Rattlers or oxygen vacancies: Determinant of high temperature plateau thermal conductivity in doped pyrochlores

Yanfei Wang, Fan Yang, and Ping Xiao

Rattlers or oxygen vacancies: Determinant of high temperature plateau thermal conductivity in doped pyrochlores

Yanfei Wang, Fan Yang, and Ping Xiao[a)]

Materials Science Centre, School of Materials, The University of Manchester, M13 9PL, United Kingdom

High temperature plateau thermal conductivity (k_{min}) remains poorly understood despite its crucial importance in thermal insulation components at elevated temperature. We report In/Sc doped $La_2Zr_2O_7$ pyrochlores with rattlers and oxygen vacancies and their effects on heat transport. Rattlers can dramatically flatten k-T curves at very low doping level; whereas, oxygen vacancies are very effective in reducing k_{min}, particularly when comparing compounds with considerably varied levels of them. Oxygen vacancies generate an electrostatic repulsion force among cations surrounding them, resulting in stronger lattice anharmonicity and weaker bonds, which is the underlying reason of them being the determinant of k_{min}. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4801319]

Heat transport at elevated temperature is extremely important in thermal insulation layers under harsh service environments such as for thermal barrier coatings (TBCs).[1] The materials capable of surviving such extreme conditions are usually ceramics. For ceramics as typical dielectric materials, heat conduction at high temperature is primarily determined by phonon-phonon Umklapp scattering. Thermal conductivity (k) becomes almost constant (termed as the high temperature plateau k_{min}) beyond a critical temperature,[2] at which the phonon mean free path Λ approaches the inter-atomic spacing Λ_0 while the specific volumetric heat capacity C_V approaches its asymptotic value ($3k_B/a^3$), as shown[3]

$$k_{min} = \frac{1}{3}\frac{3k_B}{a^3}\Lambda_0 v,$$ (1)

where a^3, v, and k_B are the average atomic volume, phonon group velocity, and Boltzmann constant, respectively. Since v and a have very weak temperature dependence, they can be taken as constant at different temperatures. Consequently, the high temperature plateau k_{min} can be treated as a temperature independent value.

For a given material, both the atomic volume (a^3) and inter-atomic spacing (Λ_0) are fixed. To lower k_{min}, the only strategy is to reduce v, which can be expressed as[4]

$$v = \xi\sqrt{\frac{E}{\rho\gamma}},$$ (2)

in which ρ is the density, E is Young's modulus, γ is Grüneisen parameter (a description of lattice anharmonicity), and ξ is a constant related to Poisson's ratio. Eq. (2) suggests a bigger γ and lower E favour a smaller v. Moreover, a stronger lattice anharmonicity leads to a greater decrease of E at high temperatures.[5] These suggest the dominance of γ over k_{min}.[4,5] Recently, Christensen et al.[6] pointed out that lattice anharmonicity could be raised by introducing rattlers. As a recently identified phonon scattering source, rattlers widely exist in a

lattice with cage-like voids, such as filled skutterudites,[7,8] hydrate clathrates,[9,10] and Y and Yb doped $La_2Zr_2O_7$ pyrochlores.[3,11] In Ref. 3, a subtle decrease of k_{min} was found in Y doped $La_2Zr_2O_7$ with a variation of dopant content, but it is not yet clear to attribute to rattlers or oxygen vacancies, the latter of which will later be identified as an effective enhancer of lattice anharmonicity besides their well-accepted role as strong phonon scatterers. Therefore, it is of theoretical and practical importance to study the effects of oxygen vacancies and rattlers on heat transport at high temperatures, and more crucially, the underlying factor determining k_{min}.

