Lone pairs in insulating pyrochlores: Ice rules and high-\(k\) behavior

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Abstract. Pyrochlore dielectric materials such as \((\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Nb}_{1.5}\text{Zn}_{0.5})\text{O}_7\) (BZN) have generated interest because they combine high dielectric constants with small dielectric loss tangents and yet are cubic at all temperatures. The recent low-temperature preparation and structural characterization of \(\text{Bi}_2\text{Ti}_2\text{O}_7\), which remains cubic down to 2 K, has provided a good model system for understanding the properties of Bi-based pyrochlores. In this contribution, the electronic structure of cubic \(\text{Bi}_2\text{Ti}_2\text{O}_7\) is visualized and compared with the electronic structure of the Aurivillius phase ferroelectric \(\text{SrBi}_2\text{Ta}_2\text{O}_9\) (SBT), which displays a ferroelectric distortion below 608 K associated with the tendency of lone pair active Bi\(^{3+}\) to move off-center. Such coherent off-centering distortions are frustrated on the pyrochlore lattice, and this prevents a ferroelectric-paraelectric phase transition in \(\text{Bi}_2\text{Ti}_2\text{O}_7\). Instead, Bi\(^{3+}\) ions in \(\text{Bi}_2\text{Ti}_2\text{O}_7\) are obliged to off-center in an incoherent manner, that is compatible with the cubic structure being retained. Frustrated lone pair behavior in the defect pyrochlore \(\text{Pb}_2\text{Sn}_2\text{O}_6\) is also described. Parallels between the well-studied frustration of certain types of magnetism in pyrochlore compounds (spin-ice) and the striking paucity of ferroelectric pyrochlores, arising from the corner-connected tetrahedral topology of the pyrochlore lattice are pointed out.
Figure 1. (Color) (a) Ideal pyrochlore $A_2B_2O_6O'$ crystal structure in the $Fd\overline{3}m$ space group showing black A atoms, orange $O'$ and the network of corner-connected $BO_6$ octahedra (blue). (b) is a view of the tetrahedral $A_2O'$ sublattice, and (c) is a view of the $B_2O_6$ sublattice. All views are looking down [110].

1. Introduction

Pyrochlore oxides[1] have attracted a great deal of recent attention as a consequence of their diverse, often unusual, physical properties. Recent examples of the diverse properties displayed by pyrochlores include the discovery of colossal magnetoresistance in $Tl_2Mo_2O_7$ in the absence of multiple valence states,[2] superconductivity in $Cd_2Re_2O_7$,[3] and in the $\beta$-pyrochlore $KOs_2O_6$,[4] and an unusual chiral magnetic ground state in $Nd_2Mo_2O_7$.[5]

In the pyrochlore crystal structure, originally associated with the mineral $Ca_2Nb_2O_6F$, the B (Nb) atoms form a network of corner-sharing octahedra. The A-site (Ca) has six O neighbors and two F neighbors. For the purpose of this work on oxide pyrochlores, the structure is best described as $A_2B_2O_6O'$ comprising two interpenetrating sublattices with the formulæ $A_2O'$ and $BO_6$. These views of the structure are displayed in figure 1. The crystal chemical principles involved in the pyrochlore structure are unusual as has recently been emphasized by Vanderah and coworkers.[6] For example, the $A_2O'$ sublattice can tolerate a great deal of displacive disorder, and consequently, does not obey the usual rules for cation substitution. These unusual principles play a significant rôle in rendering the pyrochlore structure suitable for the storage of ions involved in radioactive waste.[7]

Another crucial feature of the structure is that when regarded separately, both
the A and B sublattices form corner-connected networks of $A_4$ and $B_4$ tetrahedra. The formation of such tetrahedral networks can result in magnetic frustration associated, for example, with the infeasibility of decorating the vertices of a tetrahedron with all four spins in an anti-parallel configuration.[8, 9] P. W. Anderson[10] first recognized the relation between the tetrahedral spin configurations of spinels and the problem of the crystal structure of ice-$I_h$. According to the Bernal-Fowler rules[11] each oxygen atom in the ice lattice is tetrahedrally bonded to four protons, with the proviso that two of the protons are proximal (covalent) and two are distal (H-bonded). There is no unique arrangement which satisfies these rules, and as a consequence, ice-$I_h$ has a residual zero-temperature entropy.[12, 13, 14] The crystal structure of ice-$I_h$ is therefore frustrated in the sense that it cannot find a perfectly crystalline zero-entropy ground state. There is great current interest in such frustrated systems, associated with a desire to understand the nature of complex potential energy landscapes, and a number of recent studies have emerged on “spin-ice” pyrochlores.[15, 16] Interestingly, when ground state structures are induced, for example through OH$^-$ doping, polar ground states become possible in water ice.[17]

