Large Low Temperature Specific Heat in Pyrochlore Bi$_2$Ti$_2$O$_7$

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Abstract

Both amorphous and crystalline materials frequently exhibit low temperature specific heats in excess of what is predicted using the Debye model. The signature of this excess specific heat is a peak observed in $C/T^3$ versus $T$. To understand the curious absence of long-range ordering of local distortions in the crystal structure of pyrochlore Bi$_2$Ti$_2$O$_7$, we have measured the specific heat of crystalline Bi$_2$Ti$_2$O$_7$ and related compounds. We find that the peak in $C/T^3$ versus $T$ in Bi$_2$Ti$_2$O$_7$ falls at a substantially lower temperature than other similar compounds, consistent with the presence of disorder. This thermodynamic evidence for disorder in crystalline Bi$_2$Ti$_2$O$_7$ is consistent with quenched configurational disorder among Bi lone pairs produced by geometrical frustration, which could represent a possible realization of “charge ice”.

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It is well known that at relatively low temperatures, typically in the range of 2 K to 30 K, amorphous systems exhibit a larger specific heat than the simple prediction of the Debye model. This excess specific heat manifests itself as a peak in $C/T^3$ versus $T$, and is generally attributed to local low energy vibrational modes not accounted for in the Debye model. These low energy modes are observed in Raman spectra and from inelastic neutron scattering, where they give rise, in glasses, to the so-called “boson peak”. The mechanisms responsible for these low energy modes have been discussed in terms of localized vibrations (“floppy modes”), domain wall motions of the glassy mosaic structure, and transverse phonon modes.

A number of crystalline materials also exhibit a low-temperature peak in $C/T^3$. This peak can be attributed to van Hove singularities where the vibrational density of states (VDOS) crosses the Debye density of states, leading to a flattening of phonon dispersion curve. This is nearly equivalent to stating that the local modes are responsible; in materials such as SiO$_2$, the nature of the vibrations responsible for the peak in crystalline and amorphous samples are similar. As low temperature specific heat measurements can provide evidence for disorder in insulating crystalline compounds, we have used thermodynamic measurements to investigate displacive disorder in Bi$_2$Ti$_2$O$_7$ and related systems.

In this contribution, we examine the excess low temperature specific heat in a series of structurally- and compositionally-related crystalline compounds of interest as polar and dielectric materials. The pyrochlore compound Bi$_2$Ti$_2$O$_6$O’ is compositionally and electronically related to the perovskite ferroelectric PbTiO$_3$, in that the A site of the structure is occupied by a main group ion with the 6s$^2$, 6p$^0$ configuration, and the B site is occupied by d$^0$ Ti$^{4+}$ (structures displayed in FIG. 1). Both the A and the B site ions in these compounds are therefore susceptible to off-centering. This so-called stereochemical activity, and this is what drives the phase transition to a coherent, polar, tetragonal ground state in PbTiO$_3$. The related pyrochlore compound Bi$_2$Ti$_2$O$_6$O’ (more simply referred to as Bi$_2$Ti$_2$O$_7$) shows no such phase transition and even at 2 K, the crystal structure is cubic. However, in a manner that is common across many pyrochlore crystal structures with Bi$^{3+}$ on the A site, Rietveld refinement of neutron diffraction data indicates that Bi is locally off-centered. This evidence for local distortion, in conjunction with the absence of ferroelectricity, suggests that the Bi ions are displaced randomly into one of several distinct, but symmetric, sites about the equilibrium position as indicated in FIG. 1(b).
FIG. 1: (a) Structure of ideal Bi$_2$Ti$_2$O$_6$O’. The 6s$^2$ lone pair around Bi$^{3+}$ atoms are visualized using the valence electron localization function (ELF) with isosurfaces of value 0.625 following methods presented in reference [15]. (b) Split atom positions of Bi and O’ (50% isotropic thermal ellipsoids displayed) as obtained from Rietveld refinement of powder neutron diffraction data indicative of local displacive disorder, following reference [10]. (c) Crystal structure of tetragonal PbTiO$_3$ (two unit cells displayed), using the ELF to locate lone pairs around Pb$^{2+}$. Note the difference in the nature of the lone pairs in (a) and (c). Black spheres are Bi or Pb, cyan spheres are Ti, and orange spheres are O.

