

Dielectric, X-Ray, and Optical Study of Ferroelectric $\text{Cd}_2\text{Nb}_2\text{O}_7$ and Related Compounds*

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Single crystals of $\text{Cd}_2\text{Nb}_2\text{O}_7$ have been grown, and dielectric, x-ray, and optical studies have been carried out on these above and below the ferroelectric Curie point. The x-ray analysis confirms the pyrochlore structure, and gives the oxygen parameter $x=0.305$ at room temperature. The symmetry below the Curie point, -85°C , is uncertain, due to the very slight lattice distortion: c/a is about 1.0005 if the ferroelectric phase is tetragonal. The spontaneous polarization along the cubic (111) axis is 6 microcoulombs/cm² at -180°C .

Partial replacement of Cd by Pb or Ca, or of Nb by Ta, decreases the Curie temperature of $\text{Cd}_2\text{Nb}_2\text{O}_7$. Dielectric measurements revealed no anomaly in several other $A_2B_2O_7$ compounds. Lattice parameters are reported for $\text{Pb}_2\text{Ta}_2\text{O}_7$, $\text{Y}_2\text{Ti}_2\text{O}_7$, and $\text{Cd}_2\text{Nb}_2\text{O}_6$.

I. INTRODUCTION

THE discovery of ferroelectricity in cadmium niobate, $\text{Cd}_2\text{Nb}_2\text{O}_7$, by Cook and Jaffe,^{1,2} introduced a new member into the family of ferroelectric compounds.

Dielectrically, the behavior of $\text{Cd}_2\text{Nb}_2\text{O}_7$ shows characteristics common to all ferroelectrics. The dielectric constant has quite a high value, and increases hyperbolically upon approaching the Curie point from the paraelectric side; thus the Curie-Weiss law is satisfied. The Curie point was first reported to lie at 170°K .¹ Further measurements by Shirane and Pepinsky,³ and independently by Hulm,⁴ established the Curie point at $185\pm 3^\circ\text{K}$. The fluctuations are the result of different firing temperatures of the ceramic specimens and thus apparently to partial evaporation of CdO. Shirane and Pepinsky³ and Hulm⁴ also discovered a second anomaly in the dielectric constant *versus* temperature curve, at 85°K , which suggests the existence of a second phase change at this temperature (see Fig. 1). Ferroelectric hysteresis loops were observed from the Curie point at 185°K down to 4°K ; the value of the spontaneous polarization is about 1.8 microcoulomb/cm² at 100°K . All the above measurements were carried out on ceramic specimens.

Structurally, $\text{Cd}_2\text{Nb}_2\text{O}_7$ represents a new type of ferroelectric. The crystal structure was examined by Bystroem⁵ by means of x-ray powder patterns, as were related substances $\text{Cd}_2\text{Ta}_2\text{O}_7$, $\text{Ca}_2\text{Ta}_2\text{O}_7$, and $\text{Pb}_2\text{Sb}_2\text{O}_7$. Bystroem found that all four compounds belong to the cubic $E8_1$ structure type,^{6,7} first known as the *koppite* type but more properly called the *pyrochlore*

type (since koppite is now discredited as a mineral species⁸).

The $E8_1$ structure type can be viewed as having a resemblance to a distorted fluorite (CI) structure. However, instead of having the composition $(A,B)_4X_8$, which would correspond to the AX_2 ratio in fluorite, the formula is $(A,B)_4X_7$; thus one of the eight anions in the fluorite-type structure is missing, and the remaining oxygens are considerably shifted.² The space group is $Fd\bar{3}m$, and there are 8 "molecules" per cell. The structural framework is a three-dimensional array of BO_6 octahedra, all sharing corners, and the framework thus has the composition $(B_2O_6)_\infty$. One parameter, x , determined the shape of the octahedra; the condition for regular octahedra is $x=\frac{5}{16}=0.312$. The seventh set of oxygens and the A ions occupy open spaces in the framework. A projection of the unit cell on (110) is shown in Fig. 2.

The existence of three-dimensionally directly-linked oxygen octahedra which encase highly polarizable ions relates $\text{Cd}_2\text{Nb}_2\text{O}_7$ to the perovskite ferroelectrics of the general formula ABO_3 . In both cases the BO_6 octahedra

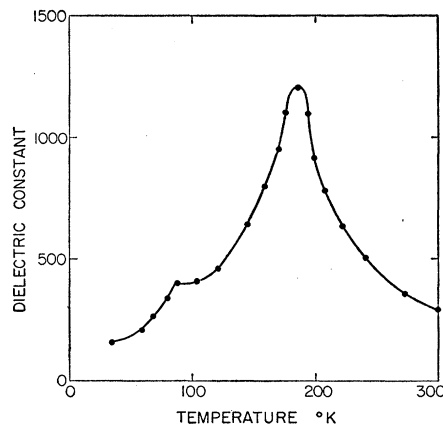


FIG. 1. Dielectric constant of ceramic $\text{Cd}_2\text{Nb}_2\text{O}_7$ vs temperature.

