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Inorganic crystals with glass-like and ultralow thermal conductivities

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Abstract:	<p>The ability to control the transport of thermal energy is critical in a wide variety of technologies. At the same time, understanding the underlying microscopic mechanisms of thermal transport in solids continues to be a central goal of condensed matter and materials physics, with many persistent challenges and unanswered questions. One of the remarkable findings has been the observation that some crystalline materials have very low, glass-like thermal conductivities despite long-range order in the arrangement of the atoms in their structure. Although examples with such unusual behavior were initially rare, the number of crystalline materials known to have glass-like thermal conductivities has grown significantly in the past two decades. Moreover, some fully dense inorganic solids have recently been discovered that possess ultralow thermal conductivities below the so-called glass limit. In this review, we use several specific examples to highlight the salient structural and lattice dynamical features of these intriguing "glass-like crystals," focusing on current understanding of the microscopic mechanisms that cause these crystals to conduct heat like a glass. The study of such materials continues to push our understanding of heat transport in solids and the roles that chemical bonding and structural order and disorder play in thermal transport processes.</p>
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Please submit a plain text version of your cover letter here. Please note, if you are submitting a revision of your manuscript, there is an opportunity for you to provide your responses to the reviewers later; please do not add them to the cover letter.	Prof. Dr. Wolfgang Neumann Editor-in-Chief, Crystal Research and Technology Humboldt-Universität zu Berlin Institut für Physik - Kristallographie Newtonstr. 15 12489 Berlin, Germany Dear Prof. Dr. Neumann: Thank you again for the invitation to contribute to the special issue of Crystal Research and Technology dedicated to the occasion of Prof. David C. Johnson's 60th birthday. It

	<p>is our pleasure to submit our manuscript, "Inorganic crystals with glass-like and ultralow thermal conductivities," for your consideration.</p> <p>Our manuscript provides an overview of current understanding of the structures and lattice dynamics of a fascinating yet still relatively poorly understood group of materials, namely those crystalline materials that exhibit thermal transport properties that are more representative of amorphous solids. Following a brief introduction to the characteristic features of typical crystals and glasses, we examine a number of specific examples of crystals with glass-like thermal conductivities, highlighting what is known thus far about the mechanisms that might be at the root of their unusual properties as well as areas where the understanding remains underdeveloped. Given the current interest in these materials in very active fields such as thermal barrier coating and thermoelectric materials research, we believe our review is timely and will be appreciated by your journal's readership.</p> <p>Thank you again and we look forward to receiving the reviewers' feedback on our paper.</p> <p>Sincerely,</p> <p>Matt Beekman, Ph.D. Assistant Professor Department of Physics California Polytechnic State University San Luis Obispo, CA 93407 Tel: (805) 756-7129 Email: mbeekman@calpoly.edu</p>
<p>Do you or any of your co-authors have a conflict of interest to declare?</p>	<p>No. The authors declare no conflict of interest.</p>

Inorganic crystals with glass-like and ultralow thermal conductivities

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The ability to control the transport of thermal energy is critical in a wide variety of technologies. At the same time, understanding the underlying microscopic mechanisms of thermal transport in solids continues to be a central goal of condensed matter and materials physics, with many persistent challenges and unanswered questions. One of the remarkable findings has been the observation that some crystalline materials have very low, glass-like thermal conductivities despite long-range order in the arrangement of the atoms in their structure. Although examples with such unusual behavior were initially rare, the number of crystalline materials known to have glass-like thermal conductivities has grown significantly in the past two decades. Moreover, some fully dense inorganic solids have recently been discovered that possess ultralow thermal conductivities below the so-called glass limit. In this review, we use several specific examples to highlight the salient structural and lattice dynamical features of these intriguing “glass-like crystals,” focusing on current understanding of the microscopic mechanisms that cause these crystals to conduct heat like a glass. The study of such materials continues to push our understanding of heat transport in solids and the roles that chemical bonding and structural order and disorder play in thermal transport processes.

1 Introduction

One of the defining characteristics that differentiates a crystal from a glass is the microscopic arrangement of the constituent atoms of the material: the periodic arrangement of atoms in conventional crystals possesses translational and rotational symmetries that result in long-range order that is lacking in the amorphous arrangement of atoms in a glass [1]. The mechanical, electrical, and thermal properties of these two types of materials are often strikingly different, a direct consequence of the ordered versus disordered arrangement of the atoms. This is especially true of thermal conductivity, a ubiquitous materials property that plays a key role in diverse technological applications such as thermal barrier coatings, thermoelectric energy conversion, thermal management in integrated circuits, and heat transfer in buildings [2-4]. The majority of crystalline solids have relatively high thermal conductivities, whereas non-metallic amorphous solids, or glasses, typically have very low thermal conductivities, with a very different temperature dependence as well [5].

Although there can exist a variety of carriers of heat in solids, including less common carriers such as photons and magnons [6], in most materials at ordinary temperatures thermal conduction is dominated by electronic charge carrier and/or lattice vibration contributions [7, 8]. For many applications, including

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thermoelectric energy conversion and thermal barrier coatings in high temperature gas turbines, crystalline materials are the best candidates due to the need for stability at high temperature and/or the simultaneous need for specific electrical properties such as high charge carrier mobility. At the same time, in applications such as thermal barrier coatings in gas turbines and thermoelectric energy conversion, irreversible heat conduction limits efficiency, thus the constituent materials need to have thermal conductivity values that are as low as possible [2, 3]. For these reasons, significant effort in materials research has focused on understanding and reducing the lattice component of thermal conductivity, resulting in gains in materials performance and a continually improving understanding of thermal transport in crystals [9, 10, 11].

One of the products of research in this area has been the observation that a variety of *crystalline* solids have lattice thermal conductivities that are unusually low, mimicking those of *glasses* in both magnitude and temperature dependence [12]. Beyond just satisfying scientific curiosity, a better understanding of this surprising behavior has the potential to improve energy conversion efficiency and positively impact a number of technologies, including those mentioned above. This paper provides an overview of inorganic crystalline materials that have glass-like thermal conductivities, in particular thermal conductivities that are near (or even below) the respective theoretical minimum for the material and exhibit the characteristic temperature dependence of a glass. We highlight the current understanding of the mechanisms underlying the atypical behavior in these materials, as well as existing gaps in our understanding of these intriguing phenomena.

2 Lattice vibrations, heat transport in solids, and the glass limit

Transport of thermal energy through atomic vibrations is present in all solids. In crystals, these vibrations are typically well described by collective normal mode excitations that behave as traveling waves propagating through the crystal, which can simultaneously be treated as quantum mechanical quasiparticles called phonons [7]. The phonon model continues to be highly successful in describing the lattice dynamics and heat transport in crystals [5-14]. Treating phonons as a gas, a relatively simple expression for the thermal conductivity can be derived from ki-

netic theory, providing a useful model for thinking about heat transport by phonons [8]:

$$\kappa_L = \frac{1}{3} \int C(\omega)v(\omega)l(\omega)d\omega \quad (1)$$

Here $C(\omega)$ is the spectral phonon heat capacity (heat capacity per frequency), $v(\omega)$ is the phonon group velocity, $l(\omega)$ is the mean free path for the phonon of frequency ω , i.e. the average length between scattering events, and the sum is over the entire phonon spectrum. In general, C , l , and v are all dependent on frequency, thus different phonons with different frequencies ω contribute to the thermal conductivity by different amounts. The total thermal conductivity is the sum of all of these individual contributions. Phonon scattering tends to restore the phonon occupation back to its local thermal equilibrium distribution, and in effect reduces l and the corresponding heat current [14].

