

Ferroelectricity in Tetramethylammonium-Trichloro-Mercurate

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Tetramethylammonium-trichloro-mercurete, $[\text{N}(\text{CH}_3)_4]_2\text{HgCl}_6$, is ferroelectric between -80° and $+200^\circ$. Above 200° it decomposes without showing a Curie point. At room temperature the spontaneous polarization is about $1.2 \mu\text{coul}/\text{cm}^2$, the coercive field 3 kv/cm and the dielectric constant 60.

WE attempted to make the compound $[\text{N}(\text{CH}_3)_4]_2\text{HgCl}_6$ (tetramethylammonium-tetrachloro-mercurete), which is reported to be isomorphous¹ with K_2BeF_4 . The latter is isomorphous with the known ferroelectric ammoniumfluoberyllate,² $(\text{NH}_4)_2\text{BeF}_4$.

The crystals obtained by slowly evaporating an aqueous solution containing tetramethylammonium-chloride $[\text{N}(\text{CH}_3)_4]\text{Cl}$ and mercury chloride, HgCl_2 , in the molar ratio 2:1 were indeed ferroelectric.

A quantitative analysis for the elements Hg, N, C, and H showed, however, that the compound obtained was not $[\text{N}(\text{CH}_3)_4]_2\text{HgCl}_6$ but tetramethylammonium-trichloro-mercurete $[\text{N}(\text{CH}_3)_4]\text{HgCl}_3$. It forms colorless, needle-like crystals which are frequently deformed into flat, elongated plates. Conoscopic observation showed the crystals to be optically biaxial. Extinction under crossed nicols occurs at an angle of 45° with respect to the needle axis. X-ray data³ indicate that the crystals are orthorhombic. ($a=7.69$, $b=8.68$, $c=15.75$ Å.)

Owing to the shape of the samples dielectric measurements were only made in the direction perpendicular to the crystal plates. The material is ferroelectric at room temperature and shows a very good square loop between electric displacement and electric field.

At room temperature the spontaneous polarization is about $1.2 \mu\text{coul}/\text{cm}^2$, the coercive field 3 kv/cm and the dielectric constant 60. Preliminary switching experiments showed that the material is slower than GASH, i.e., very slow as compared to barium titanate.

Ferroelectricity is observable between -80°C (or lower) and $+200^\circ\text{C}$. Around -80°C the coercive field becomes so high that the loop can no longer be observed. Around $+200^\circ\text{C}$ the crystals decompose without showing a Curie point. The spontaneous polarization P_s is only slightly temperature dependent. Between room temperature and $+200^\circ\text{C}$, P_s increases by 15%. The coercive field barely varies between -70°C and $+200^\circ\text{C}$ but rises steeply at -80°C . The small-signal dielectric constant is almost temperature independent.

The compound is to our knowledge the first ferroelectric containing the elements mercury and chlorine; it is one of the few ferroelectrics containing no oxygen. The rather complicated composition suggests many isomorphous substitutions which might lead to other ferroelectrics having the same structure. Substitution of the Cl by Br gave crystals which were also ferroelectric. Other replacements will be tried.

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¹ A. Barker, J. Chem. Soc. **101**, 2484 (1912).

² R. Pepinsky and F. Jona, Phys. Rev. **105**, 344 (1957).

³ J. G. White, RCA Laboratories, Princeton, New Jersey (private communication).