Poster Presentation

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Crystal structures and dielectric responses of guanidinium – sulfonate salts

Takahiro Kobayashi[1], Norihisa Hoshino[1], Takashi Takeda[1], Tomoyuki Akutagawa[1]
[1]*Graduate School Of Engineering, Tohoku University, Sendai, Japan*
E-mail: tkoba@mail.tagen.tohoku.ac.jp

Ferroelectric property has been reported in simple organic cation-anion salt of guanidinium $C(NH_2)_3^+$ aluminum sulfate hexahydrate. Six hydrogen-bonding protons of planar $C(NH_2)_3^+$ cation has been utilized for the construction of supramolecular cation-anion structures. Large number of layered $C(NH_2)_3^+$ salts have been prepared by conventional combining with various type of sulfonate anions, in which $-SO_3^{2-}$ unit is topologically fitted with $C(NH_2)_3^+$ cation.

Among them, simple salt of $C(NH_2)_3^+$ (C_2H_5O-SO_3^-) showed the ferroelectricity through the molecular rotation of C_2H_5O- group in anions.[1] Herein, we prepared simple $C(NH_2)_3^+$ (R-SO_3^-) with R = CH_3, C_2H_5, C_2HF_4, C_4F_9, C_4F_9O, 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 1000×10^3 Hz.

1:1 salts of $C(NH_2)_3^+$ (C_2H_5-SO_3^-) (**1**) and $C(NH_2)_3^+$ (CH_3-SO_3^-) (**2**) were obtained as centrosymmetrical space group of *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 (ΔS) 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 ε_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 C_2H_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 C_2H_5- group. The phase transition, crystal structure, and dielectric response of the other guanidine-sulfonate salts will be discussed.

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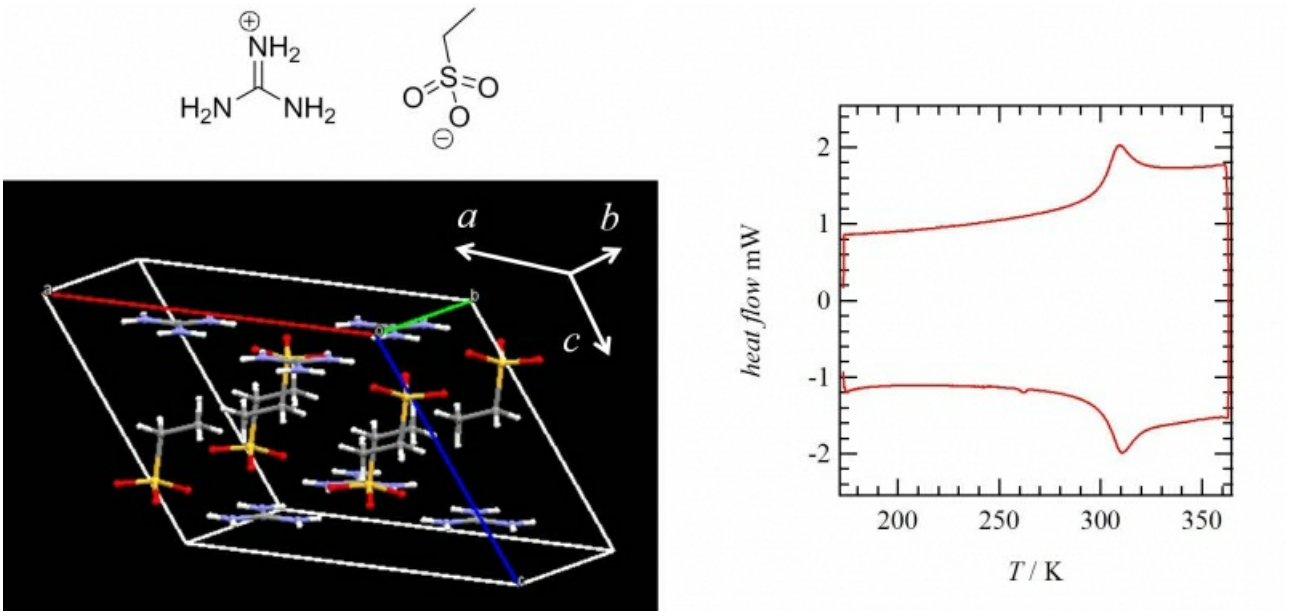

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