

DIELECTRIC CHARACTERISTICS OF THE AMMONIUM ZINC FORMATE WITH ALKALI METAL DOPING

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Recently, the scientific community has shown significant interest in $[\text{NH}_4][\text{Zn}(\text{HCOO})_3]$ metal-organic framework. Guan-Cheng Xu et al. reported a phase transition from a paraelectric phase (P₆₃₂₂) to a ferroelectric phase (P₆₃) at a temperature of 181 K [1]. Additionally, metal organic frameworks (MOFs) hold promise for magnetism, given the flexibility to modify metal centers, making them potential candidates for single crystal multiferroic materials. Our initial investigations indicated a propensity for alkali metals to diffuse into the $[\text{NH}_4][\text{Zn}(\text{HCOO})_3]$ structure. Consequently, this study aims to explore the impact of potassium impurities on the dielectric properties within the crystal structure of $[\text{NH}_4][\text{Zn}(\text{HCOO})_3]$. Dielectric measurements were conducted within the temperature range of 130 K to 300 K and a frequency range of 10 Hz to 1 GHz, utilizing an HP 4284A LCR meter and Agilent 8714ET vector network analyzer. The crystals were carefully oriented to ensure the electrical field was aligned with the z-axis during measurements. Experiments were conducted at cooling/heating rates of 1 K/min. The preliminary investigation demonstrated a subtle shift in the phase transition temperatures from 180 K to 161 K. Furthermore, the results revealed a noticeable relaxation below the phase transition temperature, likely associated with domain wall motion. Finally, the experimental data was fitted using a superposition of several Cole-Cole functions. The obtained relaxation times were then approximated using the Arrhenius law. The calculated activation energies for the low-temperature relaxation were found to be $E_A=0.15 \pm 0.02$ eV for the pure sample and $E_A=0.34 \pm 0.02$ eV for the sample containing 5% potassium impurities. The considerable increase in activation energies could be attributed to the pinning of domain walls to point defects induced by potassium, hindering the motion of domain walls.

References

[1] Xu, Guan-Cheng, et al. *Journal of the American Chemical Society* 133.38 (2011): 14948-14951.