Unlike ABO$_3$ perovskite oxides where ferroelectricity is not uncommon and is a well-studied phenomenon,[18] there exist very few ferroelectric pyrochlores. The few known system seem to be based on Cd$_2$Nb$_2$O$_7$,[19] and its variants.[20, 21] These compounds remain the subject of study.[22] “High-k” pyrochlore oxides with large dielectric constants exemplified by (Bi$_{1.5}$Zn$_{0.5}$)(Nb$_{1.5}$Zn$_{0.5}$)O$_7$ (BZN) however do exist and are attracting considerable attention. BZN is a cubic pyrochlore at all temperatures,[23] with considerable short-range order in the structure.[24] Ceramic samples are known to combine high dielectric constants with low dielectric losses.[25, 26] A combination of spectroscopic techniques reveal that the unusual properties of BZN arise due to local hopping of the Bi and O’ atoms among several potential minima.[27] Interestingly, from the viewpoint of applications, these desirable characteristics are retained in thin films.[28, 29, 30, 31]

It is intriguing that BZN exhibits all the characteristics of a compound about to undergo a phase transition, such as the need to split the Bi and O’ for satisfactory Rietveld refinements of neutron diffraction data,[23] and yet remains cubic till the lowest temperature. The absence of a phase transition is an important ingredient in the usefulness of BZN. For example, in a material with no phase transition, there is little fatigue, and the temperature coefficient of the dielectric constant is small.

The preparation of a slightly off-stoichiometric pyrochlore phase related to Bi$_2$Ti$_2$O$_7$ by Sleight and coworkers, [32] and the more recent preparation of stoichiometric, cubic Bi$_2$Ti$_2$O$_7$ by Hector and Wiggin[33] provide a good model system for understanding polar phenomena in the bismuth pyrochlores. Stoichiometric Bi$_2$Ti$_2$O$_7$ has been prepared by a low-temperature route and established by powder neutron diffraction to be a cubic pyrochlore down to 2 K, but with extensive site disorder at both the Bi and O’ sites.[33] Site disorder on the pyrochlore A-site is well-known for lone pair active cations such as Tl$^+$. [34]
Sn\(^{2+}\)[35, 36] and Bi\(^{3+}\)[23, 32, 37] and will be discussed in further detail.

We have for some time been interested in the stereochemistry of lone pairs in extended solids,[38, 39, 40, 41, 42] and have used density functional calculations of electronic structure in conjunction with the electron localization function[49, 50] for visualizing lone pair electrons in the real space of crystal structures. Here such analysis is extended to the electronic structure of cubic Bi\(_2\)Ti\(_2\)O\(_7\). For comparison, LMTO calculations have been performed on the Aurivillius phase ferroelectric SrBi\(_2\)Ta\(_2\)O\(_9\)[43, 44] where the transition from a paraelectric to a ferroelectric phase at 608 K is driven in large part by the off-centering tendency of the Bi\(^{3+}\) ions. The electronic structures of paraelectric[45] and ferroelectric SrBi\(_2\)Ta\(_2\)O\(_9\)[46, 47] have been described previously, but no discussion of the disposition of lone pairs in the ferroelectric phase has been presented. The disposition of Pb\(^{2+}\) lone pairs in the cubic defect pyrochlore Pb\(_2\)Sn\(_2\)O\(_6\)[48] are also examined.

