

# Thermomagnetic and Spectroscopic Studies of the Mechanism of Multiferroelectric Behavior in the Cr (V) Peroxychromates $(\text{NH}_4)_3 \text{Cr} (\text{O}_2)_4$ and the Effect of Cation Substitution on the Phase Transition

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**Abstract:** The Cr (V)-based antiferromagnetic compounds  $\text{M}_3 \text{Cr}(\text{O}_2)_4$ ,  $\text{M} = \text{K}, \text{Rb}$  and  $\text{Cs}$ , are known to become ferroelectric when the  $\text{M}$  cation is replaced by the  $\text{NH}_4^+$  ion, but the underlying mechanism is not fully understood. Here we report detailed x-ray structural, heat capacity, dielectric relaxation, polarization current, Raman scattering and variable frequency EPR measurements with a view to understand the mechanism underlying the multiple solid-solid phase transitions in the  $\text{M}_{3-x} (\text{NH}_4)_x \text{Cr}(\text{O}_2)_4$  family. At 295 K,  $(\text{NH}_4)_3 \text{Cr} (\text{O}_2)_4$  crystals exhibit tetragonal ( $I\bar{4}2m$ ) symmetry, with the  $\text{NH}_4^+$  cations occupying two distinctly different sites. At site 1,  $\text{NH}_4^+$  ions have usual tetrahedral symmetry with two equal  $\text{N—H} \dots \text{O}$  distances whereas at site 2, there are orientationally disordered  $\text{NH}_4^+$  ions with a time-averaged (seemingly) *octahedral* site symmetry. Ordering of the  $\text{NH}_4^+$  ions at site 1 leads to a ferroelectric transition at 250 K, followed by slowing down of site 2 cations at 207 K, and finally the third phase transition occurs at 137 K due to the ordering of the  $\text{NH}_4^+$  ions at site 2. The lattice symmetry is lowered to  $Cmc2(1)$  below 250 K. The  $\text{N—H} \dots \text{O}$  bond distances become unequal as a result of hydrogen bonding. Specific heat measurement exhibits a  $\lambda$  type anomaly at 250 K, accompanied by anomalies in dielectric constant and pyroelectric current. High frequency EPR spectra of the  $[\text{Cr}(\text{O}_2)_4]^{3-}$  ion also confirmed the transition temperature of 250 K. Raman studies confirmed the role of the  $\text{NH}_4^+$  ion's rotational and translational modes in the transition mechanism. The transition temperatures of the mixed Rb and Cs compounds vary linearly with the  $\text{NH}_4^+$  content. It is thus seen that the phase transitions are guided by the rotational and translational dynamics of the  $\text{NH}_4^+$  ions..., via hydrogen bonding. The same principles should lead to the development of other classes of multiferroics.