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INFLUENCE OF UMKLAPP SCATTERING PROCESS ON THERMAL TRANSPORT PROPERTIES OF TETRAGONAL TUNGSTEN BRONZE MATERIALS

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ABSTRACT

Thermal transport in tetragonal tungsten bronze (TTB) materials has attracted significant attention due to their structurally complex frameworks and tunable functional properties. These materials, which include single crystals, thin films, and especially ceramics, exhibit low thermal conductivity primarily governed by phonon-mediated transport. In ceramic forms, microstructural features such as grain boundaries, defects, porosity, and compositional disorder further enhance phonon scattering. Among intrinsic phonon–phonon interactions, Normal (N-Process) and Umklapp (U-Process) scattering processes play a critical role in determining the total and lattice thermal conductivities. While N-processes conserve crystal momentum and redistribute phonon populations without directly impeding heat flow, U-processes involve momentum transfer to the lattice via reciprocal lattice vectors, thereby introducing thermal resistance. In TTB materials, strong lattice anharmonicity, multi-site occupancy, crystallographic symmetry, CS planes and natural chemical disorder significantly increase the probability of Umklapp scattering, particularly at elevated temperatures. This paper provides a detailed theoretical and materials-oriented analysis of phonon transport in TTB systems, with emphasis on ceramics. The influence of crystal structure, defect chemistry, and processing routes on thermal transport is examined. The experimental thermal behaviour of Sm-doped Sr5LaTi3Nb7O30 TTB ceramic system is discussed to illustrate how compositional, doping and microstructural engineering can tailor phonon scattering and thermal properties. The findings highlight the importance of Umklapp processes in suppressing thermal conductivity and underscore the potential of TTB ceramics for thermoelectric and thermal (energy) management applications.

KEYWORDS: Umklapp scattering; phonon transport; tetragonal tungsten bronze; thermal conductivity; defect scattering.

INTRODUCTION

Tetragonal tungsten bronze (TTB) materials are the largest class of dielectrics after perovskites (Zhu et al.,2015; Jason et al., 2017; Zhu et al., 2011). The TTB structure is a complex oxide system with open framework lattice structure and partially occupied lattice sites (Shi & Khansur, 2023). It has a distorted, corner-sharing oxygen-octahedra (B1O6 and B2O6) which forms three different interstices/tunnels or sites (Zhu et al., 2015; Fang et al., 2014; Jason., 2017; Lin et al., 2014; Smirnov and Saint-Grégoire, 2013). These tunnels are square (also called perovskite), A1 with a coordination number of 12, pentagonal, A2 with 15-coordinated sites and trigonal/triangular (which is the smallest channel) C containing 9-coordinated sites. A typical TTB structure is represented with the general formula:

$[A1_2A2_4C_4][B1_2B2_8]O_{30}$

Generally, the A1 and A2 sites are occupied by metal cations of alkali/alkaline earth elements, p-block elements (e.g. Pb, Bi) or RE elements. C-sites are narrow and can be empty in most TTB compounds or occupied by small cations like Li^+. B octahedra sites are often occupied by Ti^{4+}, Nb^{5+} and Ta^{5+}. Because of the capacity to accommodate large cations and possession of great flexibility (or degrees of freedom) for tuning the chemical composition, the TTB family shows excellent properties for diverse applications (Zhu et al., 2015; Lin et al., 2014; Raju and Choudhary, 2003) such as electro-optic, pyroelectric, piezoelectric, semiconductivity (and metallic conductivity), superconductivity and high permittivity. Their structural flexibility enables a wide range of electrical and thermal properties (Setter and Waser, 2000). Heat transport in these materials is dominated by phonons (Kittel, 2005), making phonon scattering mechanisms critical. These features lead to mass fluctuation, local strain fields and broken translational symmetry. Thus, the structural complexity significantly limits phonon propagation (Graetsch et al., 1985; West, 2014). A prototype TTB crystal structure showing the sites and the corner-sharing oxygen octahedra is presented in Figure 1 (Jason et al., 2017).

