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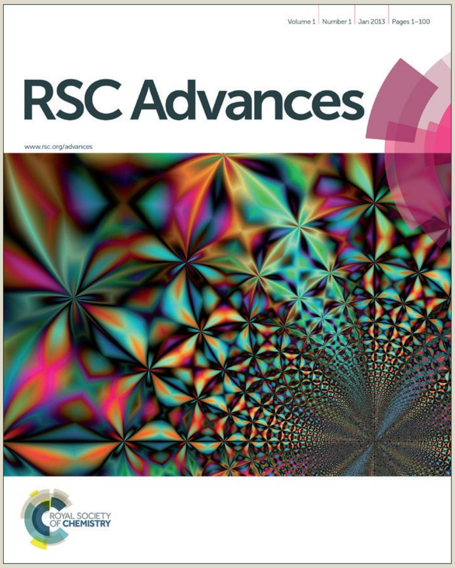

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ARTICLE

Two reversible ferroelectric phase transitions in Diisopropylammonium Perchlorate

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Two reversible first-order phase transitions were found in an improper ferroelectric, diisopropylammonium perchlorate (DIPAP), due to that the crystal symmetry transforms from $P2_1/c$ to P1 at 296 K, and subsequently to $P2_1/c$ at 338 K in heating process, which is similar to the structure transitions of the first discovered ferroelectric, Rochelle Salt. The dielectric behavior shows two remarkable dielectric step-like rising at 296 K and 338 K, which is the substantive characteristic of improper ferroelectrics. The mechanism of the two improper ferroelectric phase transitions is due to the transformation of diisopropylammonium cations and perchlorate anions as confirmed by X-ray diffraction and Raman spectrum..

Introudction

Materials with phase transition, especially switchable dielectric materials, have potential applications in the data storage, signal processing, sensing, etc [1-5]. The compounds containing polar molecules and/or dipolar reorientation have large possibility of phase transition due to that the motions of the dipoles can be switched on or off by external conditions, such as temperature, pressure. Switchable dielectrics as responsive materials undergo a transition between high and low dielectric constant states at the Curie temperature (T_c).[6, 7] The dielectric constant switching is basically due to the motional changes of polar molecules or ions between melt-like and frozen states.[8-11] So far, lots of switchable organic dielectrics have been discovered, although most of them have low dielectric Curie temperature, which restricts their applications.[12-18] Therefore, further explorations of switchable dielectrics with high transition temperature are very important for applications in the electronic technology fields. Among the discovered switchable dielectric materials, few have sequentially switchable dielectric tuned in three different states. For example, Zhou et al. reported diisopropylammonium trifluoromethanesulfonate has a sequentially switchable molecular dielectric tuned by a stepwise ordering[13]. The switchable dielectric constant is remarkable at the high phase transition temperature; however, it changes little around the low phase transition temperature, which would restrict the application of sequentially switchable dielectric in electrronic device. Herein, we present a novel organic compound diisopropylammonium perchlorate (DIPAP, $C_6H_{16}NClO_4$) with sequentially switchable dielectric behavior. It is even more amazing that the difference between the two phase transition temperatures is only 42 K, and both of the transition temperatures are above or near room temperature.

It was reported that the order-disorder transformation of diisopripylammonium cations induce excellent high-temperature ferroelectricity and large dielectric constants.[19-22] DIPAP was first discovered by us to be an improper ferroelectric with transition temperature of about 338 K.[23] According to the Landau theory of phase transition, the order parameter of improper ferroelectrics is not polarization, which is different from the traditional ferroelectric.[24, 25] The dielectric phase transition of improper ferroelectric is step-like which does not obey Curie-Weiss theory.[26] An additional phase transition at 296 K is discovered here after measurement methods have been modified to avoid water vapor influence at low temperature. Both phase transitions of DIPAP from $P2_1/c$ to P1 to $P2_1/c$ companying amazing sequentially switchable dielectric properties will be discussed here. The mechanism of the phase transitions and switchable dielectric behaviors will be analyzed by x-ray diffraction and Raman spectrum.

