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$M_{3-x}(NH_4)_xCrO_8$ (M = Na, K, Rb, Cs): A New Family of Cr^{5+}-Based Magnetic Ferroelectrics

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S *Supporting Information*

ABSTRACT: Upon consideration of the hydrogen-bonding properties of the NH_4^+ cation, we synthesized a new class of compounds, $M_{3-x}(NH_4)_xCrO_8$ (M = Na, K, Rb, Cs). These magnetic compounds with the simple $3d^1$ ground state become ferroelectric. X-ray studies confirmed that the phase transition involves a symmetry change from $I\bar{4}2m$ to $Cmc2_1$ to $P1$. The transition temperature depends linearly on the composition variable x. The transitions are of the order–disorder type, with N–H···O bonding playing the central role in the mechanism. Extension of this idea to the introduction of ferroelectricity in several other classes of materials is suggested.

The discovery of new multiferroic materials, compounds that exhibit both magnetic and electrical ordering, is an area of high current interest in part because multiferroics offer a fundamentally new method of data storage and manipulation.[1] Most of the known multiferroic materials are based on transition-metal oxides, mainly of the perovskite family ABO_3, where A is a divalent metal that is usually in a diamagnetic oxidation state and B is a paramagnetic metal in a tetravalent state. The perovskite-based multiferroic field has been recently extended to compounds known as metal–organic frameworks.[2] An important component of these systems is a molecule or ion that exhibits dynamic disorder at high temperatures but slows down and becomes ordered below a particular temperature T_c, leading to long-range order with electric polarization (i.e., ferroelectricity).[2]

In an attempt to open up a new avenue of multiferroic materials, we have investigated compounds of Cr in its (unusual) pentavalent oxidation state. These are compounds with the formula M_3CrO_8, (M = NH_4^+, Na^+, K^+, Rb^+, Cs^+), which have been known for over a century[3,4] but have only recently been reported as antiferromagnets with novel quantum critical spin dynamics.[5,6] To look for ferroelectric characteristics in these materials, we first focused on $(NH_4)_3CrO_8$,[7] because many ionic salts of the NH_4^+ ion are ferroelectric, while the corresponding ones with alkali-metal ions are not.[8] An example is $(NH_4)_2SO_4$ versus K_2SO_4: the former exhibits ferroelectricity below ~225 K, while the latter is essentially inert.[8] $(NH_4)_3CrO_8$ indeed exhibited ferroelectricity below 250 K, a rather elevated temperature. We then surmised that perhaps ferroelectric behavior could be induced in the other members by substituting the alkali metal with NH_4^+. As shown below, this was indeed found to be the case for several new mixed lattices $M_{3-x}(NH_4)_xCrO_8$. Variable-temperature single-crystal X-ray diffraction (XRD) studies showed that the ferroelectric transitions involve a lowering of the lattice symmetry via N–H···O hydrogen bonding. The transition temperature varied linearly with x, the composition ratio of the NH_4^+ ion, suggesting that the transition mechanism is based on the cooperativity of hydrogen bonding, providing a possible avenue for optimizing the ferroelectric properties.

Preparation of the title compounds was accomplished by the reaction of H_2O_2 with an ice-cold solution of basic CrO_3, as described previously.[3,5] The mixed compounds $M_{3-x}(NH_4)_3CrO_8$ were prepared by using the appropriate molar concentrations of the alkali-metal hydroxide and NH_4OH bases. Single crystals were grown by slow cooling, and their authenticity was ascertained using single-crystal XRD at various temperatures down to 100 K and powder XRD down to 6 K. Dielectric measurements were made using a standard ac bridge with an attachment for variable-temperature measurements. For the spontaneous polarization measurements, samples were poled through the phase transition temperatures at an electric field of 25 kV/cm. A Quantum Design Physical Properties Measurement System (PPMS) was used to measure the temperature dependence of the magnetic susceptibility and specific heat (C_p) at constant pressure.

Figure 1a depicts the structure of the $3d^1$ CrO_8^{3-} ion, which is the source of paramagnetism in these lattices. Figure 1b–e show schematics of the crystal structures of $(NH_4)_3CrO_8$, Rb_3CrO_8, $Rb_{1.36}(NH_4)_{1.64}CrO_8$, and $Cs(NH_4)_2CrO_8$, respectively. At room temperature, all of the crystals crystallize in the tetragonal space group $I\bar{4}2m$. It is known that the M_3CrO_8 compounds with M = Na, K, Rb, Cs (or their alloys) exhibit antiferromagnetic phase transitions only at cryogenic temperatures (below 3 K).[5,6] On the other hand, in our preliminary search, $(NH_4)_3CrO_8$ was found[7] to exhibit a structural phase transition at 137 K, but no further attempts to search for ferroelectricity were made at that time. We thus first investigated $(NH_4)_3CrO_8$ for its dielectric behavior, because as mentioned earlier, other types of NH_4^+-containing lattices exhibit a multitude of dynamic phenomena and even ferroelectricity.[8]