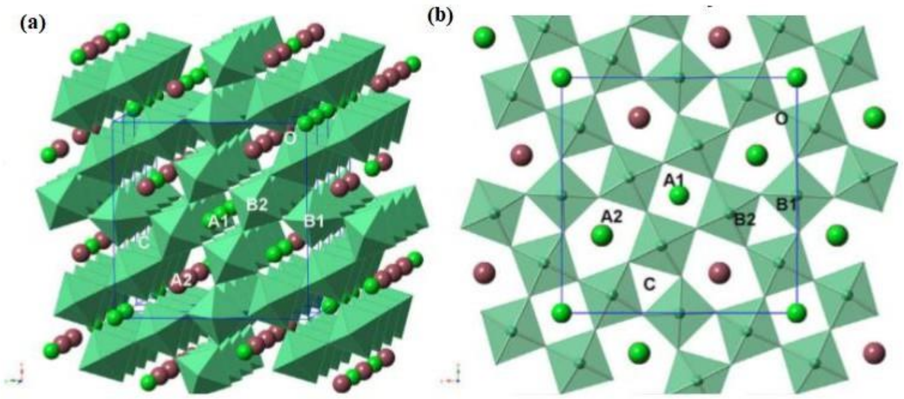

Figure 1. (a) Tilted view of a prototype tetragonal tungsten bronze (TTB) structure (b) a-b plane projection (// c-axis) illustrating the tunnels described by the corner-sharing oxygen octahedra.

Phonon Transport Fundamentals

The energy of a given lattice vibration in a rigid crystal lattice is quantised into a quasiparticle called a phonon. This is analogous to a photon in an electromagnetic wave; thermal vibrations in crystals can be described as thermally excited phonons, which can be related to thermally excited photons. Phonons are a major factor governing the electrical and thermal conductivities of a material. A phonon is a quantum mechanical adaptation of normal modal vibration in classical mechanics. A key property of phonons is that of wave-particle duality; normal modes have wave-like phenomena in classical mechanics but gain particle-like behaviour under quantum mechanics.

Thermal conductivity, k is the description of energy transport in the form of heat through a material because of temperature gradient. In thermoelectrics or solid state in general, thermal conductivity is the transfer of heat via a material either by charge carriers (electrons and holes) or by phonons travelling through the lattice. Therefore, total thermal conductivity, k is associated with carrier or electronic thermal conductivity (kE) and lattice thermal conductivity (kL) (Tritt and Subramanian, 2006), hence;

$k = k_E + k_L$ 2.0

In metals, the total thermal conductivity is dominated by kE which is attributed to presence of high carrier concentration. Therefore, metals are the best electrical and thermal conducting materials. Unlike metals, kL dominates the total thermal conductivity in non-metals (insulators and semiconductors). Conversely, in TTB systems, the dominant factor reducing thermal conductivity is the strong suppression of phonon mean free path due to scattering (Kittel, 2005). The lattice contribution to the total thermal conductivity is given by a classical kinetic theory as:

$$K_L = \frac{C_v l V_s}{3} \qquad 3.0$$

where C is the specific heat capacity, l is the mean free path of the phonons and Vg is the group velocity of the phonons. Equation 3 shows that not only kL depends on the electronic structure of the material. For a low k to be obtained, low C, short l and a low Vg are required.

Theoretical Background of Phonon Scattering

The efficiency of phonon-mediated heat conduction depends strongly on scattering mechanisms that limit phonon mean free path. These include boundary scattering, impurity scattering, and phonon–phonon interactions. Among these, normal (N) processes and umklapp (U) processes are the most fundamental intrinsic mechanisms (Ziman, 1960; Callaway, 1959; Ward et al., 2009).

Normal processes conserve crystal momentum within the first Brillouin zone and therefore do not directly contribute to thermal resistance. The momentum conservation equation is given by:

$K_1 + K_2 + K_3$ 4.0

where; k1, k2 and k3 are phonon wave vectors, also known as crystal momentum vectors. Thus; k1 and k2 are vectors of initial phonons while k3 is the vector resultant phonon after interaction (Kittel, 2005; Ashcroft & Mermin, 1976).

Whereas Umklapp processes result in effective momentum loss and thus limit heat flow. The interplay between these processes explains the characteristic temperature dependence of thermal conductivity in ceramics, including the peak at intermediate temperatures and the decline at high temperatures (Berman, 1976; Slack, 1979). Understanding these mechanisms is essential for designing ceramics with tailored thermal properties for applications such as thermal barrier coatings, electronic substrates, and thermoelectric devices. Although N-processes do not directly impede heat flow, they play an indirect role by redistributing phonon populations and facilitating equilibrium conditions that influence other scattering mechanisms (Callaway, 1959; Ziman, 1960; Ward et al., 2009).