Experimental

DIPAP crystals were obtained by reaction of diisopropylamine with perchloric acid. The crystalline slice was grown on the surface of the liquid by slow evaporation of the aqueous solution in methanol for several days. Powder X-ray diffraction (PXRD) data are collected using Rigaku (Tokyo, Japan) Dmax-rBX-ray diffractometer and Rigaku D/MAX 2000 PC X-Ray

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Diffractometer. Differential scanning calorimetry (DSC) measurements upon cooling and heating scans were measured on a NETZSCH DSC 200F3 in the temperature range 250K−400 K and the DSC curves obtained from polycrystalline. The complex permittivity was recorded using a Tonghui TH2828A LCR meter. Raman spectra were taken using a Horiba Jobin Yvon HR800 spectrometer system with 488 nm laser line of an air cooled Ar-ion laser. The DIPAP single crystal samples with area of 5~7 mm^2 and thickness of about 0.2 mm were used to measure complex permittivity and Raman spectra.

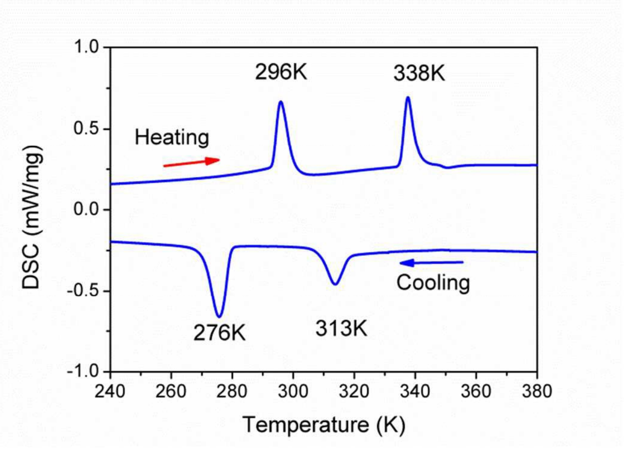

Fig. 1 Differential scanning calorimetry measurements of DIPAP as a function of temperature.

Results and Discussion

Differential scanning calorimetry (DSC) was carried out to effectively detect the existence of reversible phase transitions triggered by temperature. DSC is a thermoanalytical technique in which the difference between the heat flow to the sample and that to the reference material is measured as a function of temperature. Polycrystalline samples were used during the DSC measurements. The heating and cooling rate during the measurements are both of 10 K/min. Two couples of exothermic and endothermic anomalies were recorded representing two reversible phase transitions (Fig. 1). During the heating process, two phase transitions were observed at 297 K (T_{cL}) and 338 K (T_{cH}), respectively. During the cooling procedure, two phase transitions at 276 K and 313 K respectively are observed. Large thermal hysteresis exceeding 10 K could be seen on both phase transitions, which is indicative of two first-order phase transitions. The integral peak area of DSC is directly proportional to the enthalpy change during the phase transition. The two entropy changes ($\Delta S = \Delta H/Tc$) are about 3.38 $Jmol^{-1}K^{-1}$ (T_{cH}) and 4.24 J/mol (T_{cL}), respectively, calculated from the integral area of DSC peak. According to the Boltzmann equation: $\Delta S = R \ln(N_1/N_2)$, it is found that N_1/N_2 = 1.50 (T_{cH}), 1.67 (T_{cL}), respectively, which indicates two uncomplicated disordered-ordered phase transition features. Where R is the universal gas constant, N_1 and N_2 are the numbers of independent positions with equal probability in the crystal phases above and below the phase transition temperature.

For convenience, the phase below T_{cL}, between T_{cL} and T_{cH}, and above T_{cH} are labeled as low-temperature phase (LTP), intermediate-temperature phase (ITP) and high-temperature phase (HTP), respectively. The crystal lattice parameters of three phases could be seen in Table S1. Based on the single crystal structure data got by Bajorat,[27] DIPAP crystallizes in the monoclinic space group $P2_1/c$ in the temperature range from 213 K to 291 K. To examine the crystal structure of LTP, PXRD of DIPAP was measured at about 253 K (Fig. 2A). The PXRD pattern was refined using the Rietveld refinement and was fitted well with the crystal structure got by Bajorat *et al.*[27] indicating the structure of LTP is $P2_1/c$. The measured PXRD pattern of ITP is also consistent to the pattern refined from the single crystal structure of DIPAP at 293 K,[21] indicating a P1 space group of ITP (Fig. 2B). However, it is hard for us to get single crystal structure of HTP because the crystal was damaged during heating process. Even though, the crystal structures of HTP can be well determined with space group $P2_1/c$ (Fig. 2C) using the Rietveld refinement[21] which shows the measured PXRD was well fitted with the refinement result. From the XRD results, it is clear that the whole phase transitions are $P2_1/c \xrightarrow{T_{cL}} P1 \xrightarrow{T_{cH}} P2_1/c$. It is amazing that the space groups of the LTP and the HTP are the same and two Curie temperature points exist there, which is similar to the first discovered ferroelectric crystal, Rochelle salt, which has crystal structure transitions from $P2_12_12$ to $P2_1$ at 255 K and from $P2_1$ to $P2_12_12$ at 297 K, respectively. It is very strange for the structure transition of both DIPAP and Rochelle salt from LTP to ITP since they change from a high symmetry to a low symmetry during warming process, which do not obey the Landau phase transition theory.

