Dielectric Properties and Phase Transitions of $Cd_2Nb_2O_7$ and $Pb_2Nb_2O_7$†

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RECENTLY Cook and Jaffe[1,2] reported a new ferroelectric $Cd_2Nb_2O_7$, which shows a Curie temperature at about 170°K The crystal structure of cadmium niobate is a face-centered cubic lattice of the pyrochlore type, which has a three-dimensional framework of linked octahedra of NbO_6.[3] A comparison of the dielectric and structural properties of this new ferroelectric with those of the well-studied $BaTiO_3$ may provide information contributing to an understanding of oxide ferroelectrics in general.

Ceramic $Cd_2Nb_2O_7$ specimens were prepared by firing the mixture of $CdCO_3$ and Nb_2O_5 at about 1250°C after preliminary heating at 1150°C. The specimens were hard, non-porous ceramics of tan color. The dielectric constant *vs* temperature curve was measured at 10 kc/sec and 5 v/cm (see Fig. 1). At room temperature the dielectric constant is about 310, and it reaches a peak value of 1200 at 185°K. This value of the Curie temperature is higher than the value reported by Cook and Jaffe. These workers reported marked difference in the Curie temperatures in disks from the same mix, with the highest Curie point at 170°K. We have checked three kinds of specimens, with different firing temperatures ranging from 1200° to 1300°C, and obtained Curie temperatures between 182° and 188°K.

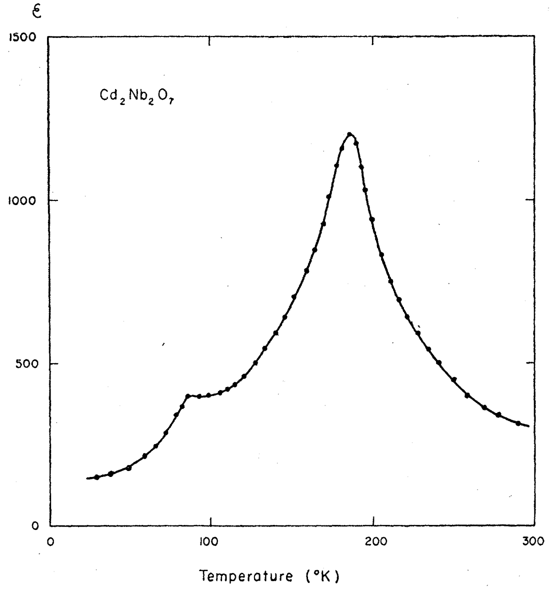
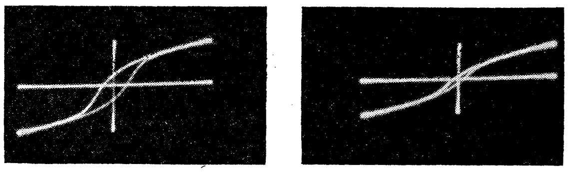


FIG. 1. Dielectric constant *vs* temperature curve of $Cd_2Nb_2O_7$ on heating.

The dielectric constant curve in Fig. 1 shows a small anomaly at 85°K, which suggests the existence of another phase change at this temperature. No other dielectric anomaly was found between 85°K and 4°K. Well-defined ferroelectric hysteresis loops were observed below the Curie temperature at 185°K down to 4°K (see Fig. 2). The spontaneous polarization estimated from these hysteresis loops under an ac field of 25 kv/cm is approximately 1.8 microcoulomb/cm² at 100°K. This value of spontaneous polarization is somewhat smaller than we expect from the remanent polarization of 3.2 microcoulomb/cm² reported previously.[2] The dielectric constant above the Curie temperature may be expressed to a good approximation by the Curie-Weiss law $\epsilon = C/(T-\theta)$, with $C = 4.6\times10^4$ and $\theta = 150$°K.

An increase in the dielectric constant of $Pb_2Nb_2O_7$ from room temperature down to liquid air temperature was reported by Cook and Jaffe, suggesting the possible existence of the Curie point below liquid air temperature. The $Pb_2Nb_2O_7$ ceramic was prepared in our laboratory by firing a mixture of $PbCO_3$ and Nb_2O_5 at 1000°C. We have measured the dielectric constant as a function of temperature down to 4°K at 10 kc/sec and 5 v/cm. The dielectric constant increases with decreasing temperature from a room temperature value of 185, and it reaches a maximum value of 360 at 14°K and decreases to 353 at 4°K. The shape of this small maximum suggests the existence of a phase transition at this temperature. However, the polarization *vs* field relation is quite linear even below 14°K under a field strength of 10 kv/cm. This leads us to doubt that $Pb_2Nb_2O_7$ is ferroelectric. Moreover, the crystal structure of $Pb_2Nb_2O_7$ at room temperature is not cubic but rhombohedral.[1] Thus any phase transition in $Pb_2Nb_2O_7$ at 14°K must be different from the upper ferroelectric phase transition in $Cd_2Nb_2O_7$.