While a variety of different phonon scattering mechanisms may be present to different extents in a given material, two mechanisms are present in *all* crystalline materials. At high temperatures, the scattering of phonons by other phonons in three-phonon resistive processes, known as anharmonic or Umklapp scattering, becomes increasingly important as the temperature increases and more phonons with larger wave vectors are excited [7]. At the same time, the heat capacity of the quantum mechanical phonon gas approaches the classical limit, and the specific heat approaches the constant Dulong-Petite value, independent of temperature. The net result is that κ_L decreases rapidly as T increases, typically with $\kappa_L \propto T^{-1}$ [7]. At low temperatures, phonon-phonon Umklapp scattering decreases with decreasing temperature, and eventually the mean free path l approaches the macroscopic length of the crystal (or crystallite in polycrystalline materials) for those phonons carrying most of the heat. The thermal conductivity is then approximately proportional to the specific heat, so that at low temperatures $\kappa_L \propto T^3$ for most crystals [7]. The resulting “peak-shaped” temperature profile of κ_L for crystalline SiO₂ (α -quartz) shown in Fig. 1 is typical for a crystal, with the height of the peak typically determined by defect levels [8].

In contrast, the magnitude and temperature dependence of the thermal conductivity of the amorphous state of SiO₂ (vitreous silica, also shown in Fig. 1) is quite different. The thermal conductivity is much lower over the entire temperature range, shows no pronounced peak, exhibits an approximately $\kappa_L \propto T^2$ dependence at very low temperatures, a plateau near 10 K, and has relatively weak dependence on temper-

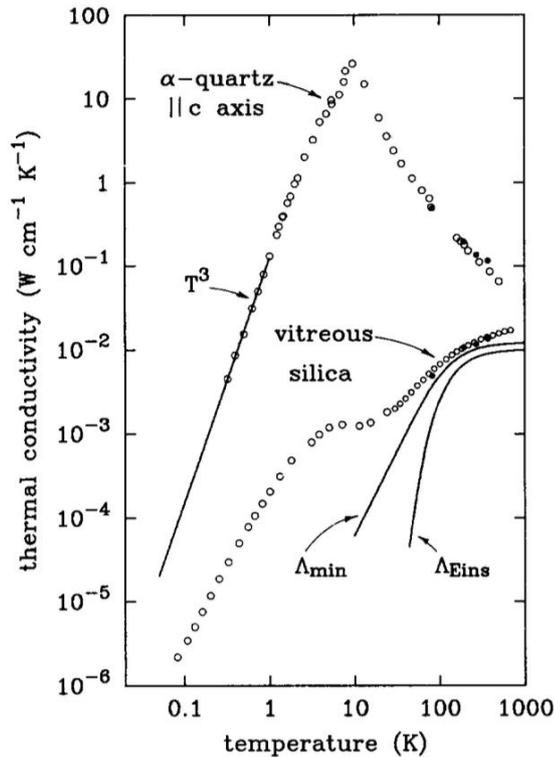


Figure 1 Thermal conductivity of crystalline (α -quartz) and amorphous (vitreous silica) SiO_2 as a function of temperature. Since both materials are electrical insulators, the total thermal conductivity is essentially equal to the lattice thermal conductivity. Also shown are the minimum thermal conductivity and thermal conductivity calculated by the “unmodified” Einstein model. Reprinted from Ref. 15, Copyright 1989, with permission from Elsevier.

ature near room temperature. A generally similar temperature dependence of κ_L is observed in nearly all other dielectric glasses, suggesting universal underlying phenomena that continue to be a very active topic of investigation [16-21]. The approximately T^2 dependence at low temperature and has been attributed to scattering of long wavelength vibrational modes by multi-level tunnel systems produced by the tunneling of atoms, groups of atoms, and/or electrons in the glass [16], though the exact nature of these states is arguably still not well understood and this picture has also recently been challenged [22]. The plateau near 10 K suggests a temperature regime in which the product of the average mean free path of the dominant heat carrying phonons and the heat capacity is constant, and has been attributed to Rayleigh-type scattering originating in the atomic scale positional disorder of the atoms [23].

Above the plateau ($T > 20$ K), the significant difference between the thermal conductivity of a crystal

and a glass can be understood using a model that historically preceded the phonon model. More than a century ago and only a few years before the periodic arrangement of atoms in crystals was experimentally elucidated by X-ray diffraction, Einstein made the first attempt at a quantum mechanical model of atomic vibrations in a solid [24]. His model assumed each atom in a crystal behaves as a quantum harmonic oscillator with the same vibrational frequency, with no phase coherence between oscillators. In applying his model to the problem of the thermal conductivity of crystals, Einstein included coupling of each oscillator to 24 nearest neighbors to maximize energy transfer, but his model nevertheless grossly under predicted the thermal conductivity for crystals [24]. The two key shortcomings in applying Einstein’s model to crystals were the assumptions that the oscillators all vibrate with the same frequency and that the oscillations were all independent, in stark contrast to the subsequently more successful phonon model that assumes collective motion of the atoms in delocalized waves. However, his model does produce relatively good agreement with the experimental data for glasses (see Fig. 1). Even better agreement is achieved if, instead of treating each individual atom as the oscillating entity with a single frequency, groups of atoms with a variety of frequencies are considered to be the oscillating entities [15]. In this picture, thermal energy diffuses through the solids *via* a random walk between localized oscillators, which is much less efficient than transport by the extended wavelike phonon excitations in crystals [12, 15]. The difference in magnitude and temperature dependence of the lattice thermal conductivity for crystals and glasses can therefore be understood.

The thermal conductivity predicted by the “modified” Einstein model for a given material has been termed the “minimum thermal conductivity,” “amorphous limit,” or “glass limit” [12]. It can also be derived from Eq. 1 by assuming that each phonon experiences such strong scattering that its mean free path is reduced to half of its wavelength, at which point the phonon concept itself begins to lose meaning [12, 25]. Such models provide one possible answer to a long-standing question: What is the lower limit to the thermal conductivity of a solid? The answer to this question of course has important implications for performance limitations in technologies such as thermoelectric energy conversion [26]. As shown in Figs. 1 and 2, the relatively simple modified Einstein model predicts the high temperature thermal conductivity of amorphous solids relatively well, providing both a physical picture for the atomic vibrations and

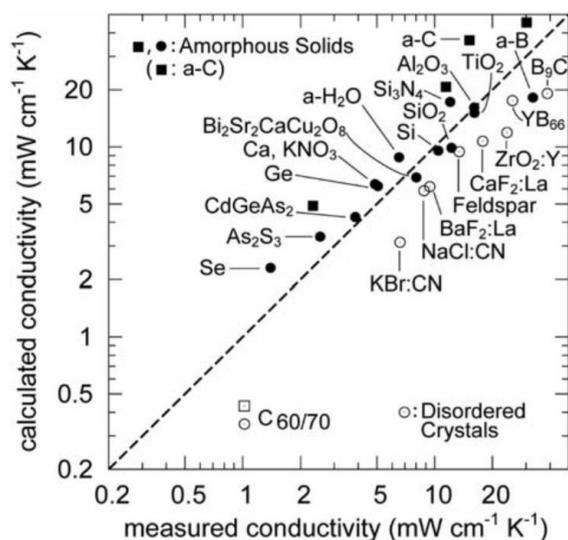


Figure 2 Thermal conductivity of various amorphous solids (closed symbols) and disordered crystals (open symbols) vs. the experimentally measured thermal conductivity for the same materials. Reprinted from Ref. 27, Copyright 2006, with permission from Elsevier.

thermal transport processes in glasses and an estimate of the minimum achievable thermal conductivity for a solid of given composition and density [12].

Remarkably, although most crystals have relatively high lattice thermal conductivities with the characteristic temperature dependence shown in Fig. 1, some crystalline materials have thermal conductivities that are actually more characteristic of a glass, both in magnitude and temperature dependence. In the following sections, we review some specific examples of such crystalline materials (Fig. 3), as well as the current understanding of the mechanisms and features that appear to be linked to this unusual behavior. We first examine how the introduction of certain types of *extrinsic* structural disorder, i.e. defects, into a crystalline material can transform its thermal conductivity from crystalline to glass-like. We then consider how some structural and lattice dynamical features that are *intrinsic* to some crystals, including low energy vibrational modes and pronounced anharmonicity, can apparently produce glass-like thermal conductivity in a crystal “naturally.” Finally, we conclude with a look at several unconventional crystals, including aperiodic crystals and so-called “ferre-crystals,” the lattice dynamics of which still remain poorly understood.