2. Details of computation

Linear Muffin-Tin Orbital calculations[51, 52] on pyrochlore Bi\(_2\)Ti\(_2\)O\(_7\) were performed within the atomic sphere approximation using version 47C of the Stuttgart TB-LMTO-ASA program.[53] Scalar-relativistic Kohn-Sham equations within the local density approximation [54] were solved taking all relativistic effects into account except for the spin-orbit coupling. The calculations were performed on 72 irreducible \(k\) points within the primitive wedge of the Brillouin zone. LMTO electronic structures were analyzed by calculating crystal orbital Hamiltonian populations (COHPs) and electron localization functions (ELFs). The crystal orbital Hamiltonian population COHP[55, 56] is a tool which permits energy-resolved analysis of bonding. The ELF provides a measure of the local influence of the Pauli repulsion on the behavior of electrons and permits the mapping in real space of core, bonding, and non-bonding regions in a crystal.[49, 50] Calculations were performed on the ideal crystal structure of pyrochlore Bi\(_2\)Ti\(_2\)O\(_7\)[33] (space group \(Fd\overline{3}m\), \(a = 10.37949\) Å), displayed in figure 1. The atom positions are Bi (0,0,0), Ti (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)), O (\(\frac{1}{2}, \frac{1}{2}, x\)) and O\(^\prime\) (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)). \(x = 0.43128\) was taken from the reported room temperature crystal structure refinement.[33] LMTO calculations were also performed on the \(A2_1\)am crystal structure of ferroelectric SrBi\(_2\)Ta\(_2\)O\(_9\) taken from the detailed structural study of Rae et al.[57] A grid of 72 irreducible \(k\) points within the primitive wedge of the Brillouin zone was used for the calculation on SrBi\(_2\)Ta\(_2\)O\(_9\). The crystal structure of the defect pyrochlore Pb\(_2\)Sn\(_2\)O\(_6\)[48] is reported in the International Crystal Structure Database (entry 15308) to be a cubic pyrochlore with \(a = 10.719\) Å. Atoms are Pb (0,0,0), Sn (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)), and O (\(\frac{1}{2}, \frac{1}{2}, x\)) with \(x = 0.4250\). O\(^\prime\) is missing in this structure. LMTO calculations on Pb\(_2\)Sn\(_2\)O\(_6\) employed a grid of 72 irreducible \(k\) points.
3. Results

3.1. \(\text{Bi}_2\text{Ti}_2\text{O}_7\)

The \(\text{Bi}_2\text{O}'\) network of \(\text{Bi}_2\text{Ti}_2\text{O}_7\) can be imagined as being formed of a diamond lattice of \(\text{O}'\), with one Bi atom at the center of every \(\text{O}'-\text{O}'\) linkage. The \(\text{Bi}_2\text{O}'\) network thus satisfies one of the Bernal-Fowler rules\cite{11} in that each \(\text{O}'\) is tetrahedrally surrounded by Bi. The network does not satisfy the “two-near and two-far” rule, meaning that ideal pyrochlore \(\text{Bi}_2\text{Ti}_2\text{O}_7\) is perfectly crystalline and has no residual entropy.

The projected Bi and oxygen LMTO densities of state (DOS), and the Bi-oxygen COHPs of cubic \(\text{Bi}_2\text{Ti}_2\text{O}_7\) are displayed in the three panels of figure 2. The band gap in cubic \(\text{Bi}_2\text{Ti}_2\text{O}_7\) is about 2 eV. Bi \(s\) states in figure 2(a) are seen to reside in a very narrow window of energy around -10 eV with respect to the top of the valence band (set as the origin of the energy axis in this and other plots). Bi \(p\) states, as expected for a formally \(\text{Bi}^{3+}\) system, are largely empty and form the conduction band which starts at 2 eV. Some Bi \(p\) states are found mixed with the valence band as a result of covalency with oxygen. Bi \(s\) and \(p\) states of \(\text{Bi}_2\text{Ti}_2\text{O}_7\) are resemble those previously observed in cubic “pre-distorted” \(\text{BiMnO}_3\).\cite{39} O \(p\) and \(\text{O}'\) \(p\) states are displayed in

![Figure 2](image-url)
figure 2(b). There are six O for every one O', giving rise to a large difference in the relative number of states. O’ states are particularly prominent around -5.5 eV, near the bottom of the valence band, where O’ p forms band with Bi p states. Bi-O and Bi-O’ COHPs are displayed per primitive unit cell (or for a single BiO₆O’₂ polyhedron) in figure 2(c). The integrated COHP which is indicative of the strength of interaction, confirms that Bi s states are quite inert in the cubic crystal structure. Stronger Bi p and O’ p interactions manifest as a large bonding COHP at the bottom of the valence band. Because of the longer distance between Bi and O (2.635 Å) compared with Bi and O’ (2.247 Å), the Bi-O interaction is weak and O obtain most of their bond valence from Ti.