The goal of this work is to explore whether there is any thermodynamic evidence for displacive disorder in Bi$_2$Ti$_2$O$_7$ driven by geometric frustration on the pyrochlore lattice. [15, 16] Frustration of ferromagnetic Ising spins in compounds with the pyrochlore crystal structure are well known, [17, 18] with analogies having been drawn with the problem of hydrogen positions in the crystal structure of cubic ice $I_c$, with its associated residual entropy. [19] A similar analogy between ice and putative polar pyrochlores was suggested in reference [15] that Bi$_2$Ti$_2$O$_7$ may be a manifestation of “charge ice”. We emphasize that this disorder is expected to be driven by purely geometrical considerations and develop on well-ordered crystalline lattices, so this “charge ice” structure should be distinguished from the “charge glass” state observed in structurally disordered La$_2$Cu$_{1-x}$Li$_x$O$_4$ and La$_{2-x}$Sr$_x$NiO$_4$. [20]

In order investigate the role of disorder on the low temperature heat capacity in crystalline systems we have measured the specific heat of Bi$_2$Ti$_2$O$_7$, two isostructural compounds
Y$_2$Ti$_2$O$_7$ and Bi$_2$NbInO$_7$, as well as the ferroelectrics PbTiO$_3$ and Bi$_4$Ti$_3$O$_{12}$. Coherent lone pair displacements in the latter two systems produce a ferroelectric ground state, which suggests that residual displacive disorder should be minimal. The compound Y$_2$Ti$_2$O$_7$ unlike the four others, has no lone pairs on the A site and can be expected to display the least disorder. All the samples are white to light yellow and highly electrically insulating in powder form.

The polycrystalline samples studied here, with the exception of Bi$_2$Ti$_2$O$_7$, were prepared by ceramic routes and phase purity was verified using powder X-ray diffraction. Perovskite PbTiO$_3$ was prepared from PbO and TiO$_2$, with a 5% stoichiometric excess of PbO to balance losses due to volatilization. Pyrochlore Y$_2$Ti$_2$O$_7$ was prepared from Y$_2$O$_3$ and TiO$_2$. The Aurivilius phase Bi$_4$Ti$_3$O$_{12}$ was obtained from appropriate stoichiometric starting ratios of Bi$_2$O$_3$ and TiO$_2$. Bi$_2$InNbO$_7$ was prepared by reacting appropriate stoichiometric amounts of Bi$_2$O$_3$, Nb$_2$O$_5$, and In$_2$O$_3$, following the method reported by Zhou et al.\textsuperscript{[13]} The Bi$_2$Ti$_2$O$_7$ sample used in this study was prepared by low temperature routes and previously subject to neutron structure determination.\textsuperscript{[9]} All specific heat measurements were carried out on Quantum Design Physical Properties Measurement Systems (PPMS). We used different techniques to extract the low temperature specific heat of these compounds. The Bi$_2$Ti$_2$O$_7$, PbTiO$_3$, and Bi$_4$Ti$_3$O$_{12}$ powders were pressed into dense pellets, mounted to a calorimeter with thermal grease. The Bi$_2$NbInO$_7$ powder was cold sintered with Ag powder, with the specific heat contribution from the silver measured separately and subtracted. The specific heat of Y$_2$Ti$_2$O$_7$ was measured both by mixing the loose powder with a small amount of thermal grease then compacted between aluminum plates with weighing paper and also by pressing it in a 1:1 ratio with silver. Both techniques yielded quantitively similar results, so we present only the data from Y$_2$Ti$_2$O$_7$ mixed with thermal grease. The Bi$_2$Ti$_2$O$_7$ and Y$_2$Ti$_2$O$_7$ samples were separately measured down to 0.5 K using a PPMS system equipped with a $^3$He refrigerator, with the relaxation measured over two time-constants.