In this paper, we study thermal conductivity of In/Sc doped $La_2Zr_2O_7$ pyrochlores because: (1) $La_2Zr_2O_7$ as a high-temperature TBC material, the high temperature k is exceptionally important; (2) the specific crystalline structure of $La_2Zr_2O_7$ allow us to investigate effects of both rattlers and oxygen vacancies on heat conduction: on one hand, one eighth of oxygen sites in $La_2Zr_2O_7$ lattice are empty, and they are ordered intrinsic oxygen vacancies (see Fig. 1); on the other hand, as illustrated in Fig. 1, the outward movement of O1 towards its adjacent oxygen vacancy forms oversized AO_8 cages and hence makes formation of rattlers possible; (3) considering the size effect of rattlers,[9] we employ much smaller octahedrally coordinated cations (In^{3+}, 0.919 Å; Sc^{3+}, 0.87 Å)[12] than Y^{3+} (1.019 Å) or Yb^{3+} (0.985 Å)[12] to occupy the oversized AO_8 cages in order to achieve an enhanced rattling effect. Meanwhile, some of In^{3+}/Sc^{3+} dopants substitute for Zr^{4+} on B-sites to produce extra oxygen vacancies. Therefore, In/Sc-$La_2Zr_2O_7$ pyrochlores are expected to have both strong rattlers and a variation of oxygen vacancies. Our study suggests that strong rattlers can effectively cause heat conduction glass-like at a very low doping level, while the oxygen vacancy concentration [V_O] controls k_{min}. The underlying reason for the dominant effect of oxygen vacancies on k_{min} is further uncovered as the repulsive electrostatic force of cations surrounding anionic vacancy sites results in an enhanced lattice anharmonicity as well as a reduced elastic modulus.

Polycrystalline pellets of $(La_{1-x_1}R_{x_1})_2(Zr_{1-x_2}R_{x_2})_2O_{7-x_2}$ ($x = x_1 + x_2$, $x = 0.02$, 0.05, 0.10, R = In, Sc) solid solutions were prepared by a conventional coprecipitation-calcination

[a)]Author to whom correspondence should be addressed. Email address: ping.xiao@manchester.ac.uk, Tel.: +44 161 3065941. fax: +44 161 3063586.
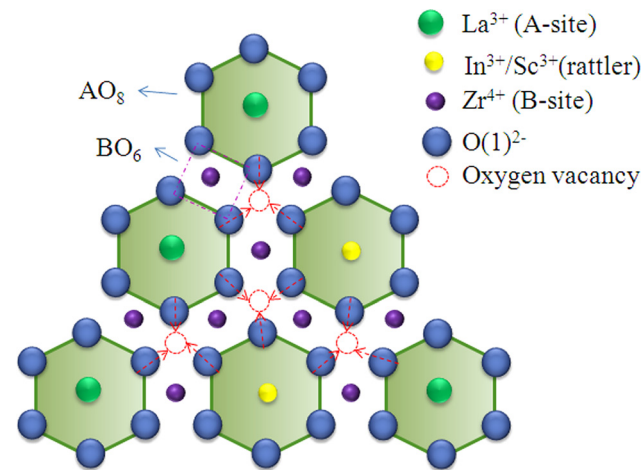
FIG. 1. Schematic drawing of a pyrochlore structure along (1 1 1) plane. The pyrochlore constitutes two interpenetrating polyhedra: AO_8 dodecahedron and BO_6 octahedron, respectively. A special feature of pyrochlores is that O1 tends to relax towards its adjacent vacancy as indicated by red arrows, which affords the formation of the oversized AO_8 cages, a necessity for the presence of rattlers.

method using $La(NO_3)_3 6H_2O$, $ZrO(NO_3)_2 8H_2O$, and $In(NO_3)_3 6H_2O$, $Sc(NO_3)_3 6H_2O$ as starting materials. The powder processing and subsequent cold-pressing and sintering were reported in detail elsewhere.[3] The phase compositions were examined by X-ray diffraction (XRD) with Cu Kα radiation and Raman spectroscopy with the 514 nm line of an argon laser. The density (ρ) was measured by the Archimedes' method and the relative densities of all compositions were above 99.4% (Table I). The thermal diffusivity (D) was measured by a laser-flash system (built-in house, Manchester, UK) in an argon atmosphere and the same procedure was followed after Ref. 3. The specific heat capacitances (C_p) were measured using a simultaneous thermal analyzer (Netzsch STA 449C) in air.

Fig. 2 shows the XRD (a) and Raman (b) patterns of In/Sc-$La_2Zr_2O_7$ solid solutions. The presence of small characteristic peaks reflects the specific cation ordering of the pyrochlore structure, suggesting all compositions crystallize into a cubic pyrochlore phase, which is further confirmed by the presence of four characteristic Raman bands of pyrochlore in (b). Neither XRD nor Raman patterns show any sign of a second phase, indicative of the complete dissolution of dopants at a given amount in the pyrochlore lattice.