Before examining the dielectric properties of $(NH_4)_3CrO_8$, we measured its heat capacity, since all ferroelectric transitions exhibit peaks in heat capacity as well.[8] As Figure 2a,b shows, $(NH_4)_3CrO_8$ exhibits at least two peaks (i.e., phase transitions), at T_{c1} = 250 K and T_{c2} = 137 K, whereas Rb_3CrO_8 shows none. Figure 2c,d depicts the effect of substituting Rb^+ and Cs^+ with NH_4^+: $Rb_{1.36}(NH_4)_{1.64}CrO_8$ and $Cs(NH_4)_2CrO_8$ exhibit peaks at 147 and 158 K, respectively, documenting that the replacement

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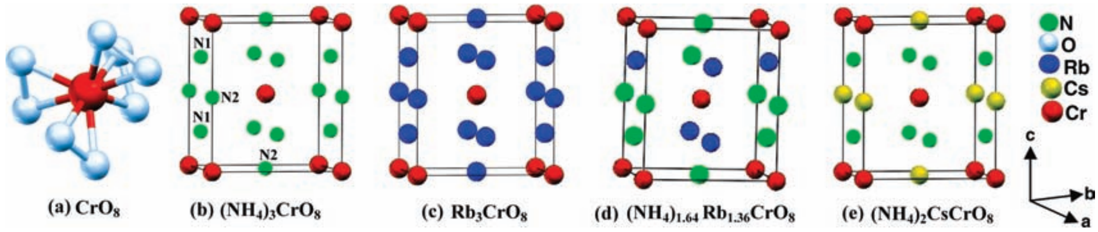

Figure 1. Structures of (a) peroxychromate, CrO_8^{3-}, having a $3d^1$ paramagnetic core; (b) $(NH_4)_3CrO_8$; (c) Rb_3CrO_8; (d) $Rb_{1.36}(NH_4)_{1.64}CrO_8$; and (e) $Cs(NH_4)_2CrO_8$. H and O atoms have been omitted for clarity. In (d), NH_4^+ ions occupy the N2 sites, whereas the N1 sites are shared by Rb^+ and NH_4^+ ions in a 2:1 ratio because of their comparable sizes. In (e), however, the NH_4^+ ions occupy the N2 sites with double occupancy at four faces, but because of its larger size, Cs^+ occupies the slightly larger N1 sites on the edges and the top and bottom faces.

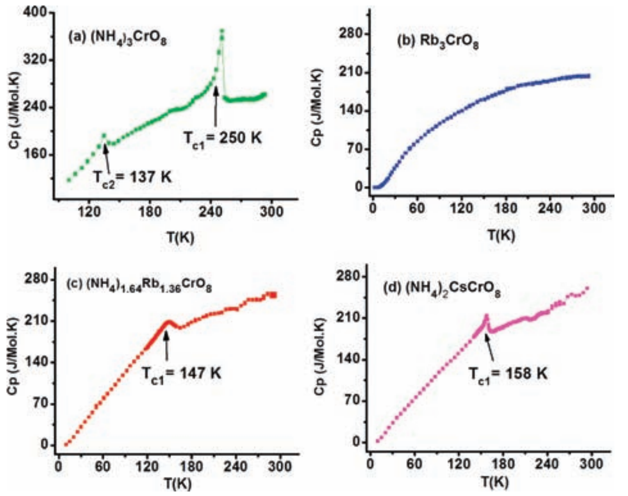

Figure 2. Temperature dependence of the heat capacities of the various $M_{3-x}(NH_4)_xCrO_8$ lattices.

of M^+ by NH_4^+ induces phase transitions. Notably, the transition temperature T_c increases in proportion to the relative amount of NH_4^+ to M^+ ions in the formula (see Figure 5).

The clear λ-type shape of the C_p peak for $(NH_4)_3CrO_8$ provided a clue to the nature of the phase transition: a typical order−disorder type. A good test for such a mechanism is that the transition entropy ΔS should be $R \ln n$, where n is the number of sites between which the molecular entity hops in the disordered phase. Thus, ΔS over each peak was calculated by graphing C_p/T versus T and then integrating, as $\Delta S = \int (C_p/T)\, dT$. For the 250 K peak in $(NH_4)_3CrO_8$, the value of ΔS was found to be 5 ± 0.05 J mol^{-1} K^{-1}. For a two-state order−disorder mixed system, the theoretical value of ΔS is $R \ln 2 = 5.76$ J/mol K.[8] Our experimental ΔS lies within ~15% of this value, strongly suggesting that the 250 K peak corresponds to the dynamical slowing (below 250 K) of the correlated motion of the NH_4^+ and CrO_8^{3-} ions between two sites as a result of hydrogen-bonding effects (see below).