* Investigation supported by a contract with Wright Air Development Center.

¹ W. R. Cook, Jr. and H. Jaffe, *Phys. Rev.* **88**, 1426 (1952).

² W. R. Cook, Jr. and H. Jaffe, *Phys. Rev.* **89**, 1297 (1953).

³ G. Shirane and R. Pepinsky, *Phys. Rev.* **92**, 504 (1953).

⁴ J. K. Hulm, *Phys. Rev.* **92**, 504 (1953).

⁵ A. Bystroem, *Arkiv Kemi, Mineral. Geol.* **18A**, No. 21 (1944).

⁶ Hermann, Lohrmann, and Philipp, *Strukturbericht II* (reprinted by Edwards Brothers, Inc., Ann Arbor, 1943); K. Hermann, *Strukturbericht VII* (reprinted by Edwards Brothers, Inc., Ann Arbor, 1943).

⁷ A. J. C. Wilson, editor, *Structure Reports X* (Oosthoek, Utrecht, 1953).

⁸ Palache, Berman, and Frondel, *Dana's System of Mineralogy* (John Wiley and Sons, Inc., New York, 1944), seventh edition, Part I.

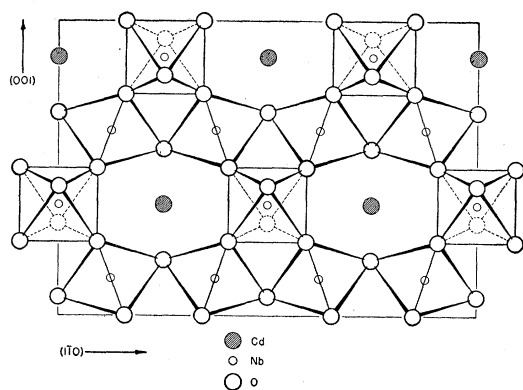


FIG. 2. NbO_6 octahedra configuration in $\text{Cd}_2\text{Nb}_2\text{O}_7$, projected on (110) plane. (The Cd ions, which overlap with the Nb ions at $(\frac{1}{2}, \frac{1}{2})$, etc., and the seventh set of oxygens, which are located above and below the Cd ions, are not shown.)

share corners only. There are essential differences between the two structure types, however. In the ABO_3 perovskites the O-B-O chains lie on straight lines which are parallel to the cubic axis; and this arrangement has been shown to be favorable for the occurrence of ferroelectricity because of the large internal field along this chain.⁹ In the pyrochlore structure the configuration of the BO_6 octahedra is much more complicated, the O-B-O chains lying on zig-zag lines along the $\langle 110 \rangle$ directions. Furthermore, in the perovskite structure the A ion only can be absent, if charge neutrality obtains as in WO_3 or Na_xWO_3 . In the pyrochlore structure, on the other hand, the A ions and the seventh oxygens are essential neither to the stability of the network of octahedra nor to the charge neutrality. It appears that the number of oxygen ions can vary from 6 to 7, if the number of the A ions varies accordingly, resulting in a general formula $A_{1+x}B_2O_{6+x}$. It is also possible partially to replace the AO group with other combinations $A'X$, according to the general formula $A_{1+x}A_{1-x}'B_2O_{6+x}X_{1-x}$. An example of the second case is pyrochlore itself, $\text{CaNaNb}_2\text{O}_6\text{F}$; an example of the first case, reported by Cook and Jaffe,² seems to be $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$. This point will be discussed in more detail below.

The ultimate aim of our investigation is an understanding of the structural mechanism leading to ferroelectricity within crystals of the pyrochlore type. To date our attention has been devoted exclusively to the phase change at 185°K . Single crystals of $\text{Cd}_2\text{Nb}_2\text{O}_7$ were first grown, and these were then studied dielectrically, optically, and by x-rays. A series of other compounds with the general formula $A_2B_2O_7$ has also been investigated.

II. CRYSTAL GROWTH

The melting point of $\text{Cd}_2\text{Nb}_2\text{O}_7$ was determined by means of an optical pyrometer as approximately 1450°C . Near 1200°C , and above, a strong smoke is

developed, very probably due to the evaporation of CdO. In attempting to grow single crystals of $\text{Cd}_2\text{Nb}_2\text{O}_7$ one must therefore take the following possibilities into account: (a) if growth can be accomplished at temperatures lower than 1200°C , no noticeable loss of CdO is to be expected; (b) if, however, the starting material must be heated above 1200°C for a considerable period, then an excess of CdO must be provided in the crucible (depending in amount on the heating time and maximum temperature) in order to compensate for CdO evaporation.