In^{3+}/Sc^{3+} dopants essentially substitute both La^{3+} on A-sites and Zr^{4+} on B-sites, supported by two pieces of
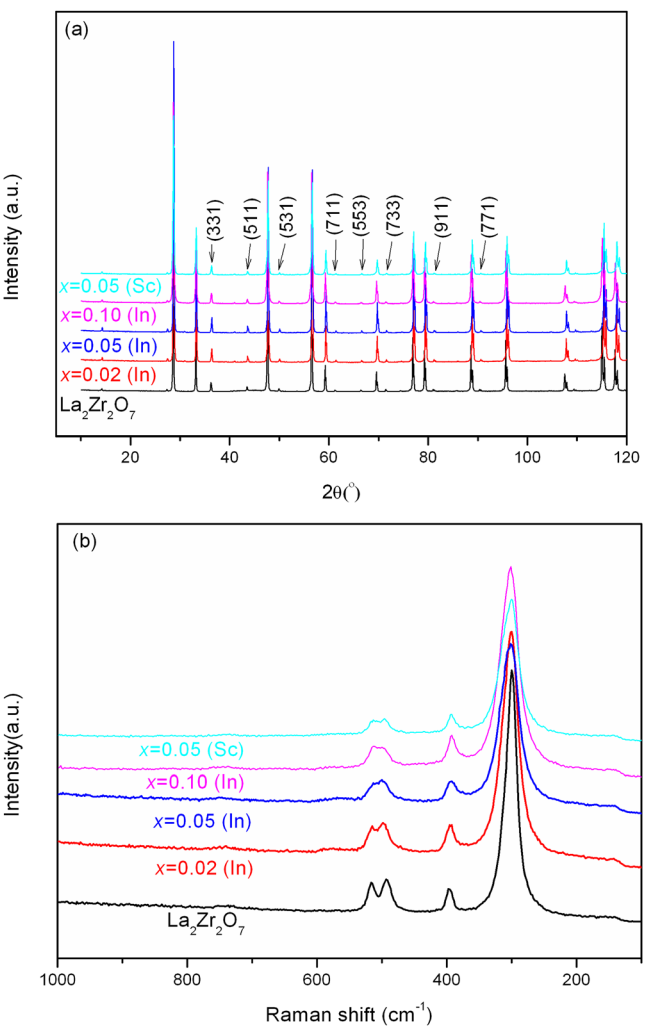

FIG. 2. X-ray diffraction (a) and Raman (b) spectra of $La_2Zr_2O_7$ and In/Sc-$La_2Zr_2O_7$ solid solutions. The small reflections labeled with their Miller indices in (a) are characteristic peaks of the pyrochlore structure. The four Raman bands of pyrochlore in (b) are present for all compositions.

evidence. First, from the absence of lattice contraction with doping of Sc/In, it can be inferred that some of the dopant cations enter the hexagonally coordinated sites (B-sites), compensating the expected contraction anticipated if these cations were to enter only the octahedral sites (A-sites), according to a slight bigger size of dopant cations (In^{3+}: 0.80 Å; Sc^{3+}: 0.745 Å) occupying the hexagonal sites than their hosts (Zr^{4+}: 0.72 Å).[12] Second, the aliovalent B-site substitutions inevitably generate additional oxygen vacancies, which can be reflected by an

TABLE I. Lattice parameter, theoretical, measured and relative densities of $La_2Zr_2O_7$ ($x = 0$) and In/Sc-$La_2Zr_2O_7$ pyrochlore solid solutions ($x = 0.02$, 0.05, 0.10).

	Lattice parameter (nm)	Theoretical density (g/cm^3)	Archimedes' density (g/cm^3)	Relative density (%)
$x = 0$	1.0801	6.035	6.04 ± 0.02	100
$x = 0.02$(In)	1.0795	$6.033 \sim 6.050^a$	6.018 ± 0.005	>99.5
$x = 0.05$(In)	1.0797	$6.014 \sim 6.038^a$	6.01 ± 0.01	>99.5
$x = 0.10$(In)	1.0808	$5.971 \sim 6.054^a$	6.02 ± 0.01	>99.4
$x = 0.05$(Sc)	1.0779	$5.971 \sim 6.013^a$	6.00 ± 0.01	>99.8
$x = 0.05$(Y)	1.0780^b	6.016	6.01 ± 0.01^b	>99.9

[a]Lowest and highest density calculated from purely A-site (In^{3+}/Sc^{3+}-La^{3+}) and B-site (In^{3+}/Sc^{3+}-Zr^{4+}) substitutions, respectively.
[b]From Ref. 3.