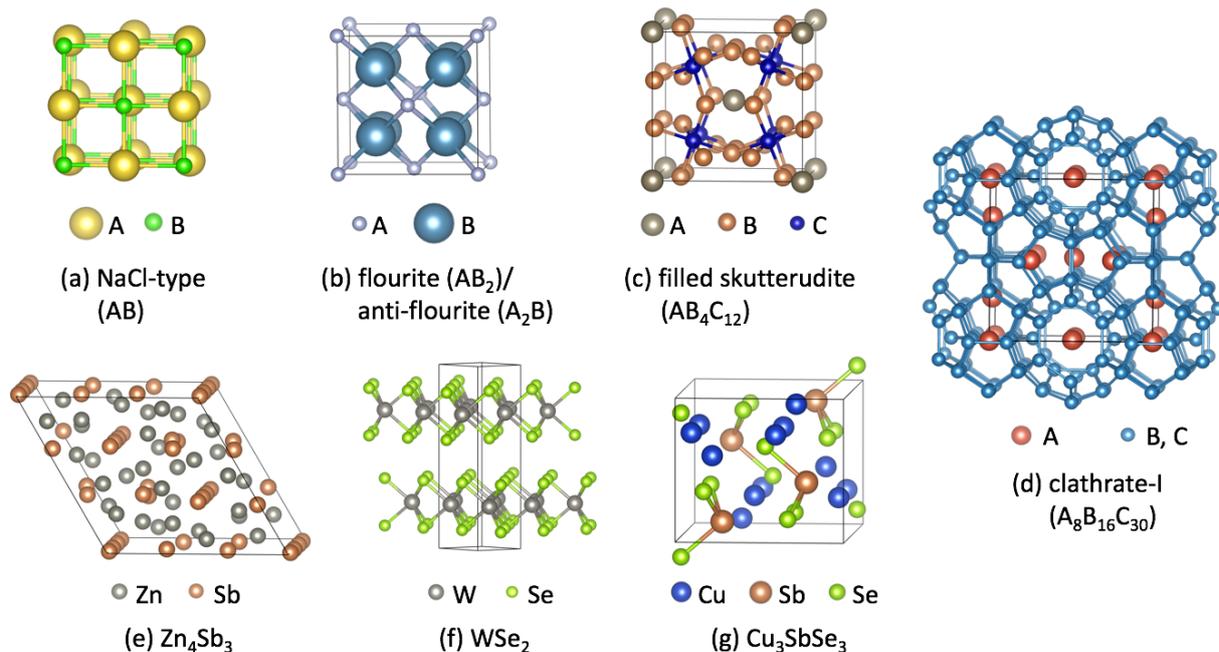


Figure 3 Selected examples of crystals with very low or glass-like lattice thermal conductivity: (a) NaCl-type solid solutions with alkali cyanides, (b) fluorite and antifluorite crystals with vacancies or interstitials (not shown), (c) filled skutterudites (A = filler atom), (d) intermetallic clathrates with “rattling” guest atoms (A = guest atom), (e) Zn_4Sb_3 (interstitial sites not shown), (f) highly anisotropic, layered WSe_2 , and (g) Cu_3SbSe_3 with stereochemically active lone pair electrons.

3 Extrinsic structural disorder in crystals

Structural disorder in crystalline materials can be broadly separated into two major classes: static disorder and dynamic disorder. The term “static” refers to some type of compositional or structural disorder that reduces long-range order in the crystal. The term “dynamic” refers to the presence of some feature of the system involving atomic motions that impedes thermal transport, often through the efficient scattering of the heat carrying acoustic phonons. Both types can have significant effects on the phonon vibrational spectrum and phonon scattering, and both types can sometimes be present simultaneously and interrelated. We illustrate this first with a structurally simple example: crystals with the NaCl structure type (Fig. 3a).

The simplest way to introduce static structural disorder in a crystal is by substitution of one constituent by another to form an alloy or solid solution. The mechanisms by which this alteration of the structure impacts the thermal conductivity of crystals are relatively well understood [6, 8, 13]. In forming $(\text{KCl})_{1-x}(\text{KBr})_x$ solid solutions between KCl and KBr, the larger, more massive Br replaces Cl in the structure. This type of random site substitution generally produces phonon scattering by mass fluctuations due to the mass difference between the atoms, as well as local strain and stress due to the difference in ionic radius and chemical bonding [6, 8, 13]. Presuming complete solubility, the effect on phonon scattering is often most pronounced near 50% substitution, corresponding to the most “disordered” composition. As shown in Fig. 4, the peak thermal conductivity value of the KCl crystal is reduced by more than one order of magnitude when $x \sim 0.5$ [12]. Although alloy site substitution can significantly lower the lattice thermal conductivity, simple isoelectronic solid solutions do not typically reduce thermal conductivities to values anywhere near the glass limit, and the lattice thermal conductivity usually retains the typical crystalline temperature dependence.

Thermal conductivities that approach the glass limit can, however, be obtained in other types of solid solutions. We again use the rock salt structure as an example. In $(\text{KBr})_{1-x}(\text{KCN})_x$, the diatomic CN^- anion replaces the Br^- anion. Although the crystal chemistry of the host structure is very similar to the preceding example, the resulting effect on the thermal conductivity is very different: as shown in Fig. 5, the thermal conductivity in this case is glass-like with a similar magnitude and temperature profile as vitreous silica [12]. Since the elongated CN^- is oriented along the $\langle 111 \rangle$ direction in the face-center cubic KBr structure,

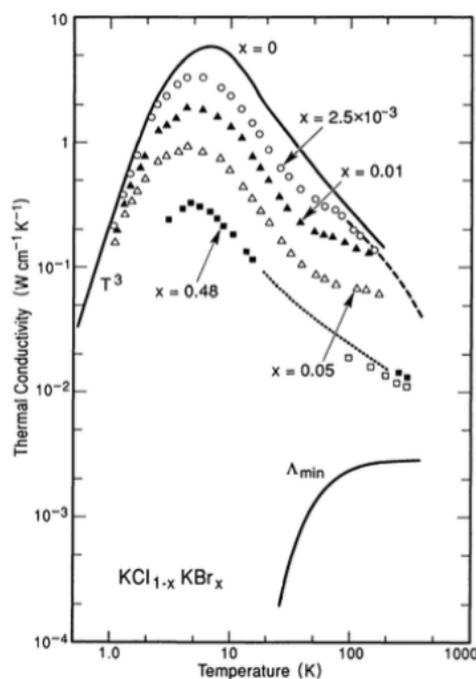


Figure 4 Thermal conductivity of $(\text{KCl})_{1-x}(\text{KBr})_x$ solid solutions. The calculated minimum thermal conductivity for KCl is also shown. Isoelectronic substitution significantly reduces the thermal conductivity, yet it remains much higher than the glass limit and retains the typical crystalline temperature dependence. Reprinted with permission from Ref. 12. Copyright 1992 by the American Physical Society.

there are eight symmetrically equivalent orientations available. At sufficiently low temperatures, the CN^- molecule can therefore quantum mechanically tunnel between these eight orientations, producing a tunnel splitting in the librational energy levels [28]. Presumably, the heat carrying acoustic phonons of the KBr host lattice are resonantly scattered by these tunnel states, which behave similarly to the tunneling states in a glass and produces the T^2 dependence at low T . At higher temperatures, the random local stresses associated with the substitution of the elongated CN^- for Br^- presumably produce lattice vibrations that are in some ways glass-like [27]. Note that, as illustrated in Fig. 5, doubling the KCN content from $x \sim 0.2$ to $x \sim 0.4$ does not appreciably affect the thermal conductivity, which is glass-like in both cases.