The first of these possibilities can be realized by using a suitable flux. Many different substances were tried as fluxes; the most successful among these turned out to be NaF and KF. Good results are obtained by mixing NaF and $\text{Cd}_2\text{Nb}_2\text{O}_7$ in molar ratio 10:1 (for example, 4.2 g of NaF and 5.2 g of $\text{Cd}_2\text{Nb}_2\text{O}_7$). The mixture is heated within a covered Pt crucible up to 1050°C , kept at this temperature for about 1 hour, and cooled down to 700°C at a rate of about 40 degrees/hour. With this procedure one obtains small plate-like crystals of hexagonal or triangular shape, with areas ranging between 2 and 6 mm^2 . If the molar ratio of flux to $\text{Cd}_2\text{Nb}_2\text{O}_7$ is changed to 20:1, only very few octahedron-shaped crystals are produced.

$\text{Cd}_2\text{Nb}_2\text{O}_7$ crystals are colored light yellow. X-ray studies show that the plate surfaces are $\{111\}$ planes. Figure 3 shows the relative orientation of the crystal plates with respect to the common octahedral habit.

The $\text{Cd}_2\text{Nb}_2\text{O}_7$ crystals obtained with NaF as a flux (in the following these are referred to as *N*-crystals) contain Na as an impurity; the ionic radii of Na^{+1} and Cd^{+2} are close enough for the first to substitute partially for the second. A qualitative spectroscopical analysis revealed the presence of Na in an amount roughly two percent by weight. An analysis for F has not been carried out, but the most probable composition of the *N* crystals appears to be $\text{Cd}_{1.6}\text{Na}_{0.4}\text{Nb}_2\text{O}_{6.6}\text{F}_{0.4}$. The

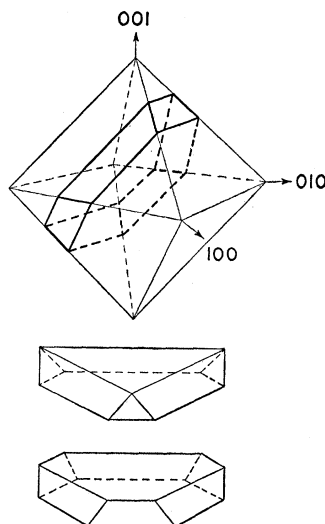


FIG. 3. Morphology of $\text{Cd}_2\text{Nb}_2\text{O}_7$.

⁹ J. C. Slater, Phys. Rev. **78**, 748 (1950).

lattice constant of $\text{Cd}_2\text{Nb}_2\text{O}_7$ was determined from the lines 10,6,6 and 12,4,4 of a powder diagram taken with a Norelco camera ($R=11.4$ cm) and $\text{Cu } K\alpha$ radiation. $\text{Cd}_2\text{Nb}_2\text{O}_7$ ceramic shows $a=10.372\pm 0.001$ Å, in agreement with previous data,⁵ whereas the lattice constant of the N crystals is slightly larger, being 10.386 ± 0.001 Å.

Crystals with the same morphology as that indicated in Fig. 3 are obtained from a binary melt of KF and $\text{Cd}_2\text{Nb}_2\text{O}_7$ in molar ratio 3.5:1 (for example, 2.0 grams of KF and 5.2 grams of $\text{Cd}_2\text{Nb}_2\text{O}_7$). The lattice constant of these (indicated as K crystals in the following) is $a=10.384\pm 0.001$ Å. The advantage of KF over NaF is that the former is very soluble in water, thus facilitating the recovering of the crystals from the melt after the growing process. No chemical or spectroscopical analysis has been carried out on the K crystals.

During the process of finding a suitable flux for the growth of $\text{Cd}_2\text{Nb}_2\text{O}_7$ crystals, the following observation was made. A mixture of B_2O_3 and $\text{Cd}_2\text{Nb}_2\text{O}_7$ in molar ratios 5:1, 2:1, or 1:1, heated to about 1200°C and cooled at a rate of 80 degrees/hour, produces perfectly transparent, colorless, needle-shaped crystals with orthorhombic habit. Under the polarizing microscope the crystals show extinction at 90° . c -axis rotation and Weissenberg photographs of these crystals gave the following values for the lattice dimensions: $a=5.85$ Å, $b=14.8$ Å, $c=5.15$ Å. The chemical composition of these crystals has not yet been directly explored; but comparison of their powder pattern with that of ceramic CdNb_2O_6 led us to assume the formula CdNb_2O_6 as the most probable one. The ($hk0$) reflections on the Weissenberg satisfy the conditions given for the columbite structure¹⁰ (space group $Pbcn$), which include such compounds as MnSb_2O_6 , MgNb_2O_6 , and ZnTa_2O_6 .