TABLE II. Ionic conductivity measured at 823 K for In/Sc-La$_2$Zr$_2$O$_7$ pyrochlores in comparison with La$_2$Zr$_2$O$_7$ and (La$_{0.95}$Y$_{0.05}$)$_2$Zr$_2$O$_7$.

	La$_2$Zr$_2$O$_7$	(La$_{0.95}$Y$_{0.05}$)$_2$Zr$_2$O$_7$	$x=0.02$ (In)	$x=0.05$ (In)	$x=0.10$ (In)	$x=0.05$(Sc)
Ionic conductivity at 823 K ($\times 10^{-5}$ S/m)	0.430 ± 0.005	0.425 ± 0.013	0.519 ± 0.006	0.724 ± 0.008	1.937 ± 0.020	1.137 ± 0.018

increase of electrical conductivity of In/Sc-La$_2$Zr$_2$O$_7$ pyrochlores (see Table II) from ac impedance spectroscopy measurements at 823 K. This is because, La$_2$Zr$_2$O$_7$ as an ionic conductor below 973 K,[13] electrical conduction is achieved by an oxygen vacancy hopping mechanism,[14] and hence a higher vacancy concentration favours a higher ionic conductivity. Therefore, In/Sc can substitute both La^{3+} on A-sites and Zr^{4+} on B-sites and the general formula can be represented as: $(La_{1-x_1}R_{x_1})_2(Zr_{1-x_2}R_{x_2})_2O_{7-x_2}$ (R = In, Sc).

Thermal conductivity of In/Sc-La$_2$Zr$_2$O$_7$ solid solutions is obtained according to

$$k = \rho \cdot C_p \cdot D. \tag{3}$$

Fig. 3 gives k-T curves of In/Sc-La$_2$Zr$_2$O$_7$ solid solutions, ZrO$_2$, yttria-stabilized zirconia (YSZ), Ba$_2$ErAlO$_5$, and La$_2$Mo$_2$O$_9$. Some of the curves are labeled by the lattice oxygen vacancy concentration [V$_O$], a ratio of all oxygen vacancies present on the basis of charge neutrality divided by all atomic sites in the lattice. For example, the proportions of vacant positions in oxygen sub-lattice ($\frac{1}{8}$, $\frac{1}{6}$, and $\frac{1}{4}$ for La$_2$Zr$_2$O$_7$,[3] Ba$_2$ErAlO$_5$,[15] and La$_2$Mo$_2$O$_9$, respectively) multiplying by anionic proportions per unit formula, can get the corresponding [V$_O$] values shown in Fig. 3. Here we find [V$_O$] determines $k_{\min}$: (1) $k_{\min}$ decreases consistently with an increase of [V$_O$] from 0 (ZrO$_2$),[16] 0.010 (3YSZ, (Y$_2$O$_3$)$_{0.03}$(ZrO$_2$)$_{0.97}$),[17] 0.014 (4.4YSZ, (Y$_2$O$_3$)$_{0.044}$(ZrO$_2$)$_{0.956}$),[16] to 0.083 (Y$_2$Zr$_2$O$_7$, La$_2$Zr$_2$O$_7$),[3] 0.1 (Ba$_2$ErAlO$_5$),[15] and 0.188 (La$_2$Mo$_2$O$_9$);[18] (2) For compounds with approximately similar [V$_O$] (around 0.083 for In, Sc, or Y lightly doped La$_2$Zr$_2$O$_7$ pyrochlores, their undoped counterpart, and Y$_2$Zr$_2$O$_7$ fluorite), they appear to exhibit similar $k_{\min}$, no matter what structures they possess: pyrochlore or fluorite, ordered or disordered (for Y$_2$Zr$_2$O$_7$) oxygen vacancies, and the presence or absence of rattlers. For In-La$_2$Zr$_2$O$_7$ (Fig. 3(b)), with an increase of x from 0.02, 0.05 to 0.10, k-T exhibit a slight decreasing trend as a result of extra oxygen vacancies generated by In^{3+}-Zr^{4+} inter-substitution. By contrast, presence of rattlers, unlike oxygen vacancies, tends to dramatically flatten the k-T curves. For those solid solutions with the same doping content ($x=0.05$ for Y, In, Sc, Fig. 3(b)), smaller rattlers show a greater capacity on driving k glass-like (i.e., enhanced rattling effect), particularly when considering that not all dopant cations act as rattlers. However, the stronger rattlers still have little influence on reducing $k_{\min}$.

