Comment on "Ferroelectric Order of Parallel Bistable Hydrogen Bonds"

Second harmonic generation (SHG) is a very sensitive probe to detect phase transitions between noncentrosymmetric (NCS) and centrosymmetric (CS) structures, since it exists only in NCS materials, unless a magnetic dipole or an electric quadrupole contributes to it [1]. Therefore, temperature dependence of second-order nonlinear optical susceptibility $\chi^{(2)}$ can be an indicator of CS-to-NCS phase transition and useful for screening inorganic-organic hybrid ferroelectrics [2–4].

Szafrański *et al.* discovered a series of ferroelectrics such as [(H-dabco)X] [$X = \mathrm{ClO_4}$ (CO4), $\mathrm{BF_4}$ (BF4), $\mathrm{ReO_4}$ (RO4), and H-dabco = 1-azonia-4-azabicyclo-(2.2.2)octane] [5,6]. Both CO4 and BF4 crystallize in NCS at room temperature and in CS above T_c [5]. Similarly, they pointed out that RO4 crystallizes in NCS space group *Cm* in the ferroelectric phase (FP) at room temperature and in CS space group $P4/mmm$ in the paraelectric phase (PP) above T_c (374 K) [6]. Actually, we consider that this assignment on space group in PP is not consistent with our experimental result of $\chi^{(2)}$ [Fig. 1(d)], since the $\chi^{(2)}$ above T_c is still nonzero. The electric configuration of Re^{7+} is $4f^{14}5d^{0}6s^{0}$, whose $4f$ orbit is full and $5d$ and $6s$ orbits are empty, which is a nonmagnetic cation. Therefore, the nonzero $\chi^{(2)}$ in RO4 can overwhelming determine noncentrosymmetry structure, since there is no magnetic dipole contributing to the SHG effect [1]. For comparison, we have measured $\chi^{(2)}$ on CO4 and BF4. As expected, above T_c their $\chi^{(2)}$ value unambiguously becomes zero [Fig. 1(b)], abiding by the symmetry breaking rule from FP to PP.

It must be NCS if a crystal is electric-dipole SHG active. We can easily understand what happens about the temperature dependence of $\chi^{(2)}$ of RO4 [Fig. 1(d)]: (a) Below 200.7 K (T_1), its structure is NCS with point group $mm2$, since $\chi^{(2)}$ has a nonzero value. (b) Above T_1, $\chi^{(2)}$ gradually increases with increasing temperature and reaches a saturated value, corresponding to a ferroelectric phase with space group *Cm*. The calculated spontaneous polarization [2] from crystal structure is 12.96 $\mu\mathrm{C\cdot cm^{-2}}$, which is consistent with Ref. [6]. (c) When the temperature is higher than 377.1 K (T_2), $\chi^{(2)}$ sharply decreases in a temperature range of 10 K and then gradually decreases to zero around 499.6 K (T_3), indicating that RO4 is still NCS. Single crystal x-ray diffraction also confirmed that the space group is $P4mm$ (Fig. 2) and not $P4/mmm$. The calculated spontaneous polarization is 9.455 $\mu\mathrm{C\cdot cm^{-2}}$ and not zero as mentioned in Ref. [6]. (d) Above T_3, $\chi^{(2)}$ becomes zero and the crystal begins to decompose as shown in the thermogravimetric analysis (TGA) curve [Fig. 1(d)]. Above 650 K, the decomposition is complete with a weight loss of 30.8%, indicating that only perrhenic acid remains. These phase transitions revealed by SHG effect are consistent with differential scanning calorimeter (DSC) results [Figs. 1(a) and 1(c)].

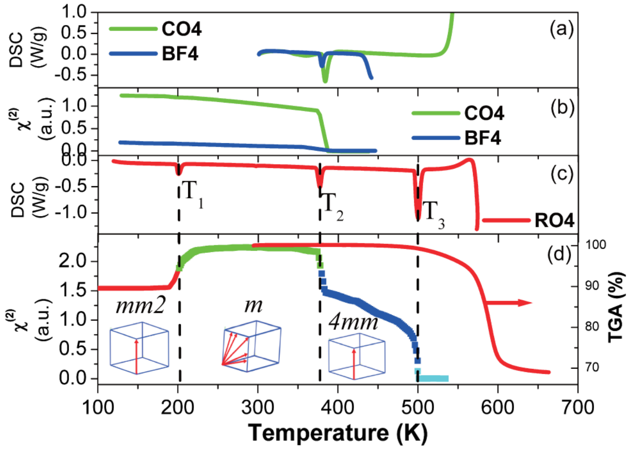

FIG. 1 (color online). Temperature dependence of DSC of CO4 and BF4 (a), $\chi^{(2)}$ of CO4 and BF4 (b), DSC of RO4 (c), and $\chi^{(2)}$ and TGA of RO4 (d). Crystal structural transition is also given in (d), and the thin red arrows indicate the directions of the polarization.

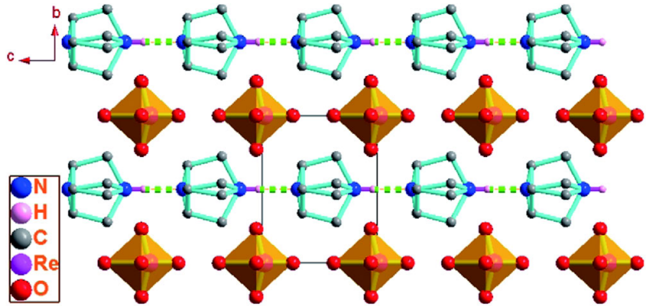

FIG. 2 (color online). Crystal structure of RO4 in the phase with space group $P4mm$ at 383 K.

In summary, RO4 undergoes two reversible FP-to-FP transitions at T_2 and T_1, respectively, like $\mathrm{BaTiO_3}$. It is notable that the correct phase transition near T_2 is a FP-to-FP transition with an Aizu notation of $4mmFm$, not a PP-to-FP transition.

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