In order to obtain pure $\text{Cd}_2\text{Nb}_2\text{O}_7$ crystals, the second of the two possibilities listed above had to be considered, i.e., growth from the pure melt. In addition to the already mentioned evaporation of CdO , another practical difficulty, in this case, is represented by the fact that it is impossible to extract the solidified mass from the Pt crucible without peeling off the latter. The best results were obtained from the following procedure: a basket of Pt foil, containing pure $\text{Cd}_2\text{Nb}_2\text{O}_7$ powder, is introduced into a larger Pt crucible containing a proper amount of CdO . The crucible, with its cover, is sealed as tightly as possible with alundum cement. The whole is heated to 1470°C , cooled to 1420°C in one hour, and further cooled very quickly. If the excess CdO is not enough to maintain a saturated CdO atmosphere within the crucible during the heating and cooling process, two types of crystals are produced in the basket; one is $\text{Cd}_2\text{Nb}_2\text{O}_7$, and the other is an orthorhombic crystal showing the same powder pattern as ceramic CdNb_2O_6 and as the crystals obtained from

¹⁰ A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, London, 1950), p. 504.

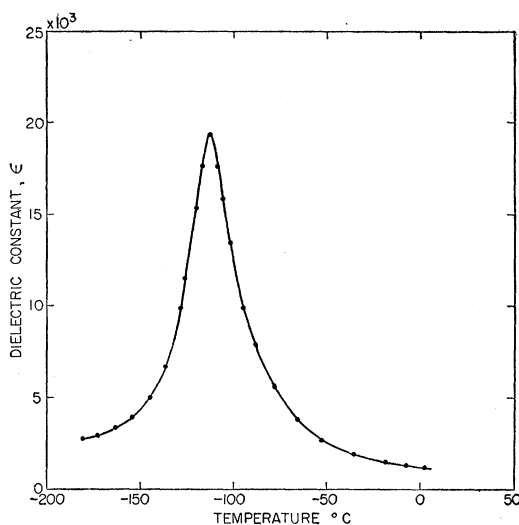


FIG. 4. Dielectric constant of $\text{Cd}_2\text{Nb}_2\text{O}_7$ crystals, grown with NaF as flux vs temperature.

B_2O_3 as a flux. This latter is again very probably CdNb_2O_6 .

The lattice constant of the $\text{Cd}_2\text{Nb}_2\text{O}_7$ crystals thus obtained is the same as for ceramic $\text{Cd}_2\text{Nb}_2\text{O}_7$: $a=10.372\pm 0.001$ Å. The crystals are too small for dielectric measurements, however, and can only be used for x-rays and optical investigations.

III. DIELECTRIC MEASUREMENTS

The study of the dielectric properties has been carried out exclusively on the N and K crystals, since crystals of pure $\text{Cd}_2\text{Nb}_2\text{O}_7$ of required size were not obtained. Unless otherwise stated, the results quoted below are those obtained with N crystals.

The crystal plates (areas ranging between 2.5 and 6 mm^2 , and thicknesses between 0.1 and 0.3 mm) were selected under the microscope for homogeneity and absence of defects. The two larger surfaces, perpendicular to the cubic $[111]$ direction, were ground parallel to each other and provided with evaporated silver electrodes.

Figure 4 shows the behavior of the dielectric constant versus temperature for a field applied along the cubic $[111]$ direction. The room temperature value is 850; the peak value, at the Curie point, is about 20 000. The measurement was made by varying the temperature slowly and continuously (about 40 degrees/hour), with a field of 50 v/cm and a frequency of 10 kc/sec. The Curie temperature is -120°C upon cooling, -112°C upon heating—showing a remarkable decrease with respect to the ceramic $\text{Cd}_2\text{Nb}_2\text{O}_7$. This decrease is no doubt due to the impurities contained in the single crystals. The dielectric constant shows the hyperbolic behavior characteristic of ferroelectric crystals above the Curie point, according to the Curie-Weiss law $\epsilon \cong C/(T-\theta)$. For ceramics the values of the Curie constant ranges from 4×10^4 to 10×10^4 °K, and θ

varies between 145° to 175°K according to different authors. For the N crystals we obtained $C = 1.1 \times 10^5$ °K, $\theta = 177$ °K.

The field dependence of the dielectric constant has been investigated by biasing the crystals with a dc field of 5 kv/cm. The shift of the Curie point towards higher temperatures is of the order of 1.5 degrees per kv/cm. The dielectric constant is decreased upon application of the dc biasing field both above and below the Curie points.

The spontaneous polarization P_s has also been measured. Because of lack of precise dimensional information for the small crystals, the value found, 6 microcoulombs/cm² at -185 °C, is only approximate. It must be noticed that the field was applied along the cubic [111] direction. If the ferroelectric axis is along the cubic [100] axis, as may be the case (see below), the value of the spontaneous polarization would be $\sqrt{3}$ times larger—that is, about 10 microcoulombs/cm².

IV. X-RAY ANALYSIS OF N , K , AND PURE $Cd_2Nb_2O_7$ CRYSTALS AT ROOM TEMPERATURE

The single crystal used for the x-ray study was a parallelepiped with the dimensions $0.03 \times 0.03 \times 0.10$ mm, grown from pure $Cd_2Nb_2O_7$ melt. As already mentioned, this type of crystal always has its [110] axis along a long edge, and (111) planes as surfaces. It was very difficult to pick up a crystal with [100] along the edge. It appeared, however, that the [110] zone is preferable for the structural study.