By combining Eqs. (1) and (2) and noticing the same order of a and Λ_0, we can obtain

$$k_{\min} = \xi' \sqrt{\frac{E}{a\bar{M}\gamma}}, \tag{4}$$

where $\bar{M}$ is average atomic weight ($\rho = \bar{M}/a^3$). Eq. (4) suggests that $k_{\min}$ can be achieved by lowering the bonding

strength E, or raising the average atomic volume (a^3) or mass ($\bar{M}$), or increasing Grüneisen parameter (γ). Table III lists parameters relating to Eq. (4), and Fig. 4(a) gives both Young's modulus and Grüneisen parameter as function of oxygen vacancy concentration. As shown in Table III, for different compounds, the adjustable ranges of a and $\bar{M}$ are relatively small. However, an increase of the oxygen vacancy concentration [V$_O$] in the lattice results in an almost linear decrease/increase of E/γ (see Fig. 4(a)), which can explain the reason why [V$_O$] is the determinant of $k_{\min}$. Fig. 4(b) gives the linear regression of $k_{\min}$ against $\sqrt{E/a\bar{M}\gamma}$ for
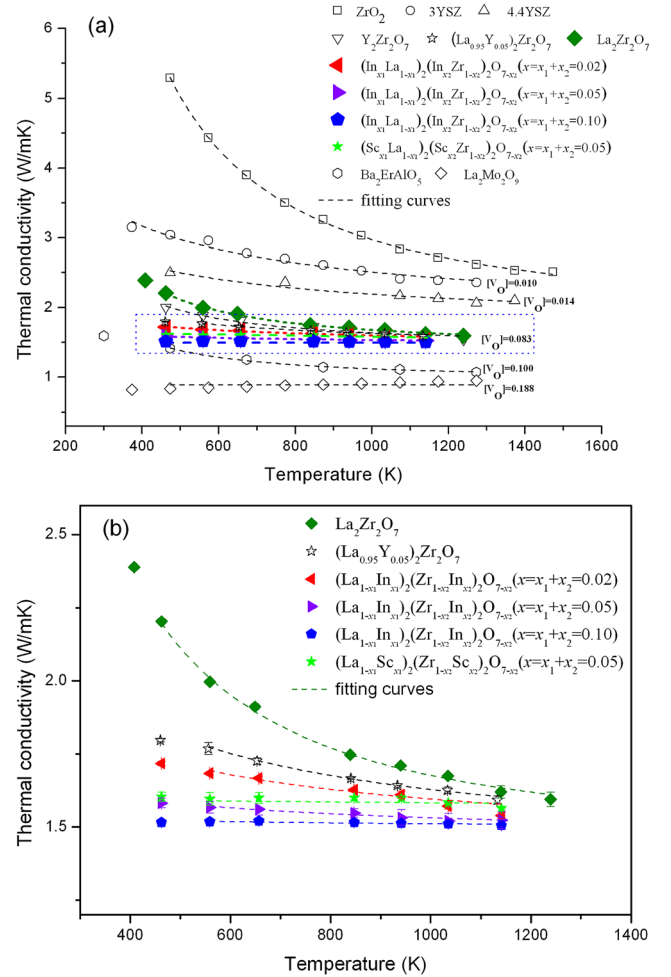

FIG. 3. (a) Thermal conductivity–temperature (k-T) curves of In/Sc-La$_2$Zr$_2$O$_7$ pyrochlore solid solutions in comparison with compounds with varied levels of oxygen vacancy concentration [V$_O$] (b) enlarged plot of k-T curves of the rectangular area in (a). Solid symbols refer to measured values in this study while hollow symbols represent those extracted from references. All values represent the k of a fully dense material. The dashed lines are fitted based on the measured k according to Eq. (4) in Ref. 3. In (a), $k_{\min}$ decreases steadily with an increase of [V$_O$] and $k_{\min}$ appears to be similar for compounds with similar [V$_O$]. (b) Smaller rattlers have a stronger capacity on flattening the k-T curves.