The dielectric constants as a function of temperature are shown in Fig. 3. A sequential switchable molecular dielectric could be clearly seen as the dielectric constants stepwise increase with the temperature increasing. The dielectric constant of HTP is about two times as that of ITP and four times as that of LTP. The sequentially switchable dielectric of DIPAP is remarkable, and the transition processes are very sharp and quick within temperature range of 1 K, which would be helpful to applications of sequentially switchable dielectrics. Both of the stepwise dielectric phase transitions may be owing to the improper ferroelectric property of DIPAP. In contrast to the ordinary ferroelectrics, the order parameter of phase transition of improper ferroelectrics is not the spontaneous polarization while other physical quantity whose transformation properties are different from those of the polarization.[28] Spontaneous polarization arises as a secondary effect in improper ferroelectric transition. The temperature dependence of the permittivity in improper ferroelectrics does not obey the Curie-Weiss law, which is significantly different from the ordinary ferroelectrics. The Landau theory of phase transitions predicts the dielectric anomaly near the phase transition temperature is step-like. It is interesting that the ITP of DIPAP is improper ferroelectric resulting in two improper ferroelectric phase transition. Both of the improper ferroelectric phase transitions lead to step-like dielectric phase transitions. Moreover, the two dielectric transition temperatures are both near room temperature, which is useful to the application of switchable dielectric.

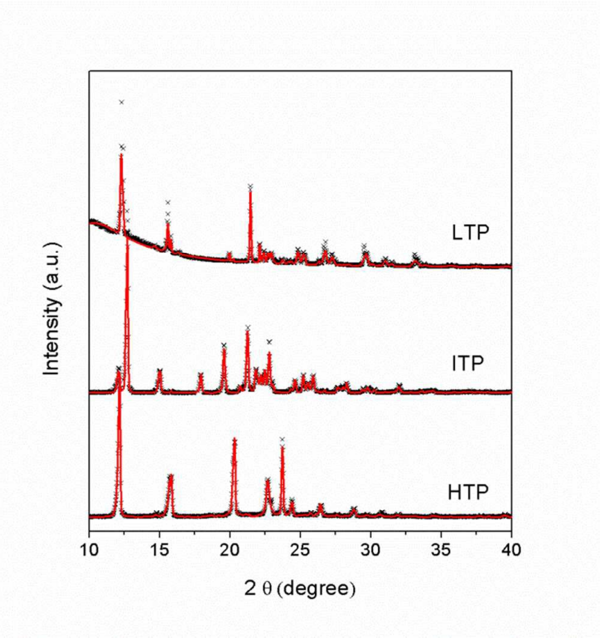

Fig. 2 The experimental (black crosses) and Rietveld refined (red lines) XRD powder patterns measured at 253 K (LTP), 303 K (ITP), and 343 K (HTP), respectively.

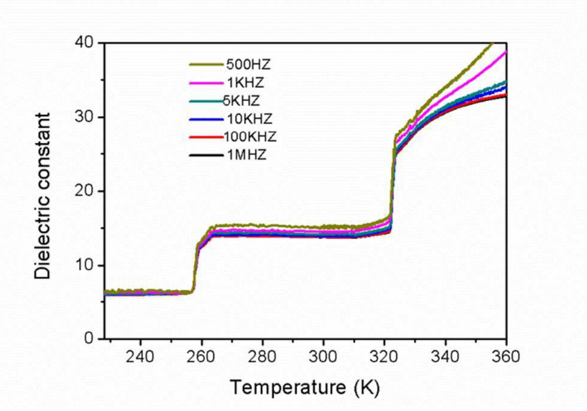

Fig. 3. The temperature dependences of dielectric constant at different frequencies in cooling process.