Weissenberg diagrams were taken for several layers of the [110] crystal, using Cu $K\alpha$ radiation; and absent reflections confirmed the space group as $Fd\bar{3}m$. General intensity relations can be explained very well by Cd and Nb positions as given by Bystroem. The intensity data for (hhl) reflections were collected using Mo $K\alpha$ radiation filtered through Zr foil. The multifilm technique with a calibrated intensity scale was used to obtain intensities, using visual estimation. Since the crystal is very small, no absorption correction was necessary; but five-day exposures were needed to obtain sufficient spot densities.

With heavy Cd and Nb atoms in a crystal, it is generally difficult to determine the exact positions of oxygen atoms. In $Cd_2Nb_2O_7$, however, the intensities of one group of reflections, of type ($4n+2, 4n+2, 4m$), depend only upon oxygen atoms; and intensities of another group, of type ($2n+1, 2n+1, 2m+1$), depend only on oxygens and differences between Cd and Nb structure factors ($f_{Cd} - f_{Nb}$), the difference being of the same order of magnitude as the factor for oxygen. From these, the oxygen parameter x was found to be $x = 0.305 \pm (0.003)$. This value is very close to the condition for regular NbO_6 octahedra. The remaining reflections are chiefly determined by $f_{Cd} + f_{Nb}$.

All structure factors were calculated with this oxygen parameter, and extinction effects observed in the strong reflections at low angles were corrected by a method

recently described by Vand.¹¹ The over-all agreement is very good, the discrepancy factor $R = (\sum ||F_0| - |F_c||) / \sum |F_0|$ being 0.06 for all reflections, and 0.11 for the two groups of reflections which were used for oxygen parameter determination only.

One of the N crystals was also studied. The crystal was ground along [110] to cylindrical form, with a diameter of 0.14 mm. Intensity data for (hhl) reflections were taken with Cu $K\alpha$ radiation. The same oxygen parameter as for pure $Cd_2Nb_2O_7$ explain intensities of the ($4n+2, 4n+2, 4m$) reflections, but do not account for those of ($2n+1, 2n+1, 2m+1$) type. The latter can be explained qualitatively if we assume that in the N crystal approximately 30 mole percent of total Cd is replaced by Na. Probably the same amount of seventh oxygen may be replaced by F, although this is difficult to establish by x-rays. The N crystal may perhaps be written as $Cd_{1.4}Na_{0.6}Nb_2O_{6.4}F_{0.6}$. The agreement of this formula with one estimated from spectroscopic analysis is as good as can be expected.

V. OPTICAL STUDY OF THE TRANSITION

The phase change in $Cd_2Nb_2O_7$ at the Curie point has also been examined by means of a new type of low-temperature stage¹² on a polarizing microscope. For pure $Cd_2Nb_2O_7$ the cubic to noncubic change occurs at 182°K, in good agreement with dielectric observations on ceramic specimens; it appears at about -123 °C for the N -type crystals, and at about -133 °C for the K -type—also in agreement with dielectric measurements.

Below the Curie point no definite extinction positions are detectable optically, nor are definite domain walls visible. This is in contrast with the case of ferroelectric $BaTiO_3$ and closely-related crystals, which reveal well-defined domain configurations with distinguishable extinction positions. Upon rotation of the $Cd_2Nb_2O_7$ plates between crossed nicols, a thin curved shadowy line rotates within the crystals; the border between light and dark regions is always diffuse and irregular. Under high magnification a fine structural pattern is visible at the surface. Near the crystal edges many small parallel wedges appear. These are elongated along the $\langle 211 \rangle$ directions, and are about 1μ wide. In the central region of the plate surface a very fine two-dimensional grid is apparent. The grid lines are probably walls of domains, the dimensions of which are very small.

The actual symmetry below the Curie point cannot be established from these observations, but a qualitative explanation can be given for them. The light travels in the cubic $\langle 111 \rangle$ direction. If the crystals become tetragonal or orthorhombic below the transition, one of

¹¹ V. Vand, "Methods for the Correction of X-Ray Intensities for Primary and Secondary Extinction in Crystal Structure Analysis," Technical Report to Office of Naval Research, July 1, 1954 (unpublished).

¹² Jona, Shirane, and Pepinsky (unpublished).

the cubic $\langle 100 \rangle$ directions will become a polar axis (see Sec. VI, below). If the domains are polarized at about 90° to each other and the walls lie at 45° to the cube edges, as in tetragonal $BaTiO_3$, a (111) plate comprised of only two domains would show extinction positions at 30° and 60° from one or the other domain. The trace of the domain wall (110) on the (111) surface is parallel to the $\langle 211 \rangle$ direction. It is in this direction that the very fine wedge-shaped domains appear elongated.