It is also possible to achieve glass-like thermal conductivity in solid solutions by introducing static disorder by the creation of vacancies and/or interstitial atoms. Examples are found in the fluorite and anti-fluorite structures (Fig. 3b). The glass-like thermal conductivity of the well-known thermal barrier coating material yttrium stabilized zirconia ($\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-x/2}$

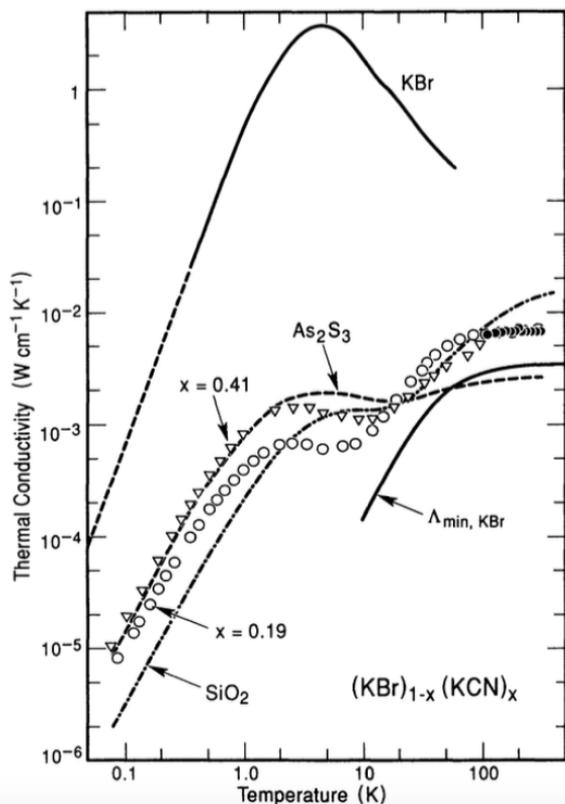


Figure 5 Thermal conductivity of $(\text{KBr})_{1-x}(\text{KCN})_x$, as well as amorphous SiO_2 and As_2S_3 . The calculated minimum thermal conductivity for KBr is also shown. Reprinted with permission from Ref. 12. Copyright 1992 by the American Physical Society.

or YSZ) with the fluorite structure has been attributed to the presence of oxygen vacancies (B atom sites in Figure 3b) [29]. Substitution of two Y^{3+} for two Zr^{4+} in the structure is charge balanced by the formation of one oxygen vacancy. The thermal conductivity of crystalline YSZ is low with the characteristic temperature dependence of a glass [12, 29]. In $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$, which also crystallizes in the fluorite structure, substitution of each La^{3+} for Ba^{2+} introduces one interstitial F^- , which again can be rationalized by simple charge balance considerations. Unlike YSZ, which is not stable at low Y content, the evolution of the thermal conductivity from crystalline to glass-like can be observed in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ as the concentration of La^{3+} and accompanying interstitial fluorine increases [12]. As shown in Fig. 6, the effect is again much more dramatic than isoelectronic substitution. Similar effects have also been observed in anti-fluorite crystals such as Mg_2Si , where substitution of Sb for Si in high concentrations produces a large concentration of Mg vacancies and nearly glass-like thermal conductivity [30]. The introduction of vacancies and interstitial at-

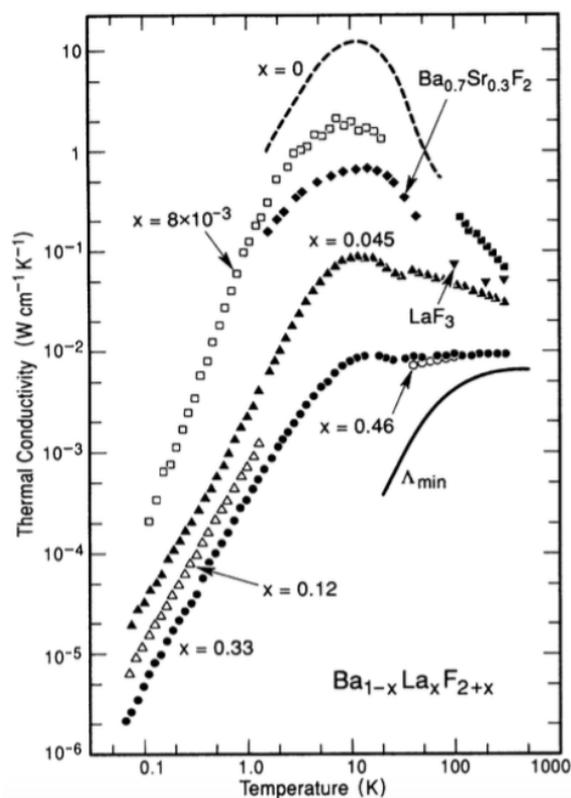


Figure 6 Thermal conductivity of $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$, illustrating the evolution from crystalline to glass-like thermal transport as the concentration of La is increased. Also shown is the thermal conductivity of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{F}_2$, an isoelectronic solid solution, and the minimum thermal conductivity for BaF_2 . Reprinted with permission from Ref. 12. Copyright 1992 by the American Physical Society.

oms in these and related materials presumably also produces random stresses throughout the crystal. The chemical disorder and random stresses in turn may induce lattice vibrations that are similar to those in a glass [27]. This contrasts with simple atomic site substitution, which can be viewed as a perturbation to the lattice dynamics of the parent crystal.

Static and dynamic disorder can also be simultaneously introduced into a material in a controlled manner. The class of materials known as filled skutterudites provides a well-studied example. Originally proposed as a potential “phonon-glass electron-crystal” thermoelectric material system [26, 31], the lattice dynamical and thermal transport properties of filled skutterudites have received much attention [32–40]. The unfilled skutterudite crystal structure (Figure 3c), of which $\text{Co}_4\text{Sb}_{14}$ is the prototypical example, contains relatively large intrinsic voids that can either remain empty or be filled with a wide variety of elements [33]. Since the ionic radius of the filler is usual-

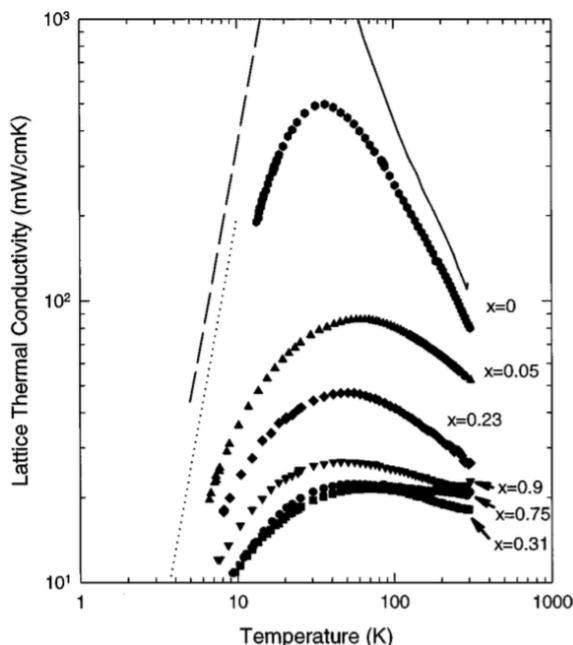


Figure 7 Effect of void filling on the lattice thermal conductivity of polycrystalline $\text{La}_x\text{Co}_4\text{Sn}_y\text{Sb}_{12-y}$ (Sn is added for charge compensation). The solid line shows experimental data for single crystal $\text{Co}_4\text{Sb}_{12}$. The dashed lines show calculated T^{-3} dependence of κ_L for grain sizes of 4 and 7 μm . Reprinted with permission from Ref. 37. Copyright 1998 by the American Physical Society.

ly significantly smaller than the effective radius of the cage, the “filler atoms” undergo large amplitude, low-energy vibrations, evidenced by a variety of crystallographic and spectroscopic techniques as well as *ab initio* calculations [32-40]. As shown in Figure 7, unfilled $\text{Co}_4\text{Sb}_{12}$ has a typical crystalline thermal conductivity. However, filling the voids with heavy La atoms dramatically reduces the lattice thermal conductivity over the entire temperature range and completely transforms the temperature dependence [37].

