

Polar and antiferroelectric behaviour of a hybrid crystal - piperazinium perchlorate.

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Streszczenie

Monoprotonated piperazinium perchlorate, $[\text{NH}_2(\text{CH}_2)_4\text{NH}][\text{ClO}_4]$, appeared to be a novel room temperature polar material (P1). Its acentric symmetry was confirmed by single-crystal X-ray diffraction, second harmonic generation (SHG) and pyroelectric measurements. Differential scanning calorimetry (DSC) measurements revealed a complex sequence of phase transitions above room temperature: $\text{I} \leftrightarrow \text{II}$ at 433/422 K (heating-cooling), $\text{II} \leftrightarrow \text{III}$ at 417/411 K, $\text{III} \leftrightarrow \text{IV}$ at 403/395 K and $\text{IV} \leftrightarrow \text{V}$ at 397 K (the lowest temperature phase transition recorded only upon heating). The characteristic feature of the structure of $[\text{NH}_2(\text{CH}_2)_4\text{NH}][\text{ClO}_4]$ is the presence of two parallel cationic chains which are connected with each other by strong $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds. In phase V, these strongly polar non-equivalent chains contribute to spontaneous polarization. ^1H NMR measurements disclosed the reorientational motions of the piperazinium $[\text{NH}_2(\text{CH}_2)_4\text{NH}]^+$ cations as well as the proton motion in the $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds along the piperazine chain. Over phase I, the overall motions of the ClO_4^- anions and reorientational motion of cations are postulated. The dielectric response, $\epsilon'(T)$, accompanying the PT $\text{I} \leftrightarrow \text{II}$ indicates possible antiferroelectricity in phase II.

Adres publiczny

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