Umklapp processes occur when the resultant phonon wavevector exceeds the Brillouin zone boundary while momentum is not conserved within the first Brillouin zone:

$$K_1 + K_2 = K_3 + G \qquad 5.0$$

where G ($G \neq 0$) is a reciprocal lattice vector and represents the periodicity of the crystal in momentum space. It is characterized with effective reversal of phonon direction, dissipation of heat-carrying momentum and a primary source of thermal resistance. These processes become significant only when sufficient thermal energy is available to excite high-frequency phonons (Peierls, 1929; Ziman, 1960; Lindsay et al, 2013). The graphical Brillouin zone boundary illustration of N-scattering and U-scattering processes is presented in Figure 2.

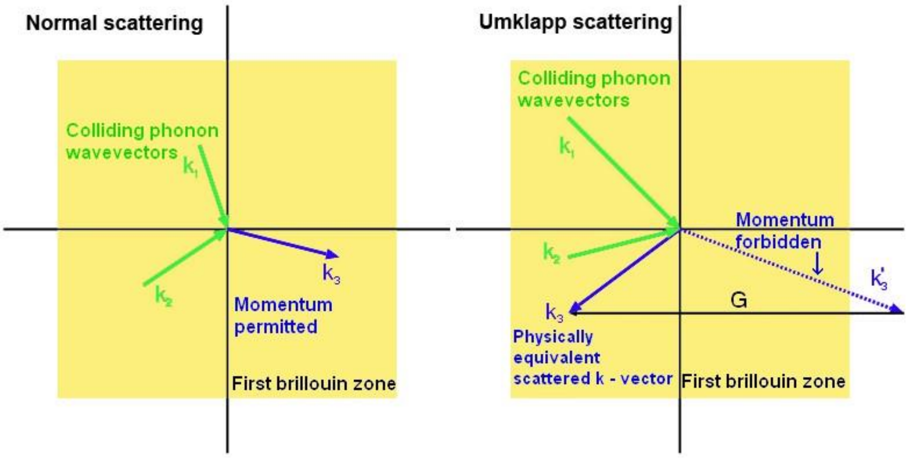

Figure 2. Graphical illustration of Brillouin zone for N-scattering and U-scattering processes.

Phonon Scattering Mechanisms in TTB Systems

Phonon scattering processes in tetragonal tungsten bronze (TTB) crystalline materials are characterized with mass disorder, anharmonic lattice dynamics, defect and vacancy scattering, grain boundary and microstructural effects and localized vibrational modes (Rattling Effects).

The presence of multiple cation species in TTB systems enhances mass fluctuation scattering (mass disorder) hence, reducing phonon transport efficiency. Also, high-entropy TTB ceramics have been shown to exhibit significantly reduced thermal conductivity due to enhanced configurational disorder (Zhong et al., 2025). The strong lattice anharmonicity exhibited by TTB systems lead to enhanced phonon–phonon interactions, increased Umklapp scattering, and reduced phonon lifetimes. Temperature-dependent Raman studies reveal phonon softening and mode broadening, indicative of strong anharmonic interactions (Srivastava, 1990).

The defect chemistry such as Oxygen vacancies and site disorder introduce localized disruptions in lattice periodicity, which scatter phonons effectively. These defects contribute significantly to thermal resistance and relaxation phenomena. Furthermore, the inherent grain boundaries, porosity and microstructural heterogeneity features act as scattering centers, reducing phonon mean free path and overall thermal conductivity (Shi & Khansur, 2023).

Large A-site channels in TTB structures allow loosely bound cations to undergo localized vibrations (“rattling”), which in turn scatter heat-carrying phonons and disrupt coherent phonon transport, resulting in phonon-glass-like behavior in crystalline materials (Sales et al., 1996).