The valence electron localization function (ELF) of Bi₂Ti₂O₇ is plotted within the real space of the crystal structure in figure 3. For clarity, Ti and O atoms are not displayed. Bi and O’ are connected to emphasize the “interrupted” diamond lattice. Isosurfaces of the ELF for a value of 0.65 manifest the lobes of s electrons around Bi. These lobes are constrained by the symmetry of the structure to form cylindrical objects with the cylindrical axis along different [111] directions, corresponding to the Bi-O’ bonds. The ELF is also displayed on the back plane of the crystal structure as a map running from deep blue (poorly localized regions) to white (strongly localized
regions). The particular manner in which the lone pairs localize around Bi atoms is an artifact of the ideal crystal structure is used here. In reality, both Bi and O’ are shifted from their crystallographic sites, albeit in an incoherent manner. To understand what the lone pair localization should more properly resemble, the disposition of lone pairs in the Aurivillius phase ferroelectric SrBi$_2$Ta$_2$O$_9$ is examined in the following subsection.

3.2. SrBi$_2$Ta$_2$O$_9$

The A2$_1$am crystal structure of SrBi$_2$Ta$_2$O$_9$[57] is displayed in figure 4 and comprises alternate stacks of double-perovskite [SrTa$_2$O$_7$]$^{2-}$ slabs interleaved with [Bi$_2$O$_2$]$^{2+}$ slabs. The latter are reminiscent of the Bi-O sublattice of BiOF[41] where Bi lone pairs organize themselves in an antiferrodistortive manner, akin to what is seen in PbO.[40, 41] In this distorted crystal structure, Bi $s$ states [figure 5(a)] are significantly more disperse than was observed for cubic Bi$_2$Ti$_2$O$_7$. Relatively few Bi $p$ states are observed in the region of filled O $p$ states [figure 5(b)]; most Bi $p$ states are empty and, starting at 2 eV, form the conduction band along with empty Ta $d$ states (not displayed). The Bi-O COHP displays quite strong bonding in the region of Bi $s$ states. Both Bi $s$ states and O $p$ states are filled, so their interaction gives rise to filled bonding states around -9 eV and filled antibonding states just below the top of the valence band. The intermediation of empty Bi $p$ states provides net stabilization.[42] The Bi-O COHP of SrBi$_2$Ta$_2$O$_9$ displayed in figure 5(c) is what the Bi-O COHP of Bi$_2$Ti$_2$O$_7$ displayed in figure 2(a) would resemble were it permitted to take on an appropriately
The valence ELF of SrBi$_2$Ta$_2$O$_9$ is displayed in the different panels of figure 6. The left panel of figure 6 displays the ELF isosurface within the space of the unit cell. For clarity, other atoms than in the Bi-O network have been let out of the depiction. The net “polarization” of the lone pair lobes is more clearly seen in projections down the c axis [figure 6(a-d)]. The ELF was been calculated on a $48 \times 48 \times 144$ ($a \times b \times c$) real-space grid within the unit cell. Figure 6(a-d) shows four sections of the ELF at four different heights along the c direction, corresponding to positions of Bi atoms in the unit cell. In this view, it is clear that all the Bi lone pairs have a component that points in the $a$ direction, meaning that the Bi are shifted slightly along $b$. It is this in-plane shift which gives SrBi$_2$Ta$_2$O$_9$ its polarization. The very different shapes of the lone pair lobes associated with centered Bi in Bi$_2$Ti$_2$O$_7$ (figure 3) and with off-centered Bi in SrBi$_2$Ta$_2$O$_9$ (figure 6) should be noted.