A macroscopic crystal plate contains a very large number of these domains. Some of these will always be in extinction position, regardless of the rotation of the plate (about $\langle 111 \rangle$) with respect to the vibration directions of the nicols. This probably accounts for the "rotating" extinction observed upon rotation of the crystal.

A (111) plate of $Cd_2Nb_2O_7$ about 100μ thick has a light yellow color of first order. The birefringence must therefore be very small—of the order of 0.004.

VI. LOW-TEMPERATURE X-RAY STUDY

Powder patterns of a ceramic (pure) $Cd_2Nb_2O_7$ specimen at $-140^\circ C$ revealed no line-splitting, even at high scattering angles, due to distortion from the former cubic lattice. A single-crystal examination of a pure $Cd_2Nb_2O_7$ crystal was then initiated at $-150^\circ C$, by means of our low-temperature Weissenberg camera,¹³ with radius = 11.4 cm and using $Cu K\alpha$ radiation. Zero-layer patterns from a crystal rotating about $[110]$ showed very slight splitting in a few high-angle reflections; but a study of these did not permit any decision concerning the new crystal system. Some very remarkable intensity changes were apparent in reflections of the $(2n+1, 2n+1, 2m+1)$ class, however. These reflections involve structure factors f_0 and $f_{Cd} - f_{Nb}$ only. Thus shifts of Cd ions with respect to Nb ions must occur; shifts in oxygens may or may not accompany these.

One of the N -type crystals was also examined at $-140^\circ C$. The splitting of high-angle reflections is larger than in pure $Cd_2Nb_2O_7$. Splitting is significant for reflections such as 4,4,12 and 9,9,3, but not detectable for 7,7,9 or 8,8,8. This suggests that the lattice is probably *not* rhombohedral, with a former cubic $[111]$ axis as the polar axis. We can account for the separations by assuming a tetragonal lattice with $a = 10.378 \text{ \AA}$, and $c/a = 1.0011$; but it is not possible to exclude an alternative orthorhombic distortion. A comparison with pure $Cd_2Nb_2O_7$ at $-150^\circ C$ suggests a possible tetragonal cell for it also, with $a = 10.364 \text{ \AA}$, $c/a = 1.0005$.

Why pure $Cd_2Nb_2O_7$ shows a smaller distortion than N -type crystals is not clear.

VII. STUDY OF OTHER $A_2B_2O_7$ TYPE COMPOUNDS

Besides $Cd_2Nb_2O_7$, a good number of other crystals have been reported as pyrochlore types.^{6,7} These are

¹³ Keeling, Frazer, and Pepinsky, Rev. Sci. Instr. 24, 1087 (1953).

TABLE I. Cell and dielectric constants for some $A_2B_2O_7$ crystals.

Composition	a (Å) ^a	Firing temperature (°C)	Dielectric constant at room temperature
$Cd_2Nb_2O_7$	10.372	1200	310
$(Cd_{0.9}, Pb_{0.1})_2Nb_2O_7$	10.407	1150	460
$(Cd_{0.8}, Pb_{0.2})_2Nb_2O_7$	10.443	1150	300
$(Cd_{0.4}, Pb_{0.6})_2Nb_2O_7$	10.550	1100	...
$(Cd_{0.2}, Pb_{0.8})_2Nb_2O_7$	10.596	1100	...
$(Cd_{0.1}, Pb_{0.9})_2Nb_2O_7$	10.615	1100	165
$Pb_2Nb_2O_7$	10.675	1050	190
	($\alpha = 88^\circ 50'$)		
$(Cd_{0.95}, Ca_{0.05})_2Nb_2O_7$	10.376	1200	600
$(Cd_{0.9}, Ca_{0.1})_2Nb_2O_7$	10.382	1200	540
$(Cd_{0.8}, Ca_{0.2})_2Nb_2O_7$	10.392	1200	380
$Cd_2(Nb_{0.95}, Ta_{0.05})_2O_7$	10.372	1200	570
$Cd_2(Nb_{0.9}, Ta_{0.1})_2O_7$	10.370	1200	380
$Cd_2(Nb_{0.8}, Ta_{0.2})_2O_7$	10.372	1200	200
$Cd_2Ta_2O_7$	10.376	1200	35
$Pb_2Ta_2O_7$	10.700	1050	51
	($\alpha = 88^\circ 25'$)		
$Y_2Ti_2O_7$	10.095	1200	65

^a All lattices are cubic except for the two for which values of α are given; the latter are rhombohedral.