The specific heat capacities for all five samples are shown in FIG. 2(a). In order to more clearly emphasize the low energy features in the system, giving rise to specific heat in excess of the Debye contribution, we have plotted the specific heat as $C/T^3$ versus $T$. All samples show a maximum when plotted in this manner, with the amplitude of the peak increasing monotonically with decreasing peak temperature. This peak indicates that the specific heat of these crystalline samples exceeds the Debye C(T) at low temperatures, and are consistent
FIG. 2: (color on-line) (a) Temperature dependence of the low temperature specific heat (plotted as $C/T^3$ versus $T$) for the five samples studied in this contribution. The values are per mole of the A-site atoms in the different formulae. For all samples, the values of $C/T^3$ in excess of about $0.5 \text{mJ mole}^{-1} \text{K}^{-4}$ are contributions not accounted for by the Debye model. (b) Scaled plots: $C/T^3/P_C$ as a function of the scaled temperature $T/T_M$.

with previous measurements on crystalline PbTiO$_3$, which has been shown to exhibit a peak at $T_M = 15 \text{K}$.

As $Y_2Ti_2O_7$ and Bi$_2Ti_2O_7$, have the same crystal structure, one would expect that both compounds should exhibit similar vibrational DOS. Contrary to this expectation, we find that Bi$_2Ti_2O_7$ has a much larger low energy density of states, which is partly due to the larger mass of Bi compared to Y. This larger mass cannot, however, fully explain the appearance of a low-energy peak; we attribute this excess heat capacity to the presence of disorder among Bi lone pairs. The lower temperature for the Bi$_2Ti_2O_7$ peak relative to the $Y_2Ti_2O_7$ peak is consistent with increasing disorder in the Bi pyrochlore arising from lone pair displacements, as discussed in more detail in the following. The other pyrochlore compound studied here, which is also expected to displacive disorder on the A site, Bi$_2NbInO_7$, shows a relatively large, low-temperature peak in $C/T^3$, although the amplitude of the peak, $P_C$ is smaller, and the temperature $T_M$ at which the peak maximum is found is higher that Bi$_2Ti_2O_7$. 


In order to compare the excess specific heat in the two pyrochlore compounds with other crystalline lone-pair active systems, we have also measured the low temperature specific heat of PbTiO$_3$ and Bi$_4$Ti$_3$O$_{12}$. It is seen in FIG.2(a) that these compounds also display a distinct peak in $C/T^3$, although the peaks fall at higher energy, and are smaller in magnitude than the peaks displayed by the two pyrochlore compounds with displacive disorder. The distinct difference in the excess specific heat of the lone-pair disordered compounds, Bi$_2$Ti$_2$O$_7$ and Bi$_2$NbInO$_7$ from the lone-pair ordered compounds, PbTiO$_3$ and Bi$_4$Ti$_3$O$_{12}$ is seen in the scaled $C/T^3$ vs. $T$ plots displayed FIG.2(b). The scaling was performed with respect to the individual peaks, $P_C$ at which $C/T^3$ is maximum, and the temperature $T_M$ where the maximum is found. While materials having both ordered and disordered distortions exhibit a specific heat peak, the lone-pair disordered compounds display a distinctly greater width in the distribution of the excess specific heat. This increase in the scaled full width half maximum (FWHM) of the Bi$_2$Ti$_2$O$_7$ and Bi$_2$NbInO$_7$ curves indicates that the modes contributing to the excess entropy in these materials have a wider distributions of energies than in the ordered compounds. As a reference, the curve computed for a single mode Einstein oscillator is plotted as a solid line in FIG.2(b). The relative width of this excess heat capacity peak, plotted on a semilog scale and measured at 70% of the maximum value, increases from 0.36 for PbTiO$_3$ to 0.71 for Bi$_2$NbInO$_7$ and 1.05 for Bi$_2$Ti$_2$O$_7$. This increase is similar to the broadening of the $C/T^3$ maximum in amorphous SiO$_2$ relative to crystalline SiO$_2$[22], and can be associated with increasing disorder of the lone pair electrons in Bi$_2$NbInO$_7$ and Bi$_2$Ti$_2$O$_7$.

