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# Chemical Control of Ferroelectric Neutral-Ionic Transition in Charge-Transfer Complexes, $TTF_{1-x}TSF_xQCl_4$ [TTF = Tetrathiafulvalene; TSF = Tetraselenafulvalene; $QCl_4$ = *p*-Chloranil]

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Some organic charge-transfer (CT) complexes with 1:1 mixed stacks of donor (D) and acceptor (A) molecules have been attracting considerable interest for the unique valence instability called the neutral-ionic (NI) phase transition.[1] The NI transition, which has been observed so far for four complexes at ambient pressure,[1,2] is characterized by the change of molecular valence and simultaneous spin-Peierls-like dimerization of the ionic DA stack. Particularly for the prototype compound tetrathiafulvalene (TTF)-*p*-chloranil ($QCl_4$), such a strongly electron-lattice-coupled nature led to the observations of current-induced switching to a negative resistance state,[3] photoinduced phase transformation,[4] and anomalous dielectric responses,[5] besides the drastic change in optical spectra reflecting the ionicity.[6] Furthermore, a recent structural study has evidenced the ferroelectric ordering of the dimerized DA stack.[7] This valence instability is sensitive to an external pressure which modifies the electrostatic interaction of the ionized lattice.[8] In the TTF-$QCl_4$ crystal, for example, application of pressure of only 1 GPa raises the $T_c$ of 82 K up to room temperature.[9] Our aim is to utilize the substitution by isostructural molecules as a source of effective pressure to tune the NI phase boundary at ambient pressure. On the basis of the TTF-$QCl_4$ crystal, we have developed a new alloy system by incorporating the selenium analogue of TTF, tetraselenafulvalene (TSF),[10] with larger molecular volume but with minimized perturbation such as the molecular shape, symmetry, and ionization energy. This paper reports on the novel dielectric properties with quantum effect as well as the phase diagram of this alloy system.

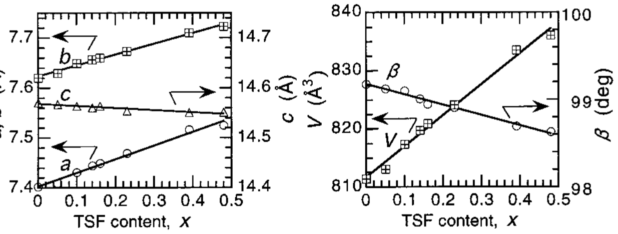

**Figure 1.** Lattice parameters for $TTF_{1-x}TSF_xQCl_4$ crystals at room temperature.

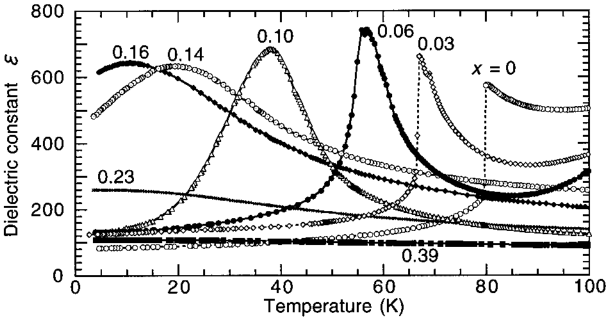

**Figure 2.** Temperature dependence of the dielectric constant at 10 kHz for $TTF_{1-x}TSF_xQCl_4$ with various *x* values.

The needle-shaped crystals were grown in the slowly cooled acetonitrile solution of components purified by repeated recrystallization and sublimation processes. The TSF fraction (*x*) could be smoothly controlled up to $x = 0.5$ with about 60−80% TSF content of the initial load of solution.[11] The X-ray diffraction measurements on the pure and alloyed single crystals gave the isostructural monoclinic ($P2_1/n$) unit cells. The lattice parameters of the DA-stacking *a* axis and the interstack *b* axis increase linearly with *x* by 1.7% and 1.3%, respectively, up to $x = 0.5$, whereas the parameter *c* is almost independent of *x* (Figure 1). The substitution of chalcogen atoms enlarges the intermolecular atomic distances involved. The observed anisotropic expansion is well explained by the observation of the corresponding distances shorter than the sum of the van der Waals radii along the *a* and *b* directions due to the S···C and S···Cl interactions but not along the *c*.[7,12]