The dramatic effect of filling the voids on κ_L of skutterudites is often attributed to a resonant phonon scattering mechanism, whereby the heat carrying acoustic phonons of the host structure are scattered by the low energy “rattling” vibrational modes associated with the filler atoms [31-40], although this explanation has been challenged for some compositions [36]. The most dramatic reduction in κ_L occurs for partial filling of the voids [37, 38], an observation that can be relatively well described by a point defect scattering mechanism that is very effective due to extremely large mass difference between vacant and occupied voids [38]. Indeed, some analyses suggest this mechanism may actually be more significant than the resonant scattering mechanism [38, 39]. Although

the lattice thermal conductivity of some filled skutterudites approaches glass-like values and temperature dependence, we note that the thermal conductivity still retains some character of the conventional temperature dependence of a crystal with values still significantly above the glass limit, consistent with lattice dynamics that are not truly glass-like [35, 36]. There is also evidence that the nature of the guest vibrations, and possibly the phonon scattering mechanisms as well, may depend on composition and/or partial versus complete filling of the cages [40].

The most profound impact that specific structural disorder introduced into a crystal can have on thermal transport has been observed in layered crystals. Indeed, there is experimental evidence that extensive structural disorder in layered crystals can actually produce thermal conductivities *below* the glass limit. David Johnson’s group at the University of Oregon has used the modulated elemental reactants synthetic approach [41, 42] to prepare thin films of layered WSe_2 (Fig. 3f) in which individual WSe_2 layers are precisely stacked yet rotationally disordered (Fig. 8) [43, 44]. The material is synthesized by sequentially depositing subnanometer thick layers of elemental W and Se in the correct ratio and with the correct thickness to form an essentially amorphous but compositionally modulated WSe_{2+x} ($0 < x < 1$) precursor, from which layered WSe_2 is formed upon gentle annealing [44]. Although the formation process is still not completely understood, the turbostratic disorder is presumably caused by independent nucleation events during annealing [45]. Cross-plane thermal conductivity measurements of WSe_2 thin films prepared by MER in this way revealed thermal conductivities as low as $0.05 \text{ Wm}^{-1}\text{K}^{-1}$ near room temperature – the lowest thermal conductivity ever reported for a fully dense solid and more than a factor of four below the calculated glass limit for WSe_2 [43]. Moreover, unlike most crystals, the thermal conductivity was observed to significantly *increase* (and approach the glass limit) after ion bombardment of the film, which presumably induces amorphization and increases disorder. These experiments challenged the conventional thinking that the lowest thermal conductivity for a material of given composition will be obtained in the amorphous phase.

The key feature contributing to the ultra-low thermal conductivity of turbostratically disordered WSe_2 appears to be the combination of rotational disorder and a layered structure with strong covalent intra-layer bonding and weak van der Waals interlayer interactions. Although it remains an open question as to whether the orientations of individual WSe_2 are truly random [45], random relative orientations

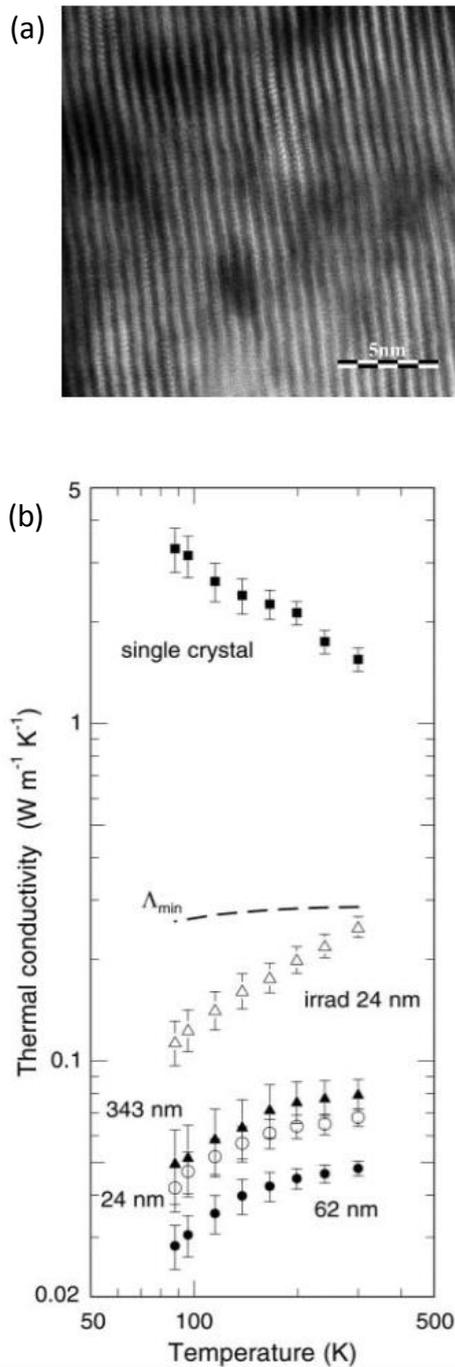


Figure 8 (a) Scanning transmission electron microscope image of WSe₂ prepared by MER, illustrating the in-plane rotational (turbostratic) disorder. Reprinted with permission from Ref. 44. Copyright 2010 American Chemical Society. (b) Cross-plane thermal conductivity of single crystal and turbostratically disorder WSe₂ films of various thicknesses. Also shown is the thermal conductivity measured after ion irradiation and the (isotropic) minimum thermal conductivity for WSe₂. From Ref. 43. Reprinted with permission from AAAS.

would produce incoherent interfaces. The reason why this material has such an extraordinarily low thermal conductivity is still not well understood. The importance of the anisotropic nature of turbostratically disordered WSe₂ has recently been highlighted in a new model for minimum thermal conductivity in anisotropic materials, which produces a minimum thermal conductivity in good agreement with the experimental data [46]. The anisotropy of the phonon dispersion is not well characterized however. The longitudinal elastic modulus of disordered layered WSe₂ along the stacking direction can be measured by conventional picosecond acoustics and is suppressed by a factor of 2 relative to typical single crystals of transition metal dichalcogenides. The shear modulus is expected to be even more strongly suppressed due to the disordered stacking of layers but has not yet been measured.

4 Intrinsically glass-like crystals: Anharmonicity, complexity, and inherent structural and dynamic disorder

In the above examples, structural disorder introduced into a crystal by static defects such as site substitutions or vacancies, localized impurity modes and tunneling states, or turbostratic disorder can reduce the thermal conductivity of an ordered crystal to values near or even below the glass limit. Some materials, however, have intrinsically glass-like thermal conductivities, which can be attributed to specific features of structure and bonding or other intrinsic structural disorder. For the materials discussed in this section, it is not needed to introduce impurities or defects into the crystal to scatter the heat carrying phonons of the host crystal or induce random stresses from chemical disorder that produces glass-like excitations. One or more intrinsic characteristics of the crystal itself somehow produce glass-like thermal conductivity.

As discussed above, the effects of anharmonicity are present in all crystals. Indeed, the 3-phonon resistive process known as Umklapp scattering is the source of the characteristic T^{-1} temperature dependence of κ_L for most crystalline solids (see Fig. 1). While this phonon scattering mechanism is present in all crystals, its effectiveness in impeding heat transport depends on structural and chemical bonding characteristics of the crystal and the resulting phonon spectrum (dispersion). Most notably, materials with pronounced anharmonic interatomic interactions have increased phonon-phonon interactions

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2 and higher probability of 3-phonon resistive processes occurring [47]. As a simple example, the ionic bonding in alkali halide crystals is more anharmonic than the covalent bonding of diamond-like crystals, which contributes to the lower thermal conductivity of the former [25]. The size of the crystallographic unit cell and Debye temperature also play important roles in anharmonic phonon-phonon scattering. Large, complex unit cells with a large number of atoms and low Debye temperature enhance phonon-phonon scattering and tend to produce lower lattice thermal conductivities [25].

