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Large low-temperature specific heat in pyrochlore $Bi_2Ti_2O_7$

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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 $Bi_2Ti_2O_7$, we have measured the specific heat of crystalline $Bi_2Ti_2O_7$ and related compounds. We find that the peak in C/T^3 versus T in $Bi_2Ti_2O_7$ falls at a substantially lower temperature than other similar compounds consistent with the presence of disorder. This thermodynamic evidence for disorder in crystalline $Bi_2Ti_2O_7$ is consistent with quenched configurational disorder among Bi lone pairs produced by the 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 2–30 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[1] and from inelastic neutron scattering,[2] where they give rise—in glasses—to the so-called "boson peak."[3,4] 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.[5–7]

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.[8] 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 is similar.[5] 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 $Bi_2Ti_2O_7$ 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 $Bi_2Ti_2O_6O'$ 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 stereochemical activity is what drives the phase transition to a coherent, polar, and tetragonal ground state in $PbTiO_3$. The related pyrochlore compound $Bi_2Ti_2O_6O'$ (more simply referred to as $Bi_2Ti_2O_7$) shows no such phase transition and, even at 2 K, the crystal structure is cubic.[9] 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 that the Bi ions

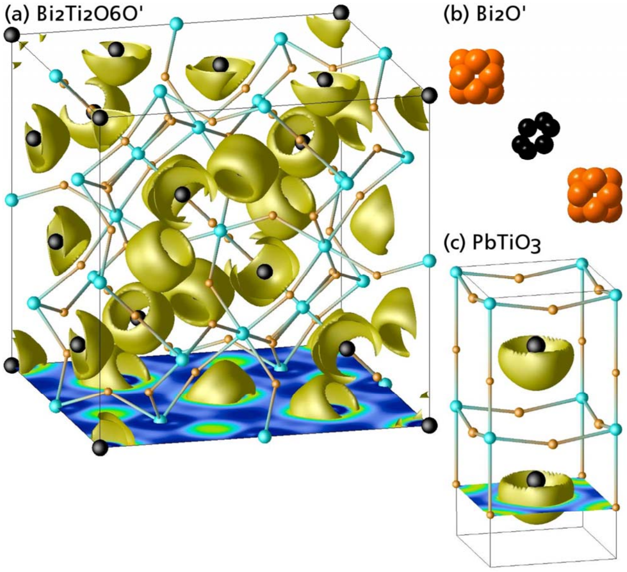

FIG. 1. (Color online) (a) Structure of ideal $Bi_2Ti_2O_6O'$. The $6s^2$ lone pair around Bi^{3+} atoms is visualized using the valence electron localization function (ELF) with isosurfaces value of 0.625, following methods presented in Ref. 15. (b) Split atom positions of Bi and O′ (50% isotropic thermal ellipsoids displayed) as obtained from Rietveld refinement of powder neutron-diffraction data indicative of local displacive disorder, following Ref. 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 (corners of panel (a) center of panel (b)) or Pb (center of panel (c)), cyan spheres are Ti (edges of panel (a) and corners of panel (c)), and orange spheres are O.

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are displaced randomly into one of several distinct—but symmetric—sites about the equilibrium position as indicated in Fig. 1(b).[9–14]

The goal of this work is to explore whether there is any thermodynamic evidence for the displacive disorder in $Bi_2Ti_2O_7$ driven by geometric frustration on the pyrochlore lattice.[15,16] Frustration of ferromagnetic Ising spins in compounds with the pyrochlore crystal structure is well known,[17,18] with analogies having being 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 Ref. 15, namely, that $Bi_2Ti_2O_7$ may be a manifestation of charge ice. Some evidence for this disordered state was obtained by structural studies on niobate pyrochlores, in which Y_2NbTiO_7 shows evidence for frustrated displacements of Nb ions along the local $\langle 111 \rangle$ directions, while the isostructural d^0 compound La_2ScNbO_7 exhibits no such disorder.[16] 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 $La_2Cu_{1-x}Li_xO_4$ and $La_{2-x}Sr_xNiO_4$.[20]

In order to investigate the role of disorder on the low-temperature heat capacity in crystalline systems, we have measured the specific heat of $Bi_2Ti_2O_7$, two isostructural compounds $Y_2Ti_2O_7$ and Bi_2NbInO_7, as well as the ferroelectrics $PbTiO_3$ and $Bi_4Ti_3O_{12}$. Coherent lone pair displacements in the latter two systems produce a ferroelectric ground state, which suggests that the residual displacive disorder should be minimal. The compound $Y_2Ti_2O_7$, 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 a powdered form.

