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Letters to the Editor

New Ferroelectric Crystal Containing No Oxygen

R. PEPINSKY AND F. JONA

X-Ray and Crystal Analysis Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania

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IT has been of interest to determine whether oxygen is essential for ferroelectricity or antiferroelectricity in ionic crystals. With one exception, that of thiourea,[1] all known ferroelectrics and antiferroelectrics have been rich in oxygen. Thiourea is the only known nonionic ferroelectric, and its dielectric behavior is perhaps due to alterations in N—H···N or N—H···S bonding. Crystal transitions in several chlorides and fluorides have been examined heretofore, but no dielectric anomalies have been found. For example, perovskite-type double halides such as $KZnF_3$ or $CsCdCl_3$ show no anomalies, in distinct contrast with the $BaTiO_3$ family; and although a transition appears in AlF_3 at 460°C, there is no associated dielectric anomaly,[2] in contrast with the anomalies observed in WO_3.[3]

Ferroelectric behavior has recently been discovered in a good number of sulfates and selenates.[4–7] Hydrogen bonding between N and O atoms apparently plays a significant role in these anomalies.[6]

It is known that $(ZnCl_4)^{-2}$ and $(BeF_4)^{-2}$ groups can partially replace $(SO_4)^{-2}$ groups in alums,[8] leading to crystals of composition $(Me^{\mathrm{I}})_2(Me^{\mathrm{III}})_2(SO_4)_3\cdot(ZnCl_4)\cdot 24H_2O$, or with (BeF_4) in place of $(ZnCl_4)$, and where Me^{I} and Me^{III} are monovalent and trivalent positive ions, respectively. We have prepared and examined several cases in which $Me^{\mathrm{I}}=CH_3NH_3$; and whereas the methylammonium sulfate alums become ferroelectric well above 77°K, the corresponding partially $ZnCl_4$-substituted alums show no transitions above 77°K. Similarly, although $NH_4Cr(SO_4)_2\cdot 12H_2O$ shows a transition (probably antiferroelectric) at 82°K, $(NH_4)_2Cr_2(SO_4)_3(BeF_4)\cdot 24H_2O$ shows no transition above 77°K.

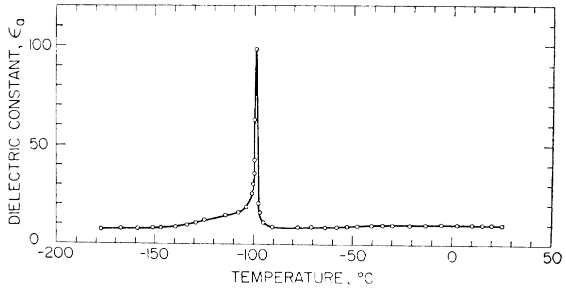

FIG. 1. Dielectric constant ϵ_a of $(NH_4)_2BeF_4$ *vs* temperature, on cooling (10 kc/sec, 1.5 v/cm).

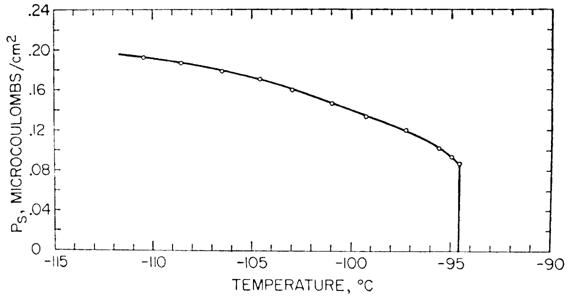

FIG. 2. Spontaneous polarization of $(NH_4)_2BeF_4$ in the neighborhood of the Curie point.

$(NH_4)_2BeF_4$ is among a group of compounds forming crystals isomorphous with $(NH_4)_2SO_4$ at room temperature.[9] It can be grown as large water-clear plates by a water-alcohol vapor-exchange method.[10] Optical examination shows a transition in the neighborhood of −100°C.[11] Dielectric measurements were made on plates prepared perpendicular to the three orthorhombic axes. The dielectric constant along the *a* axis is shown in Fig. 1, as a function of temperature. Spontaneous polarization and a ferroelectric hysteresis loop appear at −99.0°C on cooling, and disappear at −94.7°C on heating. Just above the Curie point, double hysteresis loops are observable, indicative of a first-order transition.[12] The spontaneous polarization is shown, as a function of temperature in the neighborhood of the transition, in Fig. 2; it has a value of 19×10^{-8} coulomb/cm² at −110.5°C. The coercive field is approximately 500 v/cm at this temperature, for an applied voltage of 10 kv/cm. At −140°C the coercive field has increased to about 10 kv/cm; and at liquid nitrogen temperature it is higher and in excess of the breakdown voltage of the crystal.

This behavior is to be compared to that of $(NH_4)_2SO_4$, as reported by Matthias and Remeika.[6] The axis of spontaneous polarization is the same. The Curie point for $(NH_4)_2SO_4$ is −49.5°C, and the spontaneous polarization is 25.4×10^{-8} coulomb/cm at −58°C. The coercive field for $(NH_4)_2SO_4$ appears to be considerably higher than for $(NH_4)_2BeF_4$. The hysteresis loops are rectangular in both crystals.

Differences between N—H···O and N—H···F bonding, polarizabilities of O and F, and thermal oscillations of $(SO_4)^{-2}$ and $(BeF_4)^{-2}$ ions must contribute to the differences in dielectric behavior of the two crystals. X-ray and neutron diffraction analyses of the low-temperature phases of both crystals are in progress, as a means to understanding of the transition mechanisms.

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