To quantitatively investigate these peaks, we fit the specific heat in FIG.3 to the sum of a Debye contribution ($C_D$), with two additional low energy Einstein modes ($C_E$). This is equivalent to supposing that the VDOS can be modeled by a delta function as it crosses the Debye DOS, rather than the finite jump expected for van Hove singularities in 3D crystals. We included two separate Einstein modes as FIG.2(b) indicates that the excess heat capacity cannot be fit by a single mode. While simplistic, this model allows us to relate the thermodynamic anomaly to microscopic properties in the samples. For all crystalline samples included in this study (Bi$_2$Ti$_2$O$_7$, Y$_2$Ti$_2$O$_7$, PbTiO$_3$, Bi$_2$NbInO$_7$, and Bi$_4$Ti$_3$O$_{12}$) we found that a suitable fit could be obtained using a Debye temperature of $\theta_D = 280$ K. This emphasizes that the underlying lattice heat capacities of these different samples are similar, so that the significant differences in the low temperature heat capacities should be
FIG. 3: (color on-line) Fits to the specific heat of Bi$_2$Ti$_2$O$_7$ using a combinations of Debye and Einstein modes, as described in the text. Data for Y$_2$Ti$_2$O$_7$ are seen to be almost completely fit by the single Debye mode using the same value of $\Theta_D$ used for Bi$_2$Ti$_2$O$_7$.

attributed to differences in the lone pair electron behaviour.

The low temperature $C(T)$ can be modeled as a sum of Debye and Einstein terms with each Einstein oscillator giving a contribution:

$$C_E = pR \frac{(\hbar \omega_0/k_BT)^2 e^{\hbar \omega_0/k_BT}}{(e^{\hbar \omega_0/k_BT} - 1)^2}$$

(1)

to the specific heat. In this expression, $p$ is the spectral weight, $R$ the gas constant, and $\hbar \omega_0$ the mode energy. For Bi$_2$Ti$_2$O$_7$ the first excitation has an energy of $E_1 = 2.3$ meV and an oscillator strength of $p_1 = 0.32$, while the second excitation falls at $E_2 = 5.5$ meV and has an oscillator strength of $p_2 = 2$. Similar fits were obtained for the other samples. We find that Bi$_2$Ti$_2$O$_7$ has the lowest energy oscillator. The values of the oscillator strengths and energies for the different samples are given in Table I. We find that $\hbar \omega_0$ for the lowest energy mode in these fits depends linearly on the temperature of the peak. Motivated by this result, which, within the constraints of our simple model, confirms that the peak temperature and vibrational mode frequencies are linearly related, we will discuss our data solely in terms of the peak temperature. This assumption allows us to avoid specific details of the fitting parameters, allowing a more general and robust analysis of the results.

To more clearly demonstrate the influence of increasing disorder on the $C/T^3$ peak in
TABLE I: Energies and number of oscillators used in fitting Einstein modes to the specific heats of the different compounds.

| Compound          | $E_1$ (meV) | $p_1$ | $E_2$ (meV) | $p_2$ |
|-------------------|-------------|-------|-------------|-------|
| Bi$_2$Ti$_2$O$_7$ | 2.3         | 0.32  | 5.5         | 2     |
| Bi$_4$Ti$_3$O$_{12}$ | 3.6     | 0.7   | 6.7         | 5     |
| Bi$_2$NbInO$_7$  | 2.8         | 0.27  | 6           | 1.6   |
| PbTiO$_3$        | 5.5         | 0.4   | 8           | 1.5   |

heat capacity in crystalline materials, we compare our measurements with some other low temperature heat capacity studies on ordered and disordered crystals. We plot the excess low temperature heat capacity as $C/T^3$ versus $\ln T$ for amorphous SiO$_2$ and crystalline quartz in FIG. 4(a), taken from Ref. [23], and for Bi$_4$Ti$_3$O$_{12}$ and Bi$_2$Ti$_2$O$_7$ in FIG. 4(b).