The polycrystalline samples studied here, with the exception of $Bi_2Ti_2O_7$, were prepared by ceramic routes and phase purity was verified using powder x-ray diffraction. Samples of $PbTiO_3$ were prepared by heating well-ground mixtures of PbO and TiO_2 with a 5% excess of PbO to account for the high vapor pressure of Pb at 1000 °C for 16 h followed by regrinding, pelletizing, and sintering at 1000 °C for 16 h. The resulting product was pale yellow. Samples of $Y_2Ti_2O_7$ were prepared from Y_2O_3 and TiO_2 by heating well-ground mixtures of the appropriate stoichiometric ratio pressed into pellets at 1400 °C for 12 h. The resulting product was white. Samples of $Bi_4Ti_3O_{12}$ were prepared from Bi_2O_3 and TiO_2 by heating well-ground mixtures of the appropriate stoichiometric ratio initially at 1000 °C for 24 h followed by regrinding, pelletizing, and sintering at 1150 °C for 36 h. The resulting product was pale yellow. Bi_2InNbO_7 was prepared by reacting appropriate stoichiometric amounts of Bi_2O_3, Nb_2O_5, and In_2O_3, following the method reported by Zhou *et al.*[13] The $Bi_2Ti_2O_7$ sample used in this study was prepared by low-temperature routes and was previously subjected to neutron structure determination.[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 $Bi_2Ti_2O_7$, $PbTiO_3$, and $Bi_4Ti_3O_{12}$ powders were pressed into dense pellets mounted to a calorimeter with thermal grease. The Bi_2NbInO_7 powder was cold sintered with Ag powder, with the specific-heat contribution from the silver measured separately and subtracted. The specific heat of $Y_2Ti_2O_7$ 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 $Y_2Ti_2O_7$ mixed with thermal grease. The $Bi_2Ti_2O_7$ and $Y_2Ti_2O_7$ 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.

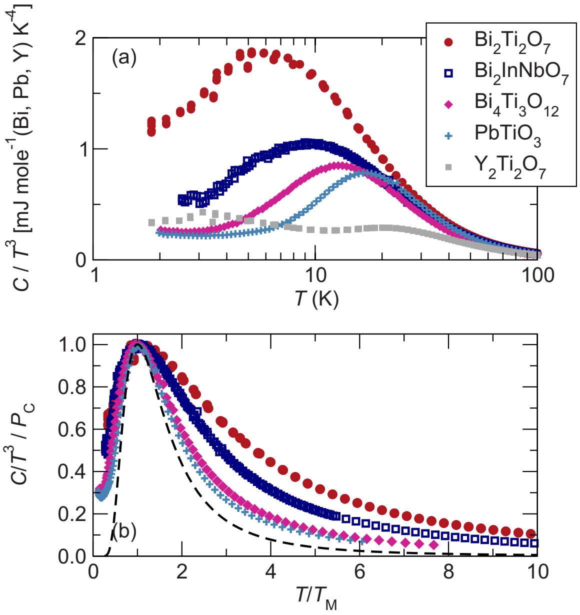

FIG. 2. (Color online) (a) Temperature dependence of the low-temperature specific heat (plotted as C/T^3 versus T) for the five samples studied in this contribution. The values are per mole of the *A*-site atoms in the different formulae. For all samples, the values of C/T^3 in excess of about 0.5 mJ mol^{-1} 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.

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 with previous measurements on crystalline $PbTiO_3$, which has been shown to exhibit a peak at $T_M = 15$ K.[21]

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 develop 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 than $Bi_2Ti_2O_7$.

