Ferroelectric property has been reported in simple organic cation-anion salt of guanidinium $\text{C(NH}_2\text{)_3}^+$ aluminum sulfate hexahydrate. Six hydrogen-bonding protons of planar $\text{C(NH}_2\text{)_3}^+$ cation has been utilized for the construction of supramolecular cation-anion structures. Large number of layered $\text{C(NH}_2\text{)_3}^+$ salts have been prepared by conventional combining with various type of sulfonate anions, in which $-\text{SO}_3^{2-}$ unit is topologically fitted with $\text{C(NH}_2\text{)_3}^+$ cation.

Among them, simple salt of $\text{C(NH}_2\text{)_3}^+(\text{C}_2\text{H}_5\text{-SO}_3^-)$ showed the ferroelectricity through the molecular rotation of $\text{C}_2\text{H}_5$- group in anions.[1]

Herein, we prepared simple $\text{C(NH}_2\text{)_3}^+(\text{R-SO}_3^-)$ with $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_4\text{F}_9,\text{C}_4\text{F}_9\text{O}$, whose phase transition behaviors and molecular arrangements were examined by single crystal X-ray diffraction analyses and DSC analyses in the temperature range from 173 K to melting point and temperature-dependent dielectric constants were measured at the frequencies range from 100 to $1000\times10^3$ Hz.

1:1 salts of $\text{C(NH}_2\text{)_3}^+(\text{C}_2\text{H}_5\text{-SO}_3^-)$ (1) and $\text{C(NH}_2\text{)_3}^+(\text{CH}_3\text{-SO}_3^-)$ (2) were obtained as centrosymmetrical space group of $\text{C}_2/m$. Two-dimensional hydrogen-bonding sheet structure was observed in the ab plane, which was stacked along the c axis. The DSC chart of salt 1 showed the reversible peaks around 310 K, which was consistent with the transition entropy ($\Delta S$) for the order-disorder type phase transition. On the contrary, there was no peaks in DSC chart of salt 2. The real part dielectric constant $\varepsilon_1$ of salt 1 in the pellet also indicated the response around 310 K, whereas there was no dielectric response in salt 2. When the dielectric responses are achieved by the molecular rotation of $\text{C}_2\text{H}_5$- group, the anisotropic dielectric responses should be observed in single crystalline salt 1. Actually, the dielectric responses of single crystalline 1 showed no response along the ab plane (//ab), whereas the dielectric response was observed along the bc plane (//bc). Therefore, the dielectric response found in salt 1 was dominated by the molecular rotation of $\text{C}_2\text{H}_5$- group. The phase transition, crystal structure, and dielectric response of the other guanidine-sulfonate salts will be discussed.


Keywords: Guanidinium, Phase Transition, Molecular Rotator