In order to understand the mechanism and dynamics of phase transitions, Raman measurements as a function of temperature were performed, which is an ideal tool for capturing the dynamics and local structural changes in the viewpoint of lattice vibrations.[29] Raman spectrum was performed at the temperature range of 268 K to 363 K (Fig.4, Fig. S1). The abruptly changes of the positions of the Raman peaks indicate two phase transitions at about 303 K and 338 K, respectively, which is consistent with the crystal structure, DSC, and dielectric results. Most of the Raman peaks rise from the internal vibrations of diisopropylammonium cations, while a few come from the internal vibrations of perchlorate. To better analyze the phase transition of DIPAP, three important Raman peaks were selected at 802 cm^{-1},824 cm^{-1} and 932 cm^{-1}. The Raman peak position shifts with reference to the peak at 303 K was shown in Fig. 4. All the three Raman peaks show significant variations nearby 303 K and 338 K due to the phase transitions. Vibrations of 802 cm^{-1} and 824 cm^{-1} are important Raman vibrations for DIPAP which are attributed to the symmetric and antisymmetric stretching vibrations of C-N-C bond in diisopropylammonium cations. Both of the two vibration frequencies shift to a higher frequency at 303 K, and then to a lower frequency at 338 K in warming process. Vibration of 932 cm^{-1} comes from the symmetric stretching of perchlorate anions, which shifts to a lower frequency at 303 K and sequently to a higher frequency at 338 K in warming process. It is known that the higher frequency of the vibration in HTP than in ITP is owing to the weaker hydrogen bond binding.[30] Since LTP and HTP of DIPAP are both $P2_1/c$ space group, the higher frequency in LTP, than that in HTP could get good explanation from contraction principle. On the basis of contraction principle, bond distance of the perchlorate anions in LTP is shorter resulting in the higher frequency of the vibration in LTP. All of the three Raman peak shifts confirming the crystal structure transitions at different temperatures. Combining the crystal structure and Raman shifts, it can be concluded that the transformation of diisopropylammonium cations plays an important role in both the phase transitions

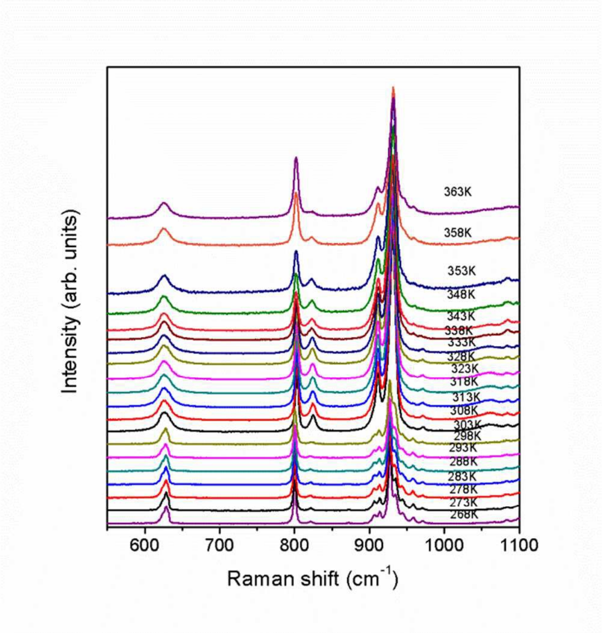

Fig. 4. The Raman spectrums of DIPAP within the selected wavenumber range at different tempertatures. The whole Raman spectrums can be seen in Fig. S1.

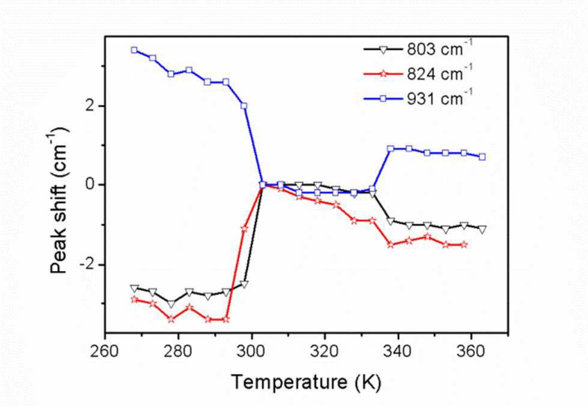

Fig. 5. The temperature dependence of Raman peak position shifts with the reference to the peak position at 303 K.