discussed exhaustively in reference 8, under the pyrochlore-microlite classification. There it is reported that, in the $A_2B_2O_6(O, OH, F)$ formula, A can include Na, Ca, K, Mg, Fe^{+2} , Fe^{+3} , Mn^{+2} , Sb^{+3} , $Pb(?)$, Ce, La, Di, Eu, Y, Th, Zr, and U; and B includes Nb, Ta, Ti, $Sn(?)$, Fe^{+3} , and $W(?)$. The number of mixed crystals which might be examined in a complete investigation of the pyrochlore-type structure is thus enormous. Bystroem⁵ prepared $Cd_2Ta_2O_7$, $Ca_2Ta_2O_7$, and $Pb_2Sb_2O_7$ artificially, and others of the species have also been prepared.⁸ Recently, $Pb_2Nb_2O_7$ was reported to have a rhombohedral lattice slightly distorted from the cubic pyrochlore lattice.¹ It is also known that although $Ca_2Sb_2O_7$, $Sr_2Sb_2O_7$, and $Cd_2Sb_2O_7$ have the same $A_2B_2O_7$ formula, they belong to the weberite species,⁵ which has an interrupted octahedra network which would presumably not be favorable for ferroelectricity.

A modest beginning has been made on a study of the dielectric and structural properties of some solid solution systems related to $Cd_2Nb_2O_7$. The ceramic specimens were prepared by firing the appropriate mixtures at temperatures listed in Table I. All of the dielectric measurements were carried out at 10 kc/sec and a field strength of about 5 v/cm. The lattice parameters were determined using the 11.4-cm diameter Norelco powder camera and $Cu K\alpha$ radiation.

From considerations of ionic size, the following systems were considered likely to form solid solution readily: $Cd_2Nb_2O_7$ - $Pb_2Nb_2O_7$, $Cd_2Nb_2O_7$ - $Ca_2Nb_2O_7$, and $Cd_2Nb_2O_7$ - $Cd_2Ta_2O_7$. The lattice constant of these compositions are shown in Fig. 5 and Table I.

All compositions of the $Cd_2(Nb, Ta)_2O_7$ system show the cubic powder patterns of pyrochlore type with little change of lattice constant, as expected from the similarity of ionic radii of Nb and Ta. The $(Cd, Pb)_2Nb_2O_7$ system also shows the pyrochlore

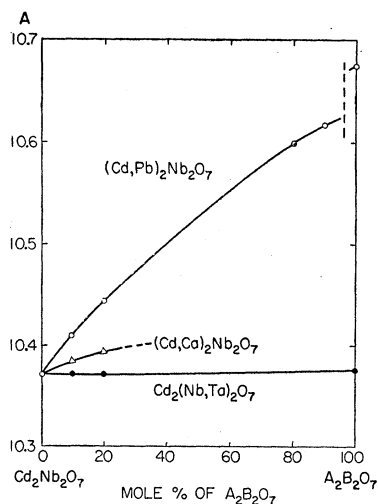


FIG. 5. Lattice parameters of solid solutions involving $\text{Cd}_2\text{Nb}_2\text{O}_7$.

lattice, except for a narrow range on the $\text{Pb}_2\text{Nb}_2\text{O}_7$ side which shows a rhombohedral lattice. This point will be discussed later.

In the $(\text{Cd}, \text{Ca})_2\text{Nb}_2\text{O}_7$ system, on the other hand, a pyrochlore-type solid solution is formed only for some compositions on the pure $\text{Cd}_2\text{Nb}_2\text{O}_7$ side. $(\text{Cd}_{0.8}, \text{Ca}_{0.2})_2\text{Nb}_2\text{O}_7$ shows, in addition to the main cubic patterns of pyrochlore type, some additional weak lines which suggest that this composition may be a mixture. Pure $\text{Ca}_2\text{Nb}_2\text{O}_7$ shows a quite different powder pattern from that of $\text{Cd}_2\text{Nb}_2\text{O}_7$, indicating that the structure is not of the pyrochlore type.

The Curie temperature of these solid solution systems were determined by dielectric measurements, as shown in Fig. 6. The results for $\text{Cd}_2(\text{Nb}, \text{Ta})_2\text{O}_7$ are not shown in the figure because they very nearly coincide with the curve for $(\text{Cd}, \text{Pb})_2\text{Nb}_2\text{O}_7$. The important result is that the Curie temperature of pure $\text{Cd}_2\text{Nb}_2\text{O}_7$ is always decreased by the replacement of Cd or Nb by other ions. The behavior of the second phase transitions in $\text{Cd}_2\text{Nb}_2\text{O}_7$ at 85°K was studied only for the system $(\text{Cd}, \text{Pb})_2\text{Nb}_2\text{O}_7$. This transition temperature was also decreased with increasing Pb concentration. It is 60°K for $(\text{Cd}_{0.95}, \text{Pb}_{0.05})_2\text{Nb}_2\text{O}_7$, and it was not observed above 10°K for $(\text{Cd}_{0.9}, \text{Pb}_{0.1})_2\text{Nb}_2\text{O}_7$.