Thermoelectric Behaviour of Selected TTB Oxide Materials

Oxides are potential thermoelectric (TE) materials due to their cheapness or abundance, non-toxicity and high chemical and/or physical stability when subjected to high temperatures. However, high crystallographic symmetry (and small unit cells) associated with oxides lead to high thermal conductivity and low dimensionless figure of merit, ZT (Heinrich, 2015). In order to improve the TE efficiency via lowering of the thermal conductivity, materials with intrinsic phonon scattering centres such as TTBs have recently attracted attention (Krumeich, 1998; Heinrich, 2015). The high crystallographic symmetry, CS planes (and small unit cells) , and the natural disorder inherent in Magneli phases and TTBs are regarded as intrinsic nanostructures (Kieslich, 2016; Heinrich, 2015) and serve as barriers to phonon propagation, hence low thermal conductivity.

$Na8-xW9+xO47-\delta$ TTB Compound

The thermal and thermoelectric properties of $Na8-xW9+xO47-\delta$ (x = 0, 0.075, 0.1, 1, 2) TTB compounds were investigated (Kieslich, 2016; Heinrich, 2015) with compositions exhibiting stability up to 1323 K, low thermal conductivity (1.6-2.0 W/m.K) , and high Seebeck coefficient, S = -240 μV/K (indication of n-type) at room temperature.

The highest power factor, PF = 0.8 μW/cm. K^2 and maximum ZT = 0.043 at 973 K were observed in $Nb_6W_{11}O_{47-\delta}$ (x = 2). The highest ZT (0.043) for $Na_{8-x}W_{9+x}O_{47-\delta}$ obtained in this study is very low compared to other n-type oxides, but the high Seebeck coefficient and very low thermal conductivity recorded show the potential of TTBs for TE applications.

$Sr_xBa_{1-x}Nb_2O_{6-\delta}$ TTB compound

Lee et al (2010) and Li et al (2015) independently investigated the thermoelectric and thermal performance of single crystal $Sr_xBa_{1-x}Nb_2O_{6-\delta}$ TTB compounds and reported a high PF (200 μW/m.K^2) at 516 K parallel to c-axis and a ZT > 0.5 along the c-direction (Jason, 2017). In a related study of TE properties of $Sr_xBa_{1-x}Nb_2O_{6-\delta}$ single crystal and ceramics, k = 1.92 W/m.K (400 K), PF = 40.8 μW/cm.K^2 (550 K), ZT = 1.12 (550 K) for single crystals; and k = 2.28 W/m.K (550 K), PF = 7 μW/cm.K^2 (550 K), ZT = 0.17 (550 K) for ceramics (Lee et al., 2012). In the recent study of the TE properties of $Nb_{8-x}W_{9+x}O_{47}$ (0<x<5) TTB ceramics, S = -95 μV/K, k = 2.6 W/m.K and ZT = 0.2 at 1173 K were reported for $Nb_4W_{13}O_{47}$ (x = 4) composition (Cerretti et al., 2017). In a related study of TE properties of $Sr_xBa_{1-x}Nb_2O_{6-\delta}$ single crystal and ceramics, k = 1.92 W/m.K (400 K), PF = 40.8 μW/cm.K^2 (550 K), ZT = 1.12 (550 K) for single crystals; and k = 2.28 W/m.K (550 K), PF = 7 μW/cm.K^2 (550 K), ZT = 0.17 (550 K) for ceramics (Lee et al., 2012) were observed.

$Nb_{8-x}W_{9+x}O_{47}$ (0<x<5) TTB Ceramics

In the recent study of the TE properties of $Nb_{8-x}W_{9+x}O_{47}$ (0<x<5) TTB ceramics, S = -95 μV/K, k= 2.6 W/m.K and ZT = 0.2 at 1173 K were reported for $Nb_4W_{13}O_{47}$ (x = 4) composition (Cerretti et al., 2017).

With these low thermal conductivities and TE results reported for TTB compounds, it is obvious to state that oxides with adaptive structures are potential candidates for TE applications (Kieslich, 2016). This is attributed in part but not limited to their complex structure, hence there is the possibility of tuning properties by cation substitution (and oxygen deficiency), (Kieslich, 2016; Heinrich, 2015).