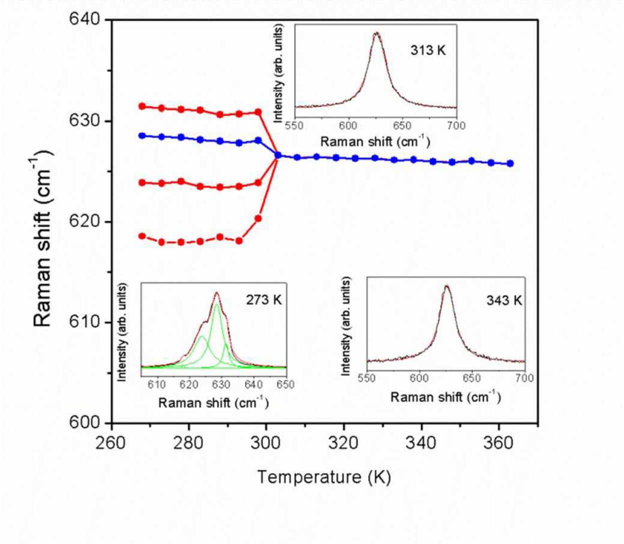

Fig. 6. The temperature dependence of Raman peak position of 628 cm^{-1} shifts with the reference to the peak position at 303 K. The red represent the vibration splitting of one of the two perchlorate anions. The insets show the fitting of the Raman peak of 628 cm^{-1} at different temperature.

Splitting of 628 cm^{-1} mode is also observed in the Raman spectrum below 298 K (Fig.S4, Fig. 5). The Raman peaks at about 628 cm^{-1} is fitted through Lorentz function. Only one peak at about 628 cm^{-1} was found above 303 K but four peaks were found below 298 K (617 cm^{-1}, 624 cm^{-1}, 628 cm^{-1} and 631cm^{-1}). The vibration of 628 cm^{-1} comes from the in-plane deformation of perchlorate anion ($\upsilon_4(F_2)$ mode) which is triplet degenerated.[31] One Raman peak indicates υ_4 mode is degenerated because of the high symmetry of perchlorate anion and crystal field effect. No significant variation of υ_4 mode was found at 338 K indicating the slight transform of perchlorate anions and crystal field effect. But the abrupt splitting below 298 K proves the deformation of perchlorate anion and crystal field effect. Below 298 K, three of the observed four peaks (617 cm^{-1}, 624 cm^{-1}, 631 cm^{-1}) belong to the non-degenerate mode of 628 cm^{-1}, which corresponds well to the result got by Marchewka[11]. But in the meantime, the Raman result tells that the triply degenerate mode of 628 cm^{-1} still exists in the LTP. It is interesting that both the degenerate mode and non-degenerate mode of the vibration of the in-plane deformation of perchlorate anion exist in the LTP. According to the crystal structure got by XRD, there are two kinds of perchlorate anions in the unit cell of LTP. The deformation and the environment of the two perchlorate anions are different. According to the Raman measurement, splitting of the vibration can only be found in one kind of the perchlorate anions, while the other is still triply degenerate. The spilt of the υ_4 mode comes from the lowering of the symmetry from the ideal configuration and the crystal field effect. As a result, the lowering symmetry of half the perchlorate anions may be one of the most important factors in driving the ITP-LTP phase transition at 276K during the cooling process.

Conclusions

In summary, there are two improper ferroelectric phase transitions at 296 K and 338 K in DIPAP, which is confirmed by DSC, XRD, dielectric anomaly, and Raman measurements. The improper phase transitions result in a remarkable sequentially switchable dielectric behavior. The crystal structure of DIPAP changes from $P2_1/c$ to $P1$ at 296 K and changes from $P1$ to $P2_1/c$ at 338 K during the heating process. XRD and Raman measurements indicate the two improper ferroelectric phase transitions rise from the transformation of diisopropylammonium cations and perchlorate anions.

Acknowledgements

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