(a) 100°K (b) 175°K

FIG. 2. Hysteresis loops of $Cd_2Nb_2O_7$ at an ac field of 25 kv/cm and 60 cycles/sec.

In order to examine a possible relation between these transitions in lead and cadmium niobates, a dielectric and structural study was made on solid solutions of $(Cd, Pb)_2Nb_2O_7$. Starting from the pure $Cd_2Nb_2O_7$ side, the Curie temperature decreases with increasing Pb concentration, appearing at 133°K in $(Cd_{0.9}, Pb_{0.1})_2Nb_2O_7$ and 41°K in $(Cd_{0.8}, Pb_{0.2})_2Nb_2O_7$. The lower transition point was not observed in these solid solutions down to 10°K. Powder photographs of solid solutions at room temperature show a cubic lattice for the compositions from pure $Cd_2Nb_2O_7$ to $(Cd_{0.1}, Pb_{0.9})_2Nb_2O_7$. Only a narrow composition range near pure $Pb_2Nb_2O_7$ shows a rhombohedral lattice. This result might be considered in conjunction with the fact[2] that $Pb_{1.5}Nb_2O_{6.5}$ shows a cubic pattern very similar to that of $Cd_2Nb_2O_7$. Exploration of the cubic *vs* rhombohedral phase line in this solid solution system, and an x-ray study of the two ferroelectric phases in pure $Cd_2Nb_2O_7$, are now underway.

Dr. Cook informed us, in a private communication, that Hulm[4] had found independently the lower phase transition in $Cd_2Nb_2O_7$ and the dielectric peak in $Pb_2Nb_2O_7$, in good agreement with the present results. We thank Dr. W. R. Cook, Jr., Dr. Hans Jaffe, and Dr. J. K. Hulm for their kind communication of unpublished data, and Mr. J. McLaughlin for the specimen preparation and dielectric measurements.

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Low-Temperature Dielectric Properties of Cadmium and Lead Niobates

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CADMIUM niobate, $Cd_2Nb_2O_7$, was reported by Wainer and Wentworth[1] to have a dielectric constant of about 500 with a high, negative temperature coefficient at room temperature; Cook and Jaffe[2] observed a ferroelectric Curie point at 170°K for this compound and also noted that its crystal structure was of the pyrochlore type rather than of the perovskite or ilmenite types in which earlier double-oxide ferroelectrics were found.[3,4] The importance of cadmium niobate as the possible fore-runner of a new class of ferroelectrics led us to investigate the dielectric properties of this compound at temperatures down to 1.2°K. Figure 1 shows the temperature variation of dielectric constant (uncorrected for porosity) for two ceramic specimens fired in cadmium oxide vapor at 1180°C (*A*, density = 4.77) and at 1260°C (*B*, density = 5.72), respectively.

Although the difference between the dielectric constants for the two specimens in Fig. 1 is mainly due to the difference in densities, the two curves do not coincide exactly when a suitable porosity correction is applied. The striking maximum at the upper Curie point shifts from 187°K to 183°K as the firing temperature is changed from 1180°C to 1260°C, perhaps owing to slight deviations from the stoichiometric formula $Cd_2Nb_2O_7$. In addition to the main peak, a small, previously unreported, dielectric constant peak is clearly visible at about 80°K for both specimens in Fig. 1, the temperature of the peak again depending slightly upon the specimen firing temperature. Since with an alternating field of about 10 kilovolts per cm, hysteresis loops were observed over the whole range from the upper Curie point down to 1.2°K, it seems possible that the small peak at 80°K marks a phase change similar to the minor transitions occurring at about 180°K and 270°K in barium titanate,[5] where a symmetry change is associated with a discrete jump in the direction and magnitude of the spontaneous electric moment without, however, the disappearance of ferroelectricity. Such transitions are obviously favored in ferroelectrics of the perovskite and pyrochlore types which are cubic in the paraelectric range and may lose several degrees of symmetry with decreasing temperature.