Experimental Thermal Study of Sm-doped $Sr_5LaTi_3Nb_7O_{30}$ TTB System

$Sr_5LaTi_3Nb_7O_{30}$ tetragonal tungsten bronze (TTB) ceramic material was investigated via two different doping mechanisms namely; electron doping, $Sr_5La_{1-x}Sm_xTi_3Nb_7O_{30}$, 0.00 ≤ x ≤ 1.00 (SLTNe) and ionic or vacancy doping, $Sr_{5-3x/2}LaSm_xTi_3Nb_7O_{30}$, 0.00 ≤ x ≤ 0.30 (SLTNv) with a view to decreasing the thermal conductivity and increasing the electrical conductivity through the use of rare earth (samarium) dopant processing strategies involving sintering in reduced atmosphere (95%/N_2/5%H_2 gas) (Iyasara, 2019).

Thermal Transport Properties

Figures 3 and 4 show the total thermal conductivity (k), and lattice thermal conductivity (k_L) of SLTNe and SLTNv TTB ceramics, respectively. Total thermal conductivity (k), and lattice thermal conductivity (k_L) of all the ceramics vary unevenly with Sm-concentration at low temperatures. The main reason for this irregularity is attributed to the influence of several factors such as defect scattering and bond angles of the Ti-O, Nb-O octahedra and the changes in phase assemblage as a function of composition. However, at low temperatures, k for most of the compositions increases with temperature. This consequence is explained using the concept of Normal scattering process (Spiteri, 2015). At low temperatures, majority of the thermally excited phonons possess small momentum and it's known as "Normal scattering process (N-process)". As a result, momentum is conserved, hence there is no contribution or effect on net energy, momentum contribution, scattering in heat transport and mean free path, MFP for total thermal conductivity, k. Thus, k increases with temperature.

Other factors that influenced the thermal conductivity include point defects; created vacancies: strontium and oxygen vacancies (V_{Sr}, V_O) in the lattice created in the lattice, and the presence of secondary phases ($SrTiO_3$ and Nb_2O_5) in the microstructure.

SLTNv TTB ceramics exhibited low k values (1.62-3.85 W/m. K) when compared to that of SLTNe TTB ceramics (2.02 to 4.17 W/m. K) in the whole measured temperature range. This observation shows that the presence of these secondary phase inclusions and the point or vacancy defects act as scattering centres (in SLTNv TTB ceramics), thereby shortening the MFP of phonons and restrict their propagation, resulting in a decrease in k (Wang et al.,2017; Zheng et al, 2012; Han et al., 2017).

It is observed that only x = 0.50 (from SLTNe TTB ceramic) and x = 0.30 (from SLTNv TTB ceramic) exhibited similar thermal behaviour; the thermal conductivity decreased with increasing temperature over the entire measured temperature range. This trend signifies a phonon scattering behaviour (Li et al., 2015) which is dominated by the Umklapp scattering process (U-process) (Wang et al.,2017; Ohta et al., 2005; Li et al., 2016). Umklapp scattering process is the name for several types of scattering mechanism that change the momentum of phonons. As previously discussed, the U-process occurs usually at high temperatures, and momentum is not conserved, resulting in a net momentum deposition in the scattering process and k being proportional to 1/kT. The lowest k (~ 2.0 W/m. K) obtained in SLTNe TTB ceramic was observed in x = 0.50 at 973 K, while in SLTNv TTB ceramic, x = 0.30 showed the lowest k (~ 1.6 W/m. K) at 873 K. The lowest k values are attributed to the Umklapp scattering which not only reduces the k, but also the electrical conductivity, σ (especially at high temperature for SLTNv, x = 0.30) as presented in Figure 3.

