Cyano-bridged perovskite $[(CH_3)_3NOH]_2[KM(CN)_6]$, [M: Fe(III), and Co(III)] for high-temperature multi-axial ferroelectric applications with enhanced thermal and nonlinear optical performance.

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Streszczenie

Highly stable ferroelectrics with reversible high-temperature phase transitions and switchable nonlinear optical behaviour are much coveted targets for emerging optoelectronic applications. Here, we demonstrate a cyano-bridged perovskite $[(CH_3)_3NOH]_2[KCo(CN)_6]$ (**TMAO-Co**), a new analogue of the multi-axial ferroelectric $[(CH_3)_3NOH]_2[KFe(CN)_6]$ (**TMAO-Fe**) with improved thermal stability and enhanced second-order nonlinear optical response. Indeed, for **TMAO-Co** the Curie temperature (T_c) is shifted to a higher value of*ca.* 416 K (improvement by *ca.* 10 K *versus* **TMAO-Fe**); the separation between T_c and the decomposition threshold is 46 K. **TMAO-Co** is a biaxial ferroelectric as revealed by $P(E)$ hysteresis loop measurements along the *a* and *c* crystallographic directions with spontaneous polarization values of 0.9 and 0.63 μC cm^{-2} at 293 K, respectively. The SHG response of **TMAO-Co** is two times higher than that of **TMAO-Fe**. The improved stability of **TMAO-Co** to thermal and optical loads allowed for demonstration of bistable switching of nonlinear optical response between SHG-on and SHG-off states by temperature sweeping. Structurally, **TMAO-Co** reproduces the unusual characteristics of **TMAO-Fe**, *i.e.* the first-order phase transition between (polar) monoclinic to (nonpolar) cubic phases involving bond switching and is assisted by the pronounced increase of disorder of the TMAO cations above T_c. Combined temperature-resolved Raman and infrared spectroscopic measurements were employed to track the symmetry increase above T_c, which is primarily associated with changes in hydrogen-bonding. Consistent with the bond-switching character of the phase transitions, a pronounced shift to higher wavenumbers is observed for the O–H stretching modes. The DFT calculations demonstrate that the system's polarization along the *a*-axis mostly comes from the rotation of the $[(CH_3)_3NOH]_2$ cluster, while the atomic displacement of the framework contributes largely to that along the *c* axis.

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