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 $Bi_4Ti_3O_{12}$. 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 $Bi_2Ti_2O_7$ and Bi_2NbInO_7 from the lone-pair-ordered compounds $PbTiO_3$ and $Bi_4Ti_3O_{12}$ is seen in the scaled C/T^3 vs T plots displayed in 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 of the $Bi_2Ti_2O_7$ and Bi_2NbInO_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_2NbInO_7 and 1.05 for $Bi_2Ti_2O_7$. This increase is similar to the broadening of the C/T^3 maximum in amorphous SiO_2 relative to crystalline SiO_2 (Ref. 22) and can be associated with increasing disorder in the lone pair electrons in Bi_2NbInO_7 and $Bi_2Ti_2O_7$.

While the main results of this paper focus on the observation that the peak in C/T^3 falls at qualitatively lower temperatures in $Bi_2Ti_2O_7$ and Bi_2NbInO_7 as compared to $Y_2Ti_2O_7$, $PbTiO_3$, and $Bi_4Ti_3O_{12}$, we briefly discuss some quantitative considerations in the following. The heat capacity for Bi_2NbInO_7 was estimated by measuring the total heat capacity for this sample mixed with silver powder and then subtracting the silver heat capacity. The contribution of the silver powder represents a significant fraction of the combined heat capacity, reaching just over 50% of the total. While subtracting this large background leads to some additionally uncertainty in the magnitude of the low-temperature heat capacity of the Bi_2NbInO_7 heat capacity, this is not expected to affect our main results. Specifically, the heat capacity for pure silver plotted as C/T^3 versus ln T is flat over the temperature range of the Bi_2NbInO_7 peak and shows a very small feature only above $T=20$ K.

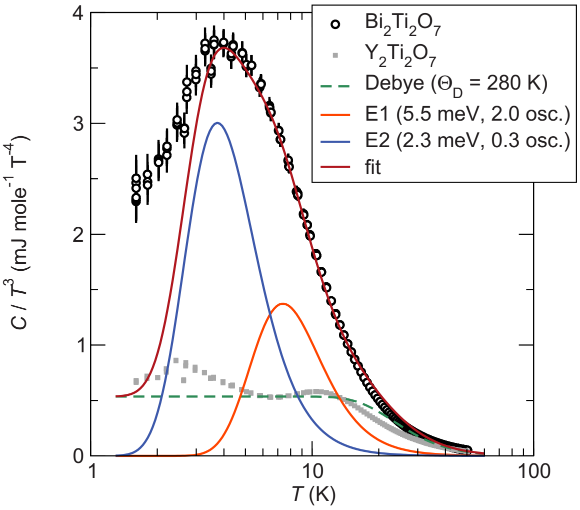

FIG. 3. (Color online) Fits to the specific heat of $Bi_2Ti_2O_7$ using a combination of Debye and Einstein modes, as described in the text. Data for $Y_2Ti_2O_7$ are seen to be almost completely fit by the single Debye mode using the same value of Θ_D used for $Bi_2Ti_2O_7$.

To quantitatively investigate these peaks in more detail, 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 three-dimensional crystals. We included two separate Einstein modes as Fig. 2 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. The low-temperature Debye temperature estimated for these materials ranged from roughly $\theta_D=240$ to 300 K. However, since the temperature range of interest falls below $\theta_D/10$, the Debye contribution is flat in this region, and the precise value used only negligibly affects the fit parameters. We also include an estimate of the uncertainty in our data in Fig. 3. This uncertainty was derived assuming an error of 2% in the heat-capacity measurement with a temperature uncertainty of 0.05 K.

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

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

to the specific heat. In this expression, p is the spectral weight, R is the gas constant, and $\hbar\omega_0$ is the mode energy. For $Bi_2Ti_2O_7$, 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 $p_2=2$. There is some uncertainty in the optimal fit values, particularly, for the higher-energy modes. Similar fits were obtained for the other samples. The values of the oscillator strengths and energies for the different samples are given in Table I. The parameters quoted indicate the values

TABLE I. Energies and number of oscillators used in fitting Einstein modes to the specific heats of the different compounds.