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As temperature is increased, a point is eventually reached where phonon-phonon scattering becomes so pronounced that the thermal conductivity of a crystal approaches the minimum value, which for many crystals occurs just before melting [25, 48]. However, in some crystals anharmonicity is present to an extent that thermal conductivity values near the glass limit are reached at much lower temperatures. Although various underlying features of structure and bonding may lead to such behavior, we highlight one feature that is currently receiving significant attention, namely the presence of stereochemically active electron lone pairs associated with one or more constituent atoms in the crystal [49-52]. Materials such as Cu_3SbSe_3 [49], AgSbSe_2 [51], and other related group 15 chalcogenides [52] have As, Sb, or Bi atoms with nominally unpaired (non-bonding) s^2 electrons. The very low thermal conductivity of these materials is somewhat surprising given that some of them adopt relatively simple crystal structures (Fig. 3). In a simple picture, increasing overlap of the wave functions of the electrons associated with adjacent atoms and the electron lone pairs produces a non-linear repulsive interaction as the atoms move closer together, resulting in strongly anharmonic bonds [49-52]. The readily deformable nature of the electron density associated with these s^2 lone pairs is evidenced by the highly directional polarizability of these electrons, which results in large mode-averaged Grüneisen parameters $2 < \gamma < 4$ (γ characterizes the volume dependence of the phonon frequency and provides a measure of the anharmonicity of the interatomic interactions) [51]. Near minimum thermal conductivities have now been observed in a number of compositions possessing stereochemically active lone pair electrons and is commonly attributed to the pronounced anharmonicity in these materials that results in such strong phonon scattering that the thermal conductivity is reduced to the glass limit [49-52]. The lattice thermal conductivity of several of these materials also has the characteristic temperature dependence of a glass, but thus far models based solely on anharmonicity that can describe the glass-like

temperature dependence of κ_L over the entire range of temperature are still lacking. It is conceivable that other mechanisms may be at play in these materials, in conjunction with anharmonic three-phonon scattering.

As mentioned above, the size and complexity of the unit cell of a crystal can significantly impact the transport of thermal energy. In essence, as the number of atoms and corresponding volume of the unit cell of the crystal increases, the number of optical modes increases and the Brillouin zone boundary decreases, such that (i) the thermal energy becomes increasingly distributed in low velocity optical modes and (ii) the probability for phonon-phonon Umklapp scattering increases [7, 25, 53]. The thermoelectric material $\text{Yb}_{14}\text{MnSb}_{11}$ provides an illustrative example: the unit cell contains 208 atoms with a unit cell volume greater than 6000 \AA^3 [54]. This feature, combined with a low sound velocity, produces a thermal conductivity near the glass limit [54, 55]. Another material with a very complex crystal structure, $\text{Gd}_{117}\text{Co}_{56}\text{Sn}_{112}$, has 285 atoms per unit cell volume of 6858 \AA^3 and an extremely low $\kappa_L < 0.3 \text{ W/m-K}$ at room temperature [56].

One of the most interesting material systems with “intrinsic” glass-like thermal conductivity are the intermetallic clathrates (Fig. 3d) [57-59]. Akin to the skutterudites, these materials also possess large cages in their structures that can accommodate heavy, loosely bound atoms that participate in low energy vibrations commonly referred to as “rattling” modes. However, with relatively few exceptions, the guest content in most intermetallic clathrates is not variable, and the phase width for most intermetallic clathrate compounds is relatively narrow [57, 58]. Since glass-like thermal conductivity and good thermoelectric transport properties were first discovered in $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ [60, 61], intermetallic clathrates have received continual attention for their potential to be used in thermoelectric power generation applications [57, 62]. As shown in Fig. 9a, the lattice thermal conductivity of $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ shows all of the telltale signs of a glass, including the T^2 dependence at low temperature, a plateau near $\sim 10 \text{ K}$, and a weakly increasing and then nearly constant κ_L above $\sim 100 \text{ K}$ that approaches the glass limit. Considerable evidence has now been amassed that indicates these features are closely linked to the structural and dynamical behavior of the guest atoms [57-75].

The presence of low energy vibrational modes associated with the guest atoms in intermetallic clathrates is now well established by extensive experimental and theoretical studies [57-59]. Nonetheless, the microscopic mechanisms that produce the glass-like thermal conductivity in these materials continue

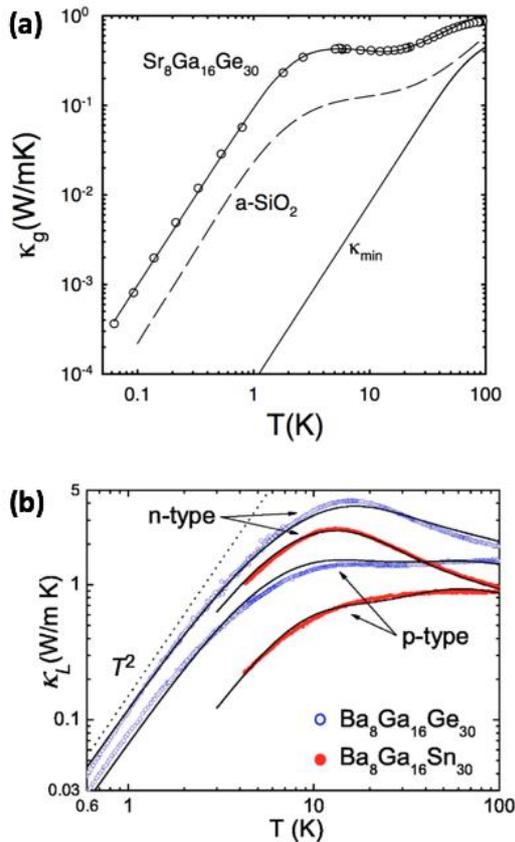


Figure 9 (a) Lattice thermal conductivity of the type I clathrate $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$. Also shown is κ_L for vitreous silica and the calculated minimum thermal conductivity for elemental Ge. Reprinted with permission from Ref. 61. Copyright 1998 by the American Physical Society. (b) Lattice thermal conductivity of n - and p -type $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ clathrates. R Reprinted with permission from Ref. 63. Copyright 1998 by the American Physical Society.

to be debated, and may even be different for different clathrate compositions [57, 59, 64, 65]. Detailed crystallographic investigations have revealed that the guest atoms in several type I clathrates, including $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$, and $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, can randomly occupy multiple symmetry-equivalent off-center sites inside the oversized cage in which they reside, resulting in static structural disorder [66-68]. The guest atoms also exhibit large amplitude thermal vibrations in addition to this random static disorder. Evidence from the Mössbauer effect, ultrasonic attenuation, and microwave absorption indicates that Eu and Sr guests may tunnel between these nearby sites, and the low temperature behavior of κ_L can be modeled well by a mechanism whereby the phonons are scattered by these tunneling states [59, 61, 69-71]. The relative size of the guest and cage has been high-

lighted as an important feature that determines whether a particular composition has a glass-like or crystal-like thermal conductivity, which may be related to the off-centering of the guest atoms. The thermal conductivity of $\text{Sr}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x}$, for example, evolves from glass-like to crystal-like as the silicon content increases and the average free volume of the cage decreases [72]. At the same time, the thermal conductivity in nominally the same composition can also be transformed from glass-like to crystal-like by adjusting the synthesis method and/or slightly adjusting the composition and resulting carrier type in semiconducting clathrates. For example, n -type clathrate-I $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ has a low but more or less crystal-like κ_L , whereas κ_L for p -type $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ is glass-like [63]. Despite composition-dependent variation between glass-like and crystalline thermal conductivity in intermetallic clathrates below room temperature, universally very low lattice thermal conductivities (~ 0.6 to 2 W/m-K) in all of these materials above the Debye temperature has been attributed to anharmonic phonon-phonon scattering, which may be enhanced by the guest-host interaction and large number of atoms ($n = 54$) in the unit cell [73-75].

In most crystalline solids, including all of those discussed above, the atoms comprising the crystal are restricted to motion primarily about their equilibrium crystallographic sites. However, in some crystals one or more of the constituent atoms can exhibit significant mobility so as to explore large regions of space, e.g. even other crystallographic sites throughout the crystal with large diffusion coefficients and over large length scales. Examples include superionic conductors such as AgI [76] and the high-performance thermoelectric materials Cu_2Se [77] and Zn_4Sb_3 [78, 79]. Interest in the seemingly simple binary compound Zn_4Sb_3 (Fig. 3e) originated in the discovery of good thermoelectric performance at intermediate to high temperatures that in part originates in its glass-like lattice thermal conductivity [78]. One of the first explanations for the glass-like thermal conductivity was based on detailed structural refinements and elucidation of disordered Zn interstitials on at least three distinct sites in the structure [79]. These interstitial Zn atoms display large and anisotropic mean square atomic displacement parameters, indicative of substantial dynamic and/or static disorder. Experimental and theoretical studies suggest a very high mobility of such atoms in these materials, which may even diffuse throughout the structure [80-82]. Such mobile, "liquid-like" behavior of one of the atomic species in a crystal, sometimes referred to as "sublattice melting," reflects substantially intrinsic dynamic disorder to which the glass-like thermal conductivity of Zn_4Sb_3 (mobile Zn ions), Cu_2Se (mo-

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bile Cu ions), and other related materials has been attributed [83]. A recent neutron scattering study of the ion transport and lattice dynamics in Cu₂Se, however, suggested that the time scales for ion diffusion are too slow to influence the lattice vibrations [84]. Those authors instead concluded that the glass-like thermal conductivity in Cu₂Se is also likely due to pronounced anharmonicity. In the case of Zn₄Sb₃, low-energy “rattling” modes associated with the Sb-Sb dumbbells in the structure have also been suggested as potential phonon scattering centers [85].

We conclude this section by noting there also exist several examples of oxide crystals that have thermal conductivities near or even below the glass limit; representatives include NaNbO₃ and CsBiNb₂O₇ [86, 87]. Both of these materials are seemingly stoichiometric crystalline compounds that are expected to be free from compositional disorder, yet show glass-like thermal conductivities over the measured temperature range. The thermal conductivity of CsBiNb₂O₇ is exceptionally low – 40% below the calculated glass limit for this material [86]. The underlying mechanisms that produce glass-like thermal conductivity in these materials are not yet understood, awaiting further experimental and theoretical study.

5 Unconventional crystals: Quasicrystals, incommensurately modulated crystals, and ferecrystals

The above examples illustrate the influence of structure, bonding, and disorder in determining the thermal transport properties of crystals and highlights how specific features can produce glass-like thermal conductivity. While most crystals have conventional three-dimensional order that can be represented by a corresponding three-dimensional reciprocal lattice, this is a sufficient but not necessary condition for a material to be crystalline. The class of materials known as aperiodic crystals, including incommensurately modulated crystals and quasicrystals, do not conform to this conventional description. Lacking periodicity in three-dimensional space, these crystals possess a different type of long-range order that still produces well-defined diffraction patterns, albeit requiring crystallographic descriptions that employ more than three dimensions [88].

The discovery of quasicrystals challenged conventional thinking on three-dimensional symmetry with the existence of periodic solids with rotational symmetries that were originally thought forbidden in crystalline solids [89]. Although quasicrystals lack

conventional translational symmetry, they nonetheless possess long-range order that can be mathematically described by space groups in more than three dimensions, evidenced by well-defined diffraction patterns [89]. In addition to their other interesting and potentially useful properties [90, 91], quasicrystals typically have low, glass-like lattice thermal conductivities. Thompson *et al.* measured thermal conductivity, transverse speed of sound, and internal friction of single-grain icosahedral Al_{72.1}Pd_{20.7}Mn_{7.2} samples [92]. The glass-like thermal conductivity, similar to an amorphous metal, and the observation that the speed of sound and internal friction data could be well described by a tunneling states model suggested that the lattice vibrations in this material may be similar to those found in glasses [92]. Umklapp scattering generalized to aperiodic crystals and strong acoustic-optic mode mixing have also been suggested as potential mechanisms that produce low thermal conductivity in quasicrystals [93, 94], though the detailed understanding is still developing.

Quasicrystals are only one subset of the broader class of aperiodic crystals. Other subsets include incommensurately modulated structures and incommensurate intergrowth structures [88, 95]. The former are characterized by a spatial modulation of the atomic positions or site occupations in an “idealized” unit cell with some spatial period, such that the equilibrium positions of the atoms from one unit cell to the next are not the same [95]. The spatial modulation period and the average lattice period in such a material are incommensurate. Although the number of known incommensurately modulated crystals is sizable and growing, the thermal conductivity of only a relatively small number of such compounds has been measured. The available data, however, suggest that these materials generally have very low and even glasslike thermal conductivities and unusual lattice vibrational properties [96].

One of the structurally most well characterized classes of incommensurate intergrowth crystals are the so-called misfit layered compounds consisting of layered intergrowths of MX and TX₂ components (M = Pb, Sn, or a rare earth, T = transition metal, and X = S or Se) with distorted rocksalt and transition metal dichalcogenide structures, respectively [97]. As illustrated in the example shown in Fig. 10, the two substructures are incommensurate along at least one crystallographic axis, and the general composition is (MX)_{1+δ}(TX₂)_n, where δ is the misfit parameter and n denotes the number of contiguously stacked TX₂ layers (typically n = 1 or 2). Wan *et al.* have investigated the thermoelectric properties of textured bulk polycrystalline specimens of several misfit layered sulfides and have found that the thermal conductivities

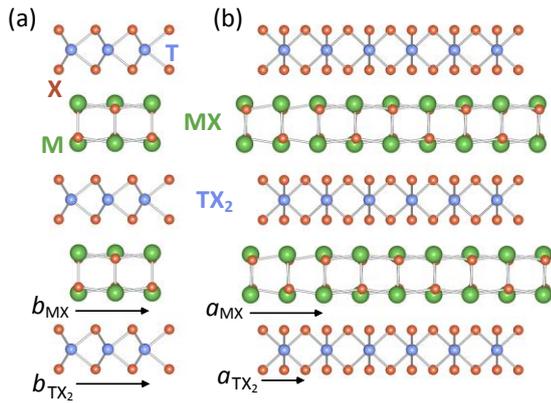


Figure 10 Representation of the crystal structure of a $(MX)_{1+\delta}TX_2$ misfit layered compound, illustrating the MX and TX_2 substructures, view along perpendicular crystallographic axes (a) and (b). Reprinted with permission from Ref. 100. Copyright 2014 IOP Publishing.

are very low [98, 99]. The lattice thermal conductivities are also very anisotropic, with κ_L measured in the direction parallel to the layers (in-plane) being a factor of two or more larger than κ_L measured in the direction perpendicular to the layers (cross-plane) [98, 99]. As shown in Fig. 11, the cross-plane lattice thermal conductivity of $(SnS)_{1.18}(TiS_2)_2$ was found to be nearly temperature independent and is lower than its corresponding glass limit over the entire measured temperature range. By comparison with the binary parent compound $TiSe_2$, insertion of the SnSe layers between the TiS_2 layers also reduces the in-plane κ_L by nearly a factor of 2. The extraordinarily low cross-plane lattice thermal conductivity was attributed to decreased transverse phonon velocity and phonon scattering enhanced by the modulated structure and translational disorder, though a well-defined description of the microscopic mechanism(s) has not been presented [99]. Experimental investigations of the lattice dynamics of misfit layered compounds are also wanting, while *ab initio* computational studies are exceedingly challenging due to the aperiodic nature of these structures. So far, the very low thermal conductivity observed in misfit layered compounds appears to be related to the highly anisotropic bonding and weak interlayer interactions in these materials.

In the past several years, a related class of novel ultralow thermal conductivity materials based on the traditional misfit layered compounds has also been conceptualized and experimentally realized *via* David Johnson's modulated elemental reactants synthetic approach [100]. Like misfit layered compounds, these materials consist of intergrowths of structurally distinct MX and TX_2 components. However, there are

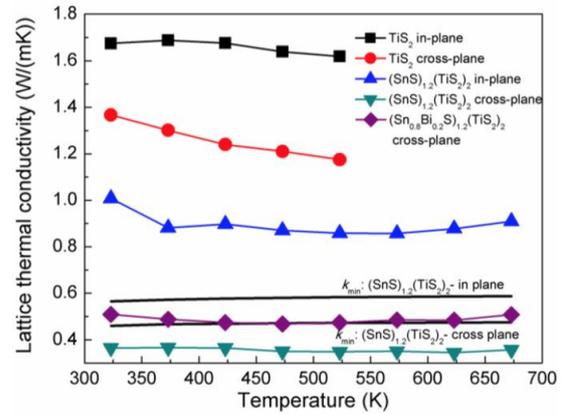


Figure 11 In-plane and cross-plane lattice thermal conductivity of layered TiS_2 and the misfit compound $(SnS)_{1.2}(TiS_2)_2$. The in-plane thermal conductivity of $(SnS)_{1.2}(TiS_2)_2$ is low but remains higher than the calculated in-plane minimum thermal conductivity. The cross-plane thermal conductivity of $(SnS)_{1.2}(TiS_2)_2$, however, is lower than the glass limit. Reprinted with permission from Ref. 99 (open access).

several aspects of Johnson's unique thin film materials that distinguish them from conventional crystalline misfit layered compounds (MLCs). Unlike conventional MLCs, an immense variety of metastable compositions can be prepared, incorporating elements that are not accessible in conventional misfit layered compound syntheses [101-103]. The number of contiguous MX or TX_2 layers in the stacking period is also not limited to 1 or 2 [100-102], and in principle any finite stacking sequence is possible. Similar to the WSe_2 films prepared by MER that are discussed above, the individual TX_2 layers are turbostratically disordered with respect to each other as well as the MX component (see Fig. 12), whereas the layers show rotational order in MLCs [100]. The individual layers are nonetheless precisely stacked with atomically abrupt interfaces, resulting in uniform intergrowth thin films that produce well defined $(00l)$ X-ray diffraction and reflectivity patterns [100]. The unusual combination of precise stacking and in-plane turbostratic disorder has prompted the name *ferecrystals* (from the latin root *fere-*, meaning "almost") to highlight the fact that these materials are structurally at the interface between crystalline and amorphous solids. The structural features of *ferecrystals* have significant impact on the lattice thermal conductivity and also allow thermal transport mechanisms in layered materials to be probed in unique ways.

The cross-plane thermal conductivity of semiconducting $[(MSe)_{1+\delta}]_m[TSe_2]_n$ thin films with $M = Pb$ or Sn , $T = Mo$ or W , and $1 \leq m, n \leq 5$ has been measured

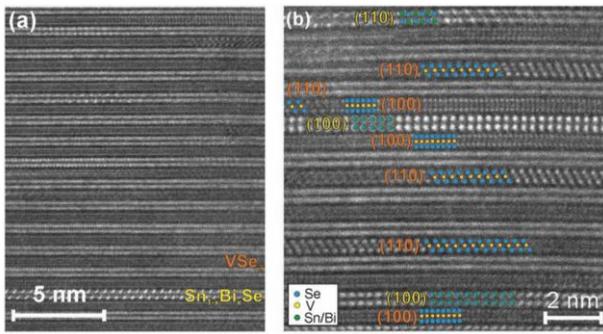


Figure 12 Scanning transmission electron microscope images of a $[\text{Sn}_{0.6}\text{Bi}_{0.4}\text{Se}]_{1+\delta}\text{VSe}_2$ ferecrystal, illustrating the rotational disorder between the MX and TX₂ layers that is commonly observed in ferecrystals. Reproduced from Ref. 104 with permission of The Royal Society of Chemistry.

by time domain thermoreflectance, revealing ultralow values between approximately 0.06 W/m-K and 0.2 W/m-K [105, 106]. These values are well below the calculated minimum thermal conductivities for the PbSe, SnSe, MoSe₂, or WSe₂ constituents [105], and also significantly lower than the values measured thus far for crystalline misfit layered compounds. Interestingly, the thermal conductivity values are higher than those obtained for turbostratically disordered WSe₂ alone, and found to be essentially independent of the MX-TX₂ interface density [105, 106], a result which is in stark contrast to conventional semiconducting superlattices. The in-plane thermal conductivity of free standing $[(\text{PbSe})_{1+\delta}]_m[\text{WSe}_2]_m$ films was found to be significantly higher (~ 0.4 W/m-K) and nearly temperature independent [107]. While much is still not understood regarding the lattice dynamics in these unique anisotropic systems, the results so far suggest that the turbostratic disorder in the TX₂ component strongly limits the cross-plane thermal transport in these materials, and the resulting lack of extended transverse modes and a decreased effective shear speed of sound may be important features. The questions regarding lattice dynamics and phonon confinement in these materials are again difficult to address via *ab initio* calculations due to their unusual disordered structure, and are only beginning to be investigated experimentally [108].

6 Concluding Remarks

While the ordered versus periodic arrangement of atoms in crystalline and amorphous solids is a defining characteristic for classification, we now know that

structural disorder to the extent found in amorphous solids is not needed to produce the universal “glass-like” thermal transport behavior associated with glasses. The features to which the universal thermal transport properties of glasses are attributed, which include low energy excitations, localized vibrational modes, and tunneling states, can be introduced in crystalline materials through structural and/or dynamic disorder, or are connected to the specific aspects of structure and chemical bonding in the crystal. The study of crystals with glass-like properties also allows insight into the unusual and still relatively poorly understood properties of amorphous solids. Systems in which disorder can be introduced in a controlled manner can be particularly illuminating [109].

In addition to the earlier examples of glass-like excitations introduced by increasing structural disorder induced by defects, crystals with large, complex unit cells, pronounced anharmonic bonding, and/or guest-host structures with “rattling” atoms or molecules provide a broader set of material systems in which thermal transport properties that are atypical of crystals are observed. In the past decade, it has become increasingly clear that materials with highly anisotropic structures and chemical bonding provide new opportunities to produce materials with ultralow thermal conductivities and perhaps other unprecedented properties. At the same time, such materials challenge both our understanding of heat transfer in solids and current modeling abilities [110]. Advancements in experimental techniques that can probe the lattice dynamics in thin film solids, the only form in which some of these intriguing materials can currently be prepared, are needed to fully address many of the interesting and important questions in this area.

Acknowledgements

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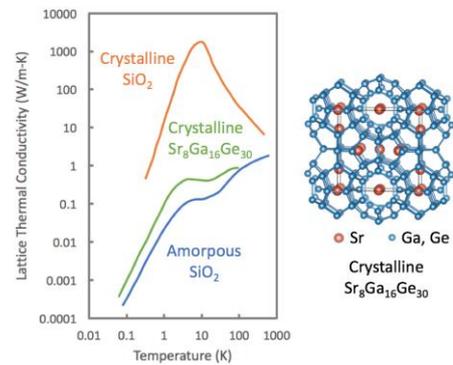
Table of Contents

Page xx-yy (for typesetter)

M. Beekman and D. G. Cahill

Inorganic crystals with glass-like and ultralow thermal conductivities

Why do some crystals conduct heat like a glass? Understanding the reasons why could help advance technologies that depend on low thermal conductivity crystalline materials, including thermal barrier coatings and thermoelectric energy conversion. In this review, we highlight what is currently known about the structure and lattice dynamics in these fascinating yet still relatively poorly understood materials.



Review