The lattice disorder present in amorphous SiO$_2$ leads to a reduction in temperature of the excess $C/T^3$ heat capacity peak as compared to structurally well-ordered quartz; this peak shift is a signature of increasing disorder in otherwise similar systems. Qualitatively, this is similar to the shift in peak temperature between Bi$_4$Ti$_3$O$_{12}$ and Bi$_2$Ti$_2$O$_7$, despite the fact that both of these materials are crystalline and have very similar Debye temperatures and elemental constituents, and hence bare oscillator spectral weights, that are roughly the same. These measurements provide thermodynamic justification to support the suggestion that crystalline Bi$_2$Ti$_2$O$_7$ has additional disorder as compared to Bi$_4$Ti$_3$O$_{12}$.

Because there is no evidence for any lattice disorder in Bi$_2$Ti$_2$O$_7$, the presence of a low-temperature $C/T^3$ peak provides empirical evidence suggesting that the lone pair electrons on Bi are disordered due to geometrical frustration, consistent with previous XRD studies[9]. Increasing disorder in other crystalline systems has been observed to shift this heat capacity peak to lower temperatures, including oxides with chemical site disorder, such as Ca replacing Sr in the CaSrFeCoO$_5$ brownmillerite[24]. This disorder-induced shift is also observed in metallic systems, although the size of the effect may be significantly smaller than in insulators[8]. It has also been noted that geometrical frustration present in systems having underconstrained degrees of freedom, such as ZrW$_2$O$_8$, can also lead to excess low temperature heat capacity in crystalline systems[25]. These results suggest that the downshift of the specific heat peak in displacively disordered, but still crystalline, Bi$_2$Ti$_2$O$_7$ may be
FIG. 4: (color on-line) (a) $C/T^3$ versus $\ln T$ amorphous SiO$_2$ and quartz\textsuperscript{[23]}, (c) $C/T^3$ versus $\ln T$ for Y$_2$Ti$_2$O$_7$ (squares) and Bi$_2$Ti$_2$O$_7$ (stars).

associated with the development of a frozen “charge-ice” state in these systems driven by geometrical frustration, rather than the frozen glassy state associated with structural disorder. Furthermore, by investigating the detailed phonon density of states in Bi$_2$Ti$_2$O$_7$ and isostructural Y$_2$Ti$_2$O$_7$ and correlating these results with heat capacity data, it may be possible to gain insight into the microscopic mechanisms giving rise to excess low temperature entropy in disordered systems.

In summary, we find that several insulating crystalline materials with lone pairs, and with the pyrochlore, perovskite, and Aurivillius crystal structures, exhibit an excess low temperature specific heat above the Debye background. The specific heat peaks in pyrochlores Bi$_2$Ti$_2$O$_7$ and Bi$_2$NbInO$_7$ are however, distinctly broader and stronger, and are found to appear at lower temperatures than those of isostructural Y$_2$Ti$_2$O$_7$ and compounds showing coherent coherent lone pair displacements (PbTiO$_3$ and Bi$_4$Ti$_3$O$_{12}$). We attribute this suppression of the excess specific heat to the presence of additional disorder in Bi$_2$Ti$_2$O$_7$ and Bi$_2$NbInO$_7$ arising from incoherent frozen displacements of the Bi lone pair electrons. This suggests that Bi$_2$Ti$_2$O$_7$ may be an example of a structurally well-ordered system with charge disorder introduced by geometrical frustration on the pyrochlore lattice.
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