To examine whether the transitions induced by NH_4^+ induce ferroelectricity, we measured the dielectric constant. Figure 3a shows the temperature dependence of ε' for $(NH_4)_3CrO_8$. A sharp λ-type peak at 250 K implying a dielectric phase transition at $T_c = 250$ K, together with other anomalies at lower temperatures, can be clearly seen. In this report, we focus only on the 250 K transition, since this transition shows clear signs of ferroelectric behavior. The T_c value of 250 K is in full agreement with the C_p data in Figure 2a. Definitive evidence of ferroelectricity

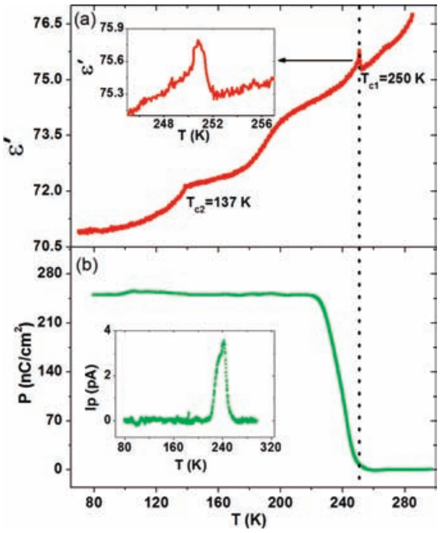

Figure 3. Temperature dependence of (a) dielectric constant and (b) spontaneous polarization of $(NH_4)_3CrO_8$. The insets in (a) and (b) respectively, show the dielectric anomaly and the critical behavior of the pyroelectric current in the vicinity of the phase transition temperature.

(or antiferroelecity) is the observation of a pyroelectric current below the T_c of a lattice.[8] Figure 3b shows the pyroelectric data: the pyroelectric coefficient γ and spontaneous polarization P_s exhibited sharp increases below 250 K when a constant heating rate was applied, as expected for a ferroelectric phase transition. A maximum polarization of 0.25 $\mu C/cm^2$ was obtained, which is comparable to those of other known ferroelectrics of similar kind.[8] The observation of the λ shape of the dielectric anomaly and the typical shape of the polarization curve are clear evidence of a ferroelectric transition.

To examine the transition mechanism at the atomic level, detailed variable-temperature powder diffraction measurements were made down to 6 K. As shown in Figure 4a, at 250 K the 220 Bragg peak splits into two peaks (indexed as 040 and 400), indicating a tetragonal to orthorhombic phase transition at that temperature, in agreement with the transition temperature observed via C_p measurements (Figure 2a). Figure 4b shows the temperature dependence of the lattice constants in the various phases. It can be seen that there is an abrupt change in the crystal symmetry and lattice parameters at 250 K, with the space group being lowered from tetragonal to orthorhombic. The transition temperature is in conformity with the those obtained from the C_p and dielectric data. There is a further

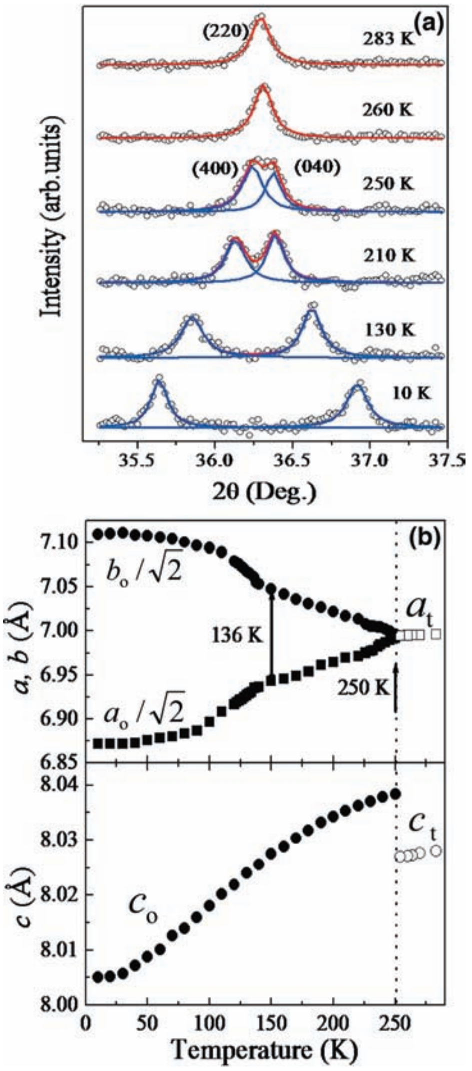

Figure 4. (a) XRD scans of typical peaks (as marked) of $(NH_4)_3CrO_8$ at several temperatures. The 220 Bragg peak splits into 400 and 040 peaks at 250 K. Circles are experimental data, and the red and blue lines are Lorentzian fits. (b) Lattice parameters as functions of temperature.

change at 137 K, as also seen in the specific heat data. However, since the polarization current showed no change at 137 K, this phase transition is strictly structural.