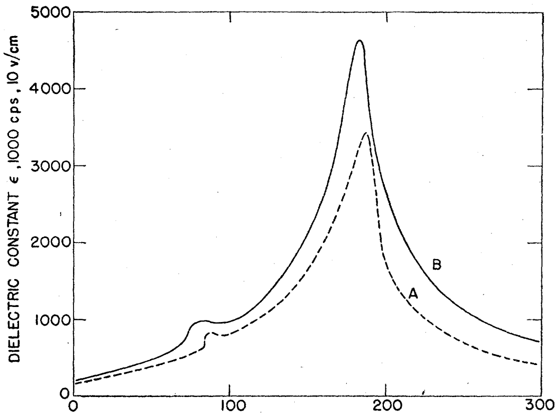

FIG. 1. Temperature variation of dielectric constant for specimens of cadmium niobate fired at 1180°C (A) and at 1260°C (B).

From dielectric observations above liquid nitrogen temperatures, Cook and Jaffe[2] suggested that lead niobate, $Pb_2Nb_2O_7$, which has an orthorhombic structure of a distorted pyrochlore type, should have a Curie point at very low temperatures. We have extended dielectric measurements on ceramic specimens of this compound down to 1.2°K, with the results shown in Fig. 2 for a specimen of density 6.53.

The dielectric constant of lead niobate rises steeply with decreasing temperature, obeying the Curie-Weiss law $\epsilon = C/(T-\theta)$, with $C = 6.26\times10^4$ and $\theta = -166$°K, down to 75°K. Below this temperature the curve flattens out, passing through a maximum at 15.4°K and dropping gradually down to 1.2°K, as shown in the enlarged inset of Fig. 2. Although the behavior of the dielectric constant is rather similar to that of potassium tantalate,[6] the polarization-field curve of lead niobate was found to be strictly linear at field strengths up to 15 kilovolts per cm and at temperatures down to 1.2°K, implying that lead niobate is not a ferroelectric crystal. While the dielectric constant peak may be associated with an antiferroelectric phase transition, it is difficult to reconcile either ferroelectric or antiferroelectric behavior with the negative Curie-Weiss temperature of lead niobate, which suggests paraelectric behavior down to absolute zero. Theory[7] indicates, however, that the dielectric constant of such a paraelectric should increase monotonically with decreasing temperature, as has been observed for strontium titanate.[8] Further work is thus required to establish the nature of the dielectric constant peak in lead niobate.

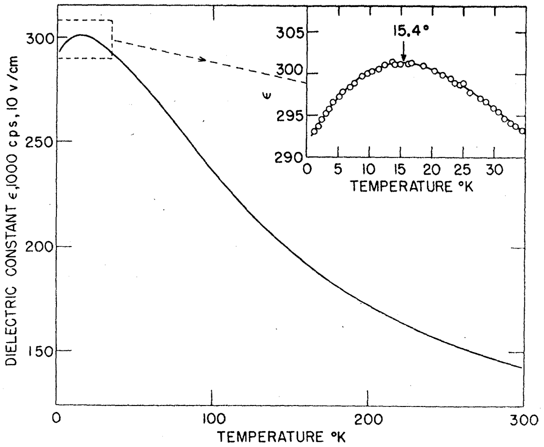

FIG. 2. Temperature variation of dielectric constant for specimen of lead niobate fired at 1180°C.

In conclusion it will be noted that no unusual dielectric properties were observed in $Cd_2Ta_2O_7$, $Pb_2Ta_2O_7$, $In_2Ti_2O_7$, $In_2Zr_2O_7$, $In_2Nb_2O_8$, $Y_2Nb_2O_8$, and $In_2Ta_2O_8$ between room temperature and liquid air temperature. The absence of ferroelectricity in the last three compounds is perhaps to be expected in view of the probable absence of NbO_6 or TaO_6 octahedra, which play such a vital role in the ferroelectricity of niobates and tantalates.[9]

I am grateful to Drs. Gen Shirane and Ray Pepinsky of Pennsylvania State College for kindly informing me of their unpublished data on cadmium and lead niobates,[10] which are in good agreement with the above results.

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Helium II Film Transport Rates over Machined Metal Surfaces*

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ONE widespread interpretation of previous transport measurements over metals maintains that ordinary, unpolished metal surfaces always show very high film transport rates (i.e., compared with glass).[1-3] The supposition is that, in contrast to glass, machined metal surfaces are characterized by a high degree of surface roughness which acts either to present a microperimeter many times larger than the measured macroperimeter,[3] or else to produce surface cracks which enhance the flow of bulk liquid.[1,2]