TABLE III. Average atomic mass ($\bar{M}$) and volume (a^3), Grüneisen parameter (γ), and elastic modulus (E) of compounds with different oxygen vacancy concentrations [V_O] in the lattice.

	$\bar{M}$ ($\times 10^{-26}$ kg)	a (nm)	γ	[V_O]	E (GPa)
ZrO_2	6.85	0.225[a]	1.37[g]	0	
3YSZ	6.85	0.225[b]	1.39[h]	0.010	220 ± 10[k]
4.4YSZ	6.87	0.225[c]	1.40[g]	0.014	
$La_2Zr_2O_7$	8.64	0.243	2.07[d]	0.083	180 ± 2[d]
$Y_2Zr_2O_7$	7.13	0.234[d]	2.08[d]	0.083	155 ± 5[d]
$x = 0.02$(In)	~8.64	0.243	~2.07	~0.083	175 ± 2[l]
$x = 0.05$(In)	~8.60	0.243	~2.07	~0.083	169 ± 4[l]
$x = 0.10$(In)	~8.57	0.243	~2.07	~0.083	165 ± 3[l]
$x = 0.05$(Sc)	~8.54	0.242	~2.07	~0.083	185 ± 2[l]
Ba_2ErAlO_5	10.13	~0.25[e]	~2.2[e]	0.100	109 ± 8[e]
$La_2Mo_2O_9$	7.84	0.243[f]	~2.6[i]	0.188	~70

[a]Ref. 19.
[b]Ref. 20.
[c]Ref. 21.
[d]Ref. 3.
[e]Ref. 20.
[f]Ref. 21.
[g]Ref. 18.
[h]Ref. 19.
[i]estimated.
[k]Refs. 22 and 23.
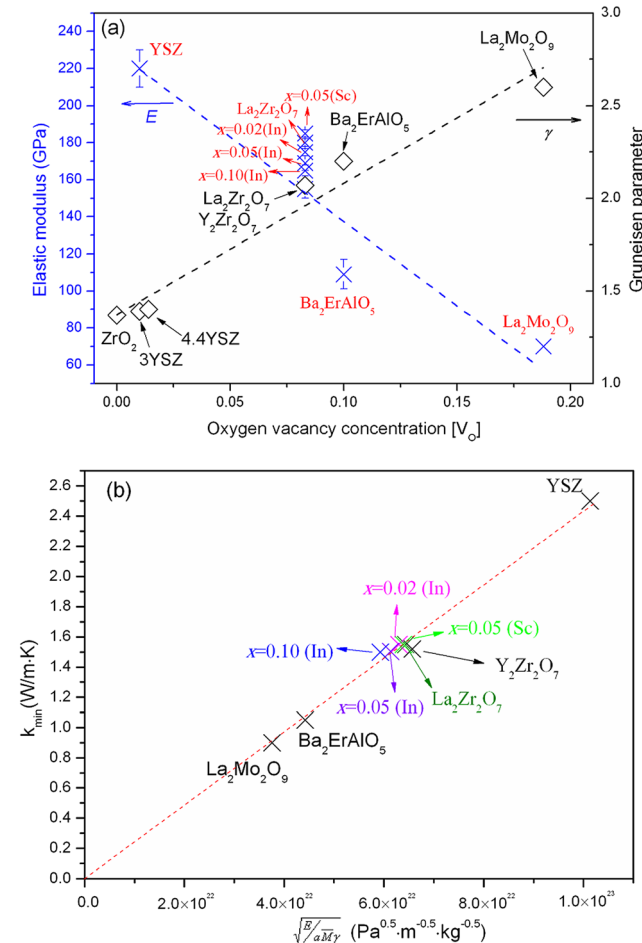[l]Measured in this study by micro-indentation.

FIG. 4. (a) The dependence of Young's modulus (E) and Grüneisen parameter (γ) on the oxygen vacancy concentration [V_O] and (b) the linear plot of $k_{\min}$ versus $\sqrt{E/a\bar{M}\gamma}$ for different materials.

different compounds, which yields ξ' in Eq. (4) around 2.43×10^{-23} m^2·kg·s^{-2}.