For further details, single-crystal X-ray studies were undertaken at the three temperatures 263, 203, and 123 K, each of which corresponds to a different phase (phases I, II, and III, respectively). The X-ray analysis clearly showed that on cooling below 250 K, the higher-temperature tetragonal phase ($I\bar{4}2m$) changed to the orthorhombic, polar phase $Cmc2_1$. The transition between phases II and III further lowered the symmetry to $P1$. These phase changes were found to be fully reversible with temperature. It can be seen (Figure 1) that phase I consists of two crystallographically independent NH_4^+ groups (containing the nitrogen atoms N1 and N2) and a CrO_8 unit. N1 is located at the $\bar{4}$ symmetry center and N2 at $\bar{4}2m$. There is a considerable difference between the two nitrogen atoms. There are eight N1 sites, located on the four faces (*ac* and *bc* planes) 2.811 Å away from 12 neighboring oxygen atoms. N2 sites are located on the *c* axis and *ab* plane and occupy more space. Each has eight nearest oxygen atoms at 2.964−3.012 Å. Below the phase transition, in phase II, the ammonium group at N1 was found to have a series of N−O distances ranging from 2.796 to 3.24 Å, in contrast to phase I, wherein all these bonds were equal. Similarly, N2 shows N−O bond distances from 2.787 to 3.361 Å. Despite the fact that the X-ray study was (as usual) unable to locate exactly the NH_4^+ H atoms, these results do reveal that there is a significant distortion of the NH_4^+ ion during the phase transition due to the N−H···O bonding. This effect is reminiscent of the mechanism of the well-established antiferroelectric phase transition in $NH_4H_2PO_4$.[8,9]

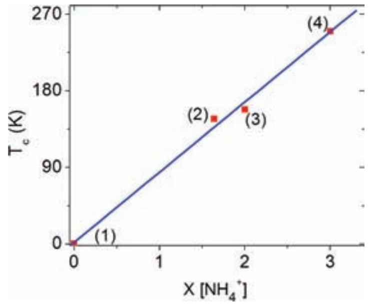

Figure 5. Evidence of the linear increase in the ferroelectric transition temperature, T_c, of M_3CrO_8 as a function of $[NH_4^+]$. Symbols are (1) Rb_3CrO_8, (2) $(NH_4)_{1.64}Rb_{1.36}CrO_8$, (3) $(NH_4)_2CsCrO_8$, and (4) $(NH_4)_3CrO_8$.

Similar X-ray diffraction, heat capacity, and dielectric measurements showed that the mixed lattice of $Rb_{1.36}(NH_4)_{1.64}CrO_8$ exhibits ferroelectricity below 147 K, while $Cs(NH_4)_2CrO_8$ becomes ferroelectric below 158 K (see Figure 2). An important observation was that the plot of T_c versus x in the above-discussed $M_{3-x}(NH_4)_xCrO_8$ lattices is strictly linear, as shown in Figure 5, suggesting that the cooperativity leading to the ferroelectric transitions in these materials indeed arises through the N−H···O hydrogen-bonding interaction. It would thus be of future interest to examine the effect of H → D isotope substitution on T_c and the saturation polarization P_s. The results suggest a possible avenue for creating more desirable characteristics. Such isotope effects are well-known in other ferroelectrics, such as the KH_2PO_4 family.[8]

In summary, we have synthesized a new class of magnetic ferroelectrics through a property-by-design approach, inducing phase transitions and dielectric polarization via hydrogen bonding. This procedure should be effective for generating ferroic characteristics in other families, such as the alkali-metal peroxyniobates (M_3NbO_8) and peroxytantalates (M_3TaO_8).[4] It certainly broadens the scope of the chemistry of Cr in its unusual oxidation states. The idea ought to apply also to the $MCuCl_3$ family (M = alkali metal), which is known to exhibit very unusual transitions (e.g, with quantum steps in magnetization),[10] but to date there are no reports of the observation of any dielectric anomaly. The present study suggests that incorporation of the NH_4^+ ion ought to induce multiferroic character in these exotic magnetic lattices.

■ ASSOCIATED CONTENT

S Supporting Information. Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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