FE-SEM) and a high-resolution transmission electron microscope (HR-TEM). Thermal conductivity was calculated using the equation $\kappa = \rho C_V \alpha$, where ρ , C_V , α are the density measured by the Archimedes method, the volumetric specific heat capacity measured by a differential scanning calorimeter (DSC-2910, TA Instruments) and the thermal diffusivity measured by a laser flash method (TC-9000V, ULVAC-RIKO), respectively.

* Corresponding author at: Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan. Tel.: +81 52 7893327; fax: +81 52 7893201.

E-mail addresses: g44233a@cc.nagoya-u.ac.jp, koumoto@apchem.nagoya-u.ac.jp (K. Koumoto).

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples. The samples were indexed to JCPDS File 46–0464 in all cases (Fig. 1).

At the micron scale, a single-phase-like cross section of the broken pellet is shown by FE-SEM observation (Fig. 2a). However, at the nanometer scale, HR-TEM analysis indicates a superlattice structure throughout the crystallite (Fig. 2b both diamond-type (domain A) and chessboard-type microstructure (domain B) are shown, which are actually identical [5]). Electron diffraction pattern (Fig. 2c) reveals a distorted perovskite structure, and the

strong satellites in the pattern suggest a secondary ordering modulation on the nanometer length scale [5, 6]. The light square nanodomains and the dark zigzagging boundary regions shown in Fig. 2d correspond to $\text{Nd}_{1/2}\text{Li}_{1/2}\text{TiO}_3$ and $\text{Nd}_{2/3}\text{TiO}_3$, respectively. Phase separation leads to the formation of this microstructure. The identification of each of the two phases and the detailed explanation of the formation mechanism of the superlattice structure have been specifically and intensively reported in References [5,7]. The formation of the two phases is believed mainly due to the different sizes of Nd^{3+} and Li^+ [7].

The samples of the $x=0.05$ and the $x=0.12$ have similar microstructures. However, different lithium contents led to different sizes of $\text{Nd}_{1/2}\text{Li}_{1/2}\text{TiO}_3$ and $\text{Nd}_{2/3}\text{TiO}_3$ (Fig. 3). Due to the smaller size of the $\text{Nd}_{1/2}\text{Li}_{1/2}\text{TiO}_3$ domain region, the $x=0.05$ specimen shows a smaller periodic length (Fig. 3), which was confirmed in reference [5]. The difference in periodic lengths would be expected to affect the thermal conductivity.

The temperature dependence of the thermal conductivity is shown in Fig. 4. The thermal conductivity is pretty low, $\sim 1 \text{ W}/(\text{mK})$ and $\sim 1.5 \text{ W}/(\text{mK})$ for the $x=0.05$ and the $x=0.12$, respectively. To exclude the effect of porosity, the thermal conductivity of a fully dense sample with zero porosity was calculated using the Klemens equation [8]

$$k_{\text{measured}}/k_{100\% \text{ dense}} = 1 - 4\phi/3 \quad (1)$$

where ϕ is the porosity of the sample. As shown in Fig. 4, the thermal conductivities for fully dense samples are below $2 \text{ W}/(\text{mK})$. The observed difference in thermal conductivities between the $x=0.05$ and the $x=0.12$ might be attributed to the difference of the periodic lengths of the superlattice structure

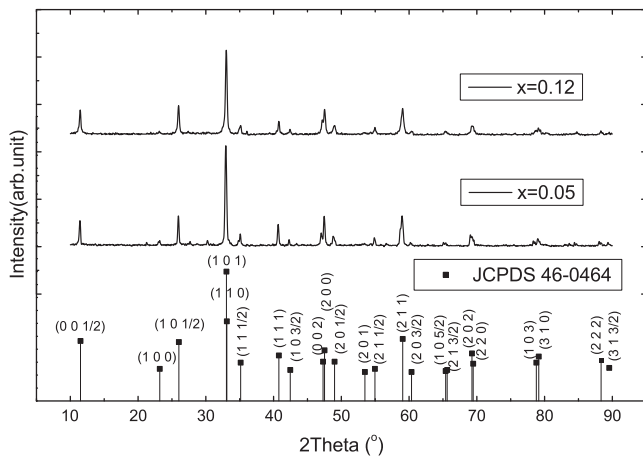


Fig. 1. XRD patterns of $\text{Nd}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ ($x=0.05$ and $x=0.12$).

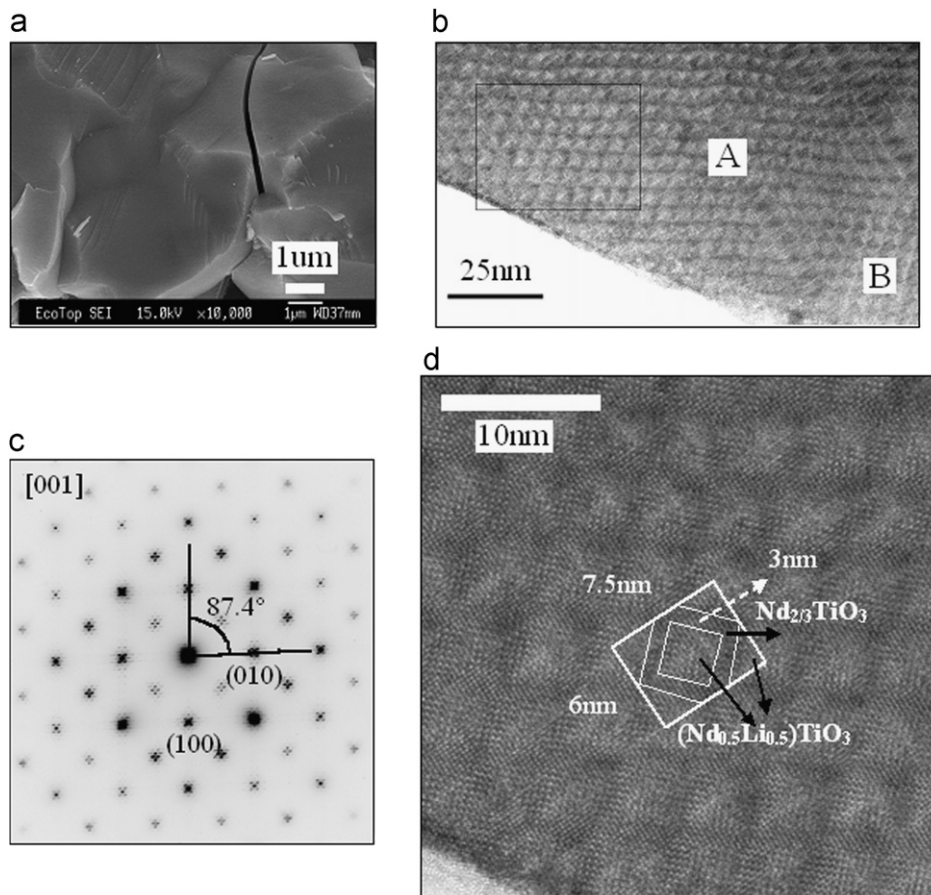


Fig. 2. (a) FE-SEM micrograph, (b) HR-TEM micrograph, (c) HR-TEM electron diffraction pattern and (d) magnification of the selected area in (b). All results are for the $\text{Nd}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ ($x=0.12$) specimen. HR-TEM observation and electron diffraction were both performed along the [001] direction.

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