The increase of γ and the decrease of E by oxygen vacancies arise from an electrostatic repulsion force of exposed cations surrounding them, because the emergence of vacancies disrupts the alternation of anions and cations in the perfect ionic lattice and therefore leads to cations/anions exposed to each other around anionic/cationic vacancies. For a normal lattice, anharmonic cubic term of the inter-atomic potential energy expansion favors lattice expansion as if it generates a repulsive component of the lattice force. Conversely, the presence of any additional repulsion of the lattice force can in turn contribute to a stronger lattice anharmonicity, which is supported by the findings of Morelli and coworkers, who reported an anomalously large γ (strong anharmonicity) in cubic I-V-VI$_2$ semiconductors and attributed it to the electrostatic repulsion of lone-pair electrons.[24,25] As an analogy, we propose the electrostatic repulsive force of the exposed cations surrounding oxygen vacancies as the underlying reason for the strong anharmonicity at oxygen vacancy sites. As an evidence, Hayashi and co-workers found a steady increase of Grüneisen parameter in YSZ with an increase of the Y$_2$O$_3$ content, or essentially [V_O].[26] Similarly, it is understandable that the repulsive lattice force introduced by vacancies can reduce the bonding strength, since the lattice repulsion force arising from neighbouring cations/anions surrounding anionic/cationic vacancies offsets a certain attractive force, which defines the strength of bond.

The remaining question is why strong rattlers, despite their amazing capability of driving k glass-like, are still not able to reduce $k_{\min}$. The fact that rattlers are good at flattening the decreasing temperature dependence of k indicates that, according to $k = \frac{1}{3}C_v v\Lambda$, they are essentially affecting Λ, or precisely the mean free path due to phonon Umklapp scattering Λ_U, since the decreasing temperature dependence of k primarily originates from Λ_U. As shown in Eq. (5), the temperature independent rattler term becomes exceptionally large when the phonon frequency ω approaches the resonant frequency ω_{Ri}, and thus overshadows the Λ_U term[27–29]

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_U(\omega)} + \frac{1}{\Lambda_{rattler}(\omega)} = \frac{\omega^2 T}{D_U} + \sum_i \frac{C_i \omega^2}{(\omega_{Ri}^2 - \omega^2)^2}, \quad (5)$$

in which D_U and C_i are temperature independent constants.

Otherwise, if rattlers effectively decreased v by raising lattice anharmonicity, as suggested in Refs. 30 and 31, k would become consistently lower at all temperatures but show an evident temperature dependent trend, i.e., parallel k-T curves rather than flattened ones. However, at high temperatures, heat is conducted by high-frequency phonons which are insensitive to rattlers, since they tend to scatter low-frequency phonons.[8,32] Therefore, rattlers are not effective, at least not as oxygen vacancies are, in raising lattice anharmonicity, and thus have little influence on $k_{\min}$.

In summary, we have revealed the importance of rattlers and their size effect on heat transport. Smaller In^{3+}/Sc^{3+} rattlers, residing in the oversized atomic AO$_8$ cages, make k of In/Sc-La$_2$Zr$_2$O$_7$ pyrochlores glass-like at an amazingly low doping content ($x = 0.05$) but still show no significant

decrease of k_{min}. By contrast, oxygen vacancies, generated by In^{3+}/Sc^{3+} substituting Zr^{4+} on B-sites, are very powerful in reducing k_{min}, especially by enumerating compounds with a wide range of oxygen vacancy concentration $[V_O]$. We have found that k_{min} decreases steadily with an increase of $[V_O]$, whereas, k_{min} is almost identical at a given $[V_O]$, with any structure details irrelevant. The underlying reason has been suggested that the electrostatic repulsive force of cations surrounding oxygen vacancies leads to stronger lattice anharmonicity as well as weaker atomic bonds. To lower k_{min}, we suggest introducing a repulsion component of the lattice force, such as with vacancies, interstitials, etc.

[1]N. P. Padture, M. Gell, and E. H. Jordan, Science **296**, 280 (2002).

[2]D. R. Clarke, Surf. Coat. Technol. **163–164**, 67 (2003).

[3]Y. Wang, F. Yang, and P. Xiao, Acta Mater. **60**, 7024 (2012).

[4]D. S. Sanditov, V. V. Mantatov, M. V. Darmaev, and B. D. Sanditov, Tech. Phys. **54**, 385 (2009).

[5]O. L. Anderson, Phys. Rev. **144**, 553 (1966).