Figure 2 shows the temperature-dependent dielectric constant $\epsilon$ measured along the DA stack using an LCR meter. For the $x = 0$ compound, the $\epsilon$ obeys a Curie−Weiss law above the $T_c$ (81−82 K), at which a discontinuous drop was observed with a thermal hysteresis of about 1−2 K in accord with the previous work.[13] This behavior is characteristic of the first-order ferroelectric phase transition. The dielectric anomaly shifts toward lower temperature, and its discontinuity and thermal hysteresis become less pronounced with increasing *x* up to 0.06. The anomaly for the $x = 0.06$ crystal shows up as a cusp-like peak without discernible thermal hysteresis, suggesting that the phase transition approaches or turns to the continuous one. For *x* from 0.06 to 0.16, the peak is gradually broadened and shifted toward zero temperature. Beyond the composition of $x = 0.16$, the saturated behavior of $\epsilon$ instead of the peak structure is characteristic of the quantum paraelectricity, a phenomenon that the

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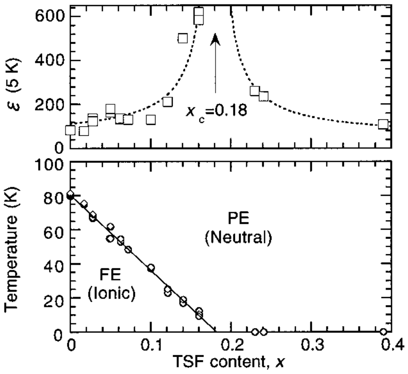

**Figure 3.** TSF concentration ($x$) dependence of the dielectric constant at 5 K (upper panel) and critical temperature for $TTF_{1-x}TSF_xQCl_4$. A solid line as guide to the eyes represents the NI or paraelectric (PE)−ferroelectric (FE) phase boundary. The dashed lines in the upper panel represent the relation $\epsilon \propto (x - x_c)^{-1}$ (see text).

ferroelectric ordering is suppressed by quantum fluctuation of the lattice as was observed for $SrTiO_3$[14] and some hydrogen-bonded molecular crystals.[15] Further TSF-doping diminishes the dielectric response at the low-temperature region, flattening the entire $\epsilon-T$ curve. The suppression of pretransitional phenomena indicates the ground state going away from the ferroelectric ionic one.

As shown in the lower panel of Figure 3, $T_c$ defined by the maximum of dielectric constant is monotonously lowered by increments of $x$. The ferroelectric ionic phase vanishes above $x = 0.18$, around which the $\epsilon$ value at low temperature (5 K) increases in a divergent manner as shown in the upper panel of Figure 3. The ferroelectric ordering, or equivalently the NI transition at such a low temperature, is affected by quantum fluctuation and can be termed as the quantum ferroelectricity. In this case, the $\epsilon$ value tends to diverge at the quantum critical point, as was confirmed for $KTa_{1-x}Nb_xO_3$, which displays the relation $\epsilon$ ($T \rightarrow 0$ K) $\propto (x - x_c)^{-1}$ with a critical Nb concentration $x_c = 0.008$.[16] The $TTF_{1-x}TSF_xQCl_4$ system shows an analogous feature, as shown by broken lines in both sides of $x_c = 0.18$. Furthermore, the quantum ferroelectricity for the present compounds is likely to accompany the valence fluctuation or quantum coexistence of the N and I molecular domains.

The expansion of the parameters $a$ and $b$ at $x = 0.18$ corresponds to the effective pressure of −0.10 and −0.37 GPa, respectively, on the basis of the data of the pressure-dependent shrinkage (0.51 and 0.12 Å/GPa, respectively[8,9]). On the other hand, linear extrapolation of the phase boundary for the pressurized TTF-$QCl_4$[9] with a slope of 3.1 MPa/K to 0 K gives the hypothetical critical pressure of −0.25 GPa. The pressure values estimated from lattice constants, although anisotropic, are comparable to this extrapolated value, confirming that the "chemical pressure" plays a dominant role in decrease of $T_c$ and resultant emergence of the quantum ferroelectricity.

In summary, by chemical substitution, we controlled the ferroelectric transition continuously down to zero temperature and demonstrated the first example of a CT complex with quantum paraelectricity. We particularly emphasize that the present novel ferroelectric transition is quite unique because the valence change is simultaneously involved.

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