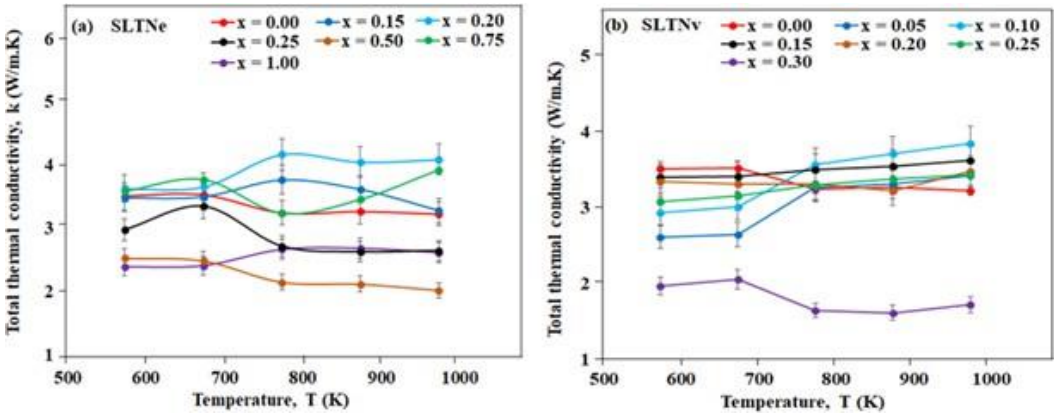

Figure 3. Temperature dependence of total thermal conductivity for (a) SLTNe (b) SLTNv TTB ceramics sintered for 6 hours in 95% N_2 /5% H_2 at 1673 K

The lattice thermal conductivity (k_L) as shown in Figure 4 exhibited the same trend as k (shown in Figure 3 above) but with slightly lower values. In general, the decrease in k experienced in SLTNe and SLTNv TTB ceramics may be linked to an additional phonon scattering resulting from impurities (or secondary phases) evidenced in the SEM images and point EDX trace (Figure 5) , cation vacancies, oxygen defects and grain boundaries (Biswas et al., 2012; Qiu et al., 2012; Wang et al., 2010).

The electronic thermal conductivity (k_E) of all ceramics showed similar temperature dependence with σ and increased with increase in temperature as presented in Figure 6. From the small k_E values (19.5 to 20.6 % of k), the electronic thermal conductivity makes a very small contribution to the total thermal conductivity. Therefore, the decrease of k of the ceramics is mainly due to the decrease of k_L via enhancement of phonon scattering.

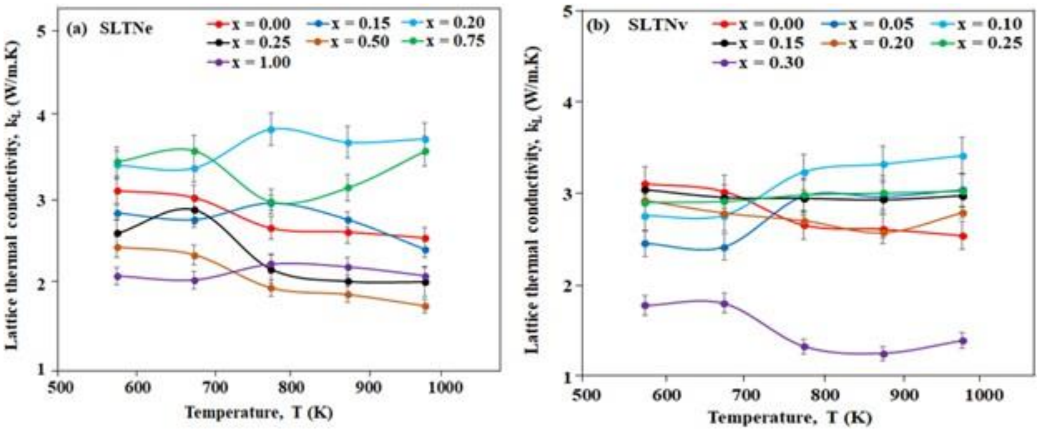

Figure 4. Temperature dependence of lattice thermal conductivity for (a) SLTNe (b) SLTNv TTB ceramics sintered for 6 hours for in 95% N_2 /5%H_2 at 1673 K.