$\text{Pb}_2\text{Nb}_2\text{O}_7$ presents an interesting problem. This compound was first studied by Cook and Jaffe,¹ and the structure was reported as a rhombohedral distortion of the pyrochlore-type structure with $a=10.570 \text{ \AA}$ and $\alpha=89^\circ 15'$.¹⁴ The dielectric measurements^{3,4} have revealed that the compound shows a flat maximum of the dielectric constant to 14°K . 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 the conclusion that $\text{Pb}_2\text{Nb}_2\text{O}_7$ is probably not ferroelectric.

The powder lines of $\text{Pb}_2\text{Nb}_2\text{O}_7$ can be explained very

¹⁴ Originally, the value $a=5.285 \text{ \AA}$ was published, (see reference 1) but later it was implied that the true cell dimension is twice as large (see reference 2).

well by assuming a rhombohedral lattice; and a comparison with the powder lines of $\text{Cd}_2\text{Nb}_2\text{O}_7$ shows that this rhombohedral lattice may be formed by a slight distortion from the cubic pyrochlore lattice. Accurate lattice constants were calculated from high angle lines 10,6,6 and 12,4,4, yielding $a=10.674 \text{ \AA}$, $\alpha=88^\circ 50'$. These values are somewhat different from the constants reported by Cook and Jaffe.¹⁵

Figure 5 shows that the phase boundary of rhombohedral $\text{Pb}_2\text{Nb}_2\text{O}_7$, and the cubic phase of $\text{Cd}_2\text{Nb}_2\text{O}_7$ lies somewhere between $(\text{Cd}_{0.1}, \text{Pb}_{0.9})_2\text{Nb}_2\text{O}_7$ and pure $\text{Pb}_2\text{Nb}_2\text{O}_7$. To explore this phase line, dielectric measurements were carried out on $\text{Pb}_2\text{Nb}_2\text{O}_7$ between 20°C and 500°C and on $(\text{Cd}_{0.1}, \text{Pb}_{0.9})_2\text{Nb}_2\text{O}_7$ between 20°C and -180°C . No anomaly indicating a phase transition was observed. Goodman also carried out dilatometric measurements of pure $\text{Pb}_2\text{Nb}_2\text{O}_7$ up to 1000°C without observing any anomaly.¹⁶

Two more compositions were studied in this range. $(\text{Cd}_{0.025}, \text{Pb}_{0.975})_2\text{Nb}_2\text{O}_7$ showed strong rhombohedral lines and some weak cubic lines; and $(\text{Cd}_{0.05}, \text{Pb}_{0.95})_2\text{Nb}_2\text{O}_7$, on the other hand, showed strong cubic lines and some weak rhombohedral lines. Although this seems to establish the existence of the mixed phase, it must be mentioned that the results immediately above might be due to nonuniformity of composition in the specimen, since the composition is very critical.

It is certain, in any case, that this rhombohedral phase is limited to the narrow range near pure $\text{Pb}_2\text{Nb}_2\text{O}_7$. In this connection it is of interest that Cook and Jaffe reported a cubic lead niobate with the approximate composition $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ ($a=10.561 \text{ \AA}$). This seems to provide an example of a general formula of pyrochlore type $A_{1+x}B_2O_{6+x}$. A further investigation of this problem is in progress.

In addition to the above-mentioned compounds, the following were prepared: $\text{Pb}_2\text{Ta}_2\text{O}_7$, $\text{Y}_2\text{Ti}_2\text{O}_7$, $\text{Sr}_2\text{Nb}_2\text{O}_7$, $\text{Y}_2\text{Zr}_2\text{O}_7$, $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{La}_2\text{Zr}_2\text{O}_7$. From powder photographs,

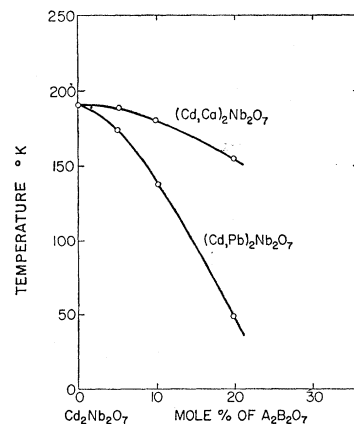


FIG. 6. Curie temperatures of solid solutions involving $\text{Cd}_2\text{Nb}_2\text{O}_7$.

¹⁵ The lattice parameters of $\text{Pb}_2\text{Nb}_2\text{O}_7$ can be calculated from the d spacings given in Goodman's paper (see reference 16). $a=10.64 \text{ \AA}$ and $\alpha=88^\circ 50'$ were obtained from 2,2,0 and 3,1,1 line groups.

¹⁶ G. Goodman, J. Am. Ceram. Soc. 36, 368 (1953).

only the first two compounds were found to have pyrochlore-type structures. The other four compounds show complicated powder patterns, and no effort was made further to interpret them. $Pb_2Ta_2O_7$ shows, as does $Pb_2Nb_2O_7$, a rhombohedral lattice; and $Y_2Ti_2O_7$ shows a cubic lattice. No dielectric anomaly was found for $Pb_2