3.3. Pb$_2$Sn$_2$O$_6$

Morgenstern-Badarau and Michel[48] have reported the defect pyrochlore crystal structure of “Pb$_2$Sn$_2$O$_6 \cdot x$(H$_2$O)”. Interestingly, the compound has long history and could be one of the components of a yellow pigment used by renaissance painters
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Figure 6. (Color) ELF isosurface projected within the unit cell of SrBi$_2$Ta$_2$O$_9$ for an ELF value of 0.65. The panels (a-d) on the right are planes of the ELF parallel to the c axis; the planes are chosen to contain Bi atoms. The values of z/c of the different planes are indicated as ratios.

called lead-tin yellow.[58] The O' atom is missing in this crystal structure and is replaced by a vacancy (□). A$_2$O' in the usual pyrochlore then corresponds to Pb$_2$□. It is natural to assume that Pb$^{2+}$ lone pairs would occupy the site that is normally taken up by O'. This would parallel the crystal-chemical relation between litharge PbO and PbO$_2$; the former having lone pairs in the place of the oxygen atoms of the latter.[59] However the A$_2$O' network of the pyrochlore lattice depicted in figure 1 allows us to recognize that for every four Pb atoms, there are two sites into which the lone pairs can localize. The problem now maps precisely on to the Bernal-Fowler rules with the lone pair-Pb connection corresponding to the short (covalent) O-H interaction. The valence ELF of cubic Pb$_2$Sn$_2$O$_6$ displayed in figure 7 support this argument. The symmetry of the crystal structure prevents localization into a single lobe, and instead, a bi-lobed lone pair is obtained. Topological frustration again prevents coherent ordering of the lone pairs in some distorted low-temperature structure. Re-examination of the crystal structure of defect pyrochlore Pb$_2$Sn$_2$O$_6$ should reveal disordering on this site; splitting every Pb atom into two along the □-Pb-□ direction (the [111] directions). The precise nature of such splitting would therefore be distinct from what is observed for Bi in Bi$_2$Ti$_2$O$_7$ where it is forms an annulus around O'-Bi-
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Figure 7. (Color) ELF isosurface projected within the unit cell of Pb$_2$Sn$_2$O$_6$ for an ELF value of 0.65. The yellow spheres are vacant positions corresponding to O’ in the ideal pyrochlore.

O’.[33]

4. Implications

To aid the rest of the discussion, the panels of figure 8 display two different views of the O’-centered tetrahedral network, also referred to as the tridimyte sublattice,[6] of the pyrochlore structure. The two views suggest that we could view the pyrochlore structure as a stellation followed by stacking of kagomé lattices of A atoms. A kagomé lattice is a lattice of corner sharing triangles. The stellation of this lattice is achieved by making each triangle a tetrahedron by alternately capping the triangles above and below the planes they are in and creating tetrahedra pointing either up or down (along [111] in the pyrochlore structure). In 2D the pyrochlore lattice should be well-represented by a kagomé lattice. This allows us to compare in a simple manner, the topologies of perovskites, which we represent by a square lattice, and the pyrochlore, which we represent using the kagomé lattice (figure 9).

A square lattice is easily distorted to a rectangular lattice [figure 9(a) and (b)] allowing coherent localization of lone pair lobes, which we indicate with arrows. This simple description is reasonably accurate in describing the pyroelectric to ferroelectric (cubic $Pm\bar{3}m$ to tetragonal $P4mm$) phase transition in perovskite
Figure 8. (Color) (a) Corner-connected $O'A'_4$ tetrahedra of the $A_2B_2O_6O'$ structure projected down [111] (b) A single slab of the network seen from the side; the pyrochlore structure described as a stellated *kagomé* network.

Figure 9. (Color) (a) is a square lattice with lone-pair active ions in the corners. Coherent localization of the lone pairs results in a polar rectangular lattice (b). (c) is a *kagomé* lattice with lone pair active ions at the corners. The lone pairs can either localize towards other vertices (d) or towards the centers of the triangle (e), but they do not do so coherently.
A *kagomé* lattice with lone pair-active ions at its corners [figure 9(a)] could localize lone pairs in two different ways: The first is for the lone pairs to localize perpendicular to the line joining the centers of the triangles, as depicted in figure 9(c). This is the case with the annular lone-pair localization in Bi$_2$Ti$_2$O$_7$. The second is for the lone pairs to localize towards the centers of triangles, as depicted in figure 9(d). This is representative of *kagomé* spin ice[60] and is similar to what is observed Pb$_2$Sn$_2$O$_6$. In neither case is it a simple matter to arrange the arrows such that a unit cell is obtained. Note that neither of these arrangements would be *ferrodistortive*. In fact, while we have focused on the paucity of ferroelectric pyrochlores, our analysis actually refers to any symmetry lowering phase transition.