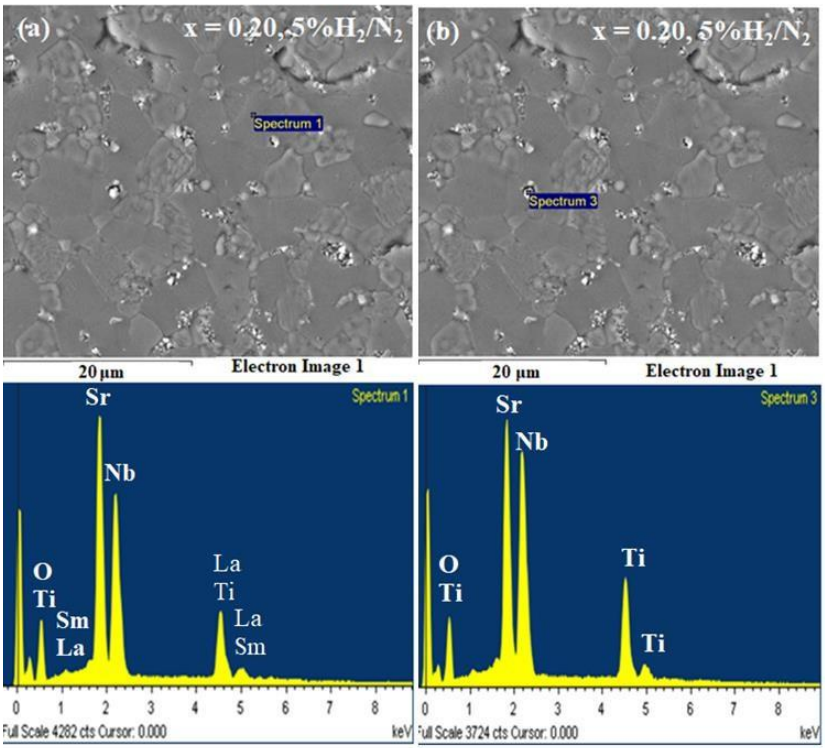

Figure 5. SEM image and point EDX trace of $Sr_5La_{0.80}Sm_{0.20}Ti_3Nb_7O_{30}$ TTB ceramic sintered 6 hours in 95% N_2 /5%H_2 at 1673 K from a (a) large grain (spectrum 1) (b) small grain or secondary phase (spectrum 3).

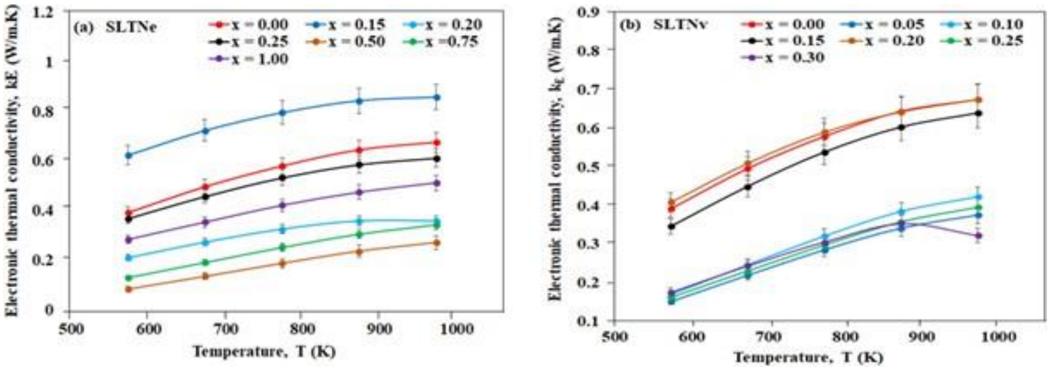

Figure 6. Temperature dependence of lattice thermal conductivity for (a) SLTNe (b) SLTNv TTB ceramic sintered for 6 hours in 95% N_2 /5% H_2 at 1673 K.

CONCLUSION

This study establishes that thermal transport in tetragonal tungsten bronze, TTB materials is fundamentally governed by Umklapp phonon scattering, which serves as the dominant intrinsic mechanism of thermal resistance, particularly at moderate to high temperatures. The complex crystal structure – featuring multiple cation sites, partial occupancies, and inherent disorder enhances lattice anharmonicity and significantly increases phonon scattering rates, thereby reducing phonon lifetimes and mean free paths.

In TTB systems, Umklapp scattering processes operate alongside defect, impurity, boundary, and localized vibrational (rattling) scattering to produce strong, multi-scale phonon suppression, leading to low and often glass-like thermal conductivity. The limited role of N-processes further emphasizes the dominance of restive scattering mechanisms.

Overall, the interplay of structural complexity and anharmonic lattice dynamics makes U-scattering process central to phonon transport in TTB systems, offering valuable opportunities for targeted phonon engineering in next-generation materials. Recent advances suggest that the combination of high-entropy design, compositional tuning, and defect engineering can further intensify Umklapp scattering process, providing effective pathways for controlling transport.

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