	E_1 (meV)	p_1	E_2 (meV)	p_2
$Bi_2Ti_2O_7$	2.3 ± 0.2	0.32 ± 0.08	5.5 ± 0.5	2 ± 0.5
$Bi_4Ti_3O_{12}$	3.6 ± 0.3	0.5 ± 0.15	6.7 ± 1.2	5 ± 1
Bi_2NbInO_7	2.8 ± 0.2	0.27 ± 0.07	6 ± 1	1.6 ± 0.5
$PbTiO_3$	5.5 ± 0.7	0.4 ± 0.1	8 ± 1.2	1.5 ± 0.5

that give the best fit by eye, with the estimated uncertainties reflect the extent to which this values can be changed while still yielding reasonable—although noticeably lower-quality—fits. We find that $Bi_2Ti_2O_7$ has the lowest-energy oscillator, falling significantly below isostructural $Y_2Ti_2O_7$ and $Bi_4Ti_3O_{12}$, having the same elemental composition. 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 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 $Bi_4Ti_3O_{12}$ and $Bi_2Ti_2O_7$ 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 the peak temperature between $Bi_4Ti_3O_{12}$ and $Bi_2Ti_2O_7$ 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 $Bi_2Ti_2O_7$ has additional disorder as compared to $Bi_4Ti_3O_{12}$.

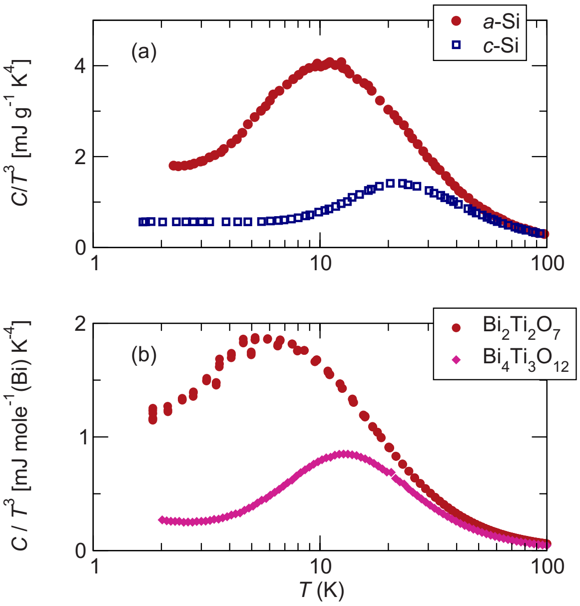

FIG. 4. (Color online) (a) C/T^3 versus ln T amorphous SiO_2 and quartz (Ref. 23), (b) C/T^3 versus T for $Bi_4Ti_3O_{12}$ (diamonds), and $Bi_2Ti_2O_7$ (circles).

Because there is no evidence for any lattice disorder in $Bi_2Ti_2O_7$, 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 x-ray diffraction 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 the geometrical frustration present in systems having underconstrained degrees of freedom, such as ZrW_2O_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 $Bi_2Ti_2O_7$ may be 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. Evidence for a similar electrically induced geometrically frustrated state has been observed in neutron studies of the niobate pyrochlores.[16] By investigating the detailed phonon density of states in $Bi_2Ti_2O_7$ and isostructural $Y_2Ti_2O_7$ 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 $Bi_2Ti_2O_7$ and Bi_2NbInO_7 are, however, distinctly broader and stronger and are found to appear at lower temperatures than those of isostructural $Y_2Ti_2O_7$ and compounds showing coherent lone pair displacements ($PbTiO_3$ and $Bi_4Ti_3O_{12}$). We attribute this suppression of the excess specific heat to the presence of additional disorder in $Bi_2Ti_2O_7$ and Bi_2NbInO_7 arising from incoherent frozen displacements of the Bi lone pair electrons. This suggests that $Bi_2Ti_2O_7$ may be an example of a structurally well-ordered system with charge disorder introduced by the geometrical frustration on the pyrochlore lattice.

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