[6]M. Christensen, A. B. Abrahamsen, N. B. Christensen, F. Juranyi, N. H. Andersen, K. Lefmann, J. Andreasson, C. R. H. Bahl, and B. B. Iversen, Nat. Mater. **7**, 811 (2008).

[7]B. C. Sales, D. Mandrus, and R. K. Williams, Science **272**, 1325 (1996).

[8]G. S. Nolas, M. Kaeser, R. T. Littleton IV, and T. M. Tritt, Appl. Phys. Lett. **77**, 1855 (2000).

[9]G. S. Nolas, J. L. Cohn, G. A. Slack, and S. B. Schujman, Appl. Phys. Lett. **73**, 178 (1998).

[10]G. S. Nolas and G. A. Slack, Am. Sci. **89**(2), 136 (2001).

[11]C. Wan, W. Zhang, Y. Wang, Z. Qu, A. Du, R. Wu, and W. Pan, Acta Mater. **58**, 6166 (2010).

[12]R. D. Shannon, Acta Cryst. A **32**, 751 (1976).

[13]J. A. Labrincha, J. R. Frade, and F. M. B. Marques, J. Mater. Sci. **28**, 3809 (1993).

[14]P. J. Wilde and C. R. A. Catlow, Solid State Ionics **112**, 173 (1998).

[15]C. L. Wan, Z. X. Qu, Y. He, D. Luan and W. Pan, Phys. Rev. Lett. **101**, 085901 (2008).

[16]R. Mevrel, J.-C. Laizet, A. Azzopardi, B. Leclercq, M. Poulain, O. Lavigne, and D. Demange, J. Eur. Ceram. Soc. **24**, 3081 (2004).

[17]K. W. Schlichting, N. P. Padture, and P. G. Klemens, J. Mater.Sci. **36**, 3003 (2001).

[18]M. R. Winter and D. R. Clarke, J. Am. Ceram. Soc. **90**, 533 (2007).

[19]F. Yang, X. F. Zhao, and P. Xiao, Acta Mater. **60**, 914 (2012).

[20]U. Martin, H. Boysen, and F. Frey, Acta Crystallogr. B **49**, 403 (1993).

[21]J. A. Krogstad, M. Lepple, Y. Gao, D. M. Lipkin, and C. G. Levi, J. Am. Ceram. Soc. **94**, 4548 (2011).

[22]S. Giraud and J. Canel, J. Eur. Ceram. Soc. **28**, 77 (2008).

[23]R. Vassen, X. Q. Cao, F. Tietz, D. Basu, and D. Stover, J. Am. Ceram. Soc. **83**, 2023 (2000).

[24]D. T. Morelli, V. Jovovic, and J. P. Heremans, Phys. Rev. Lett. **101**, 035901 (2008).

[25]E. J. Skoug and D. T. Morelli, Phys. Rev. Lett. **107**, 235901 (2011).

[26]H. Hayashi, T. Saitou, N. Maruyama, K. Inaba, K. Kawamura, and M. Mori, Solid State Ionics **176**, 613 (2005).

[27]Y. G. Wang, X. F. Xu, and J. H. Yang, Phys. Rev. Lett. **102**, 175508 (2009).

[28]G. S. Nolas, J. L. Cohn, B. C. Chakoumakos, and G. A. Slack, *Proceedings of the 25th International Thermal Conductivity Conference*, edited by C. Uher and D. T. Morelli (Technomic Publishing Co., Lancaster, PA, 2000), p. 122.

[29]X. Shi, H. Kong, C.-P. Li, C. Uher, J. Yang, J. R. Salvador, H. Wang, L. Chen, and W. Zhang, Appl. Phys. Lett. **92**, 182101 (2008).

[30]J. S. Tse, D. D. Klug, J. Y. Zhao, W. Sturhahn, E. E. Alp, J. Baumert, C. Gutt, M. R. Johnson, and W. Press, Nat. Mater. **4**, 917 (2005).

[31]O. Delaire, J. Ma, K. Marty, A. F. May, M. A. McGuire, M. H. Du, D. J. Singh, A. Podlesnyak, G. Ehlers, M. D. Lumsden, and B. C. Sales, Nat. Mater. **10**, 614 (2011).

[32]J. S. Tse, V. P. Shpakov, V. R. Belosludov, F. Trouw, Y. P. Handa, and W. Press, Europhys. Lett. **54**, 354 (2001).