In the rare instances when pyrochlore oxides distort as a result of coherent ordering of stereochemically active lone pairs, the resulting crystal structures can be be quite complex, for example, as determined recently for Bi$_2$Sn$_2$O$_7$.[61] However, retention of the cubic structure is important for properties. For instance, the pyrochlore composition Bi$_2$Zn$_{1/3}$Nb$_{4/3}$O$_7$ crystallizes in a monoclinic structure related to zirconolite,[62] and the material is not as interesting as (Bi$_{1.5}$Zn$_{0.5}$)(Nb$_{1.5}$Zn$_{0.5}$)O$_7$ for high-$k$ applications. Wang *et al.*[25] have presented a simple and powerful argument for when A$_2$B$_2$O$_7$ pyrochlores with lone pair active A cations distort. They point to a relative competition between covalency in the A-O and B-O networks. Pyrochlores with strongly covalent B-O networks tend to retain the cubic structures.

The arguments presented here bear close similarities to the frustration of soft modes in ZrW$_2$O$_8$, proposed by Ramirez and coworkers[65] as being responsible for its negative thermal expansion behavior.[66] Recently, Loidl and coworkers[67] reported unusual magnetoferroelectric properties of spinel CdCr$_2$S$_4$. In this compound, relaxor ferroelectricity is observed in the absence of any substitutional disorder. The authors suggest that the origin of such relaxor behavior could be the topological frustration of a true ferroelectric ground state. In the superconducting β-pyrochlore oxides, Kuneš, Jeong, and Pickett[68] have used first principles calculations to determine that local displacements of the A cation are critical in determining superconducting $T_c$s. One could argue that in the absence of the topological frustration provided by the pyrochlore lattice, these local displacements would lead to a distorted ground state structure. In a related vein, for macroscopic materials built up from bars and pins, the unusual properties of *kagomé* lattices with respect to the applications of stresses have already been noted.[69]

To summarize, it is proposed that in pyrochlores such as (Bi$_{1.5}$Zn$_{0.5}$)(Nb$_{1.5}$Zn$_{0.5}$)O$_7$, properties are dominated by topological frustration rather than cation site disorder. Bi$_2$Ti$_2$O$_7$ itself is therefore a candidate for high-$k$ behavior, and should be regarded as a parallel of systems such as cubic, *predistorted* PbTiO$_3$. In relaxor ferroelectrics, substitutional disorder frustrates long-range ordering and gives rise to unusual behavior, such as broad dielectric anomalies as a function of temperature.[63, 64] If re-
laxor ferroelectrics with site disorder are the ferroelectric equivalent of substitutional spin glasses such as Cu:Mn, then pyrochlore dielectrics could be considered the ferroelectric analogues of topologically frustrated magnets. In analogy with topologically frustrated magnets, the recording of low-temperature heat capacity of Bi$_2$Ti$_2$O$_7$ should permit the residual entropy to be measured and compared with values found in pyrochlore spin-ice.[15] Finally, in analogy with spin-ice, it is proposed that the term “charge-ice” is used to describe frustrated pyroelectric phenomena in systems such as spinels and pyrochlores. Topological frustration in polar materials could constitute a powerful design parameter for useful and novel materials properties.

5. Acknowledgements

I thank Susanne Stemmer for bringing (Bi$_{1.5}$Zn$_{0.5}$)(Nb$_{1.5}$Zn$_{0.5}$)O$_7$ to my attention, and for valuable discussions and references. Tony Evans, Alois Loidl, Bob McMeeking, Art Ramirez, Ivana Radosavljevic-Evans, Nicola Spaldin, Roser Valentí, Terrell Vanderah, and Pat Woodward are also thanked for discussions. Support from the National Science Foundation through the MRSEC program under award no. DMR00-80034, and through a Chemical Bonding Center (Chemical Design of Materials) under award no. CHE04-34567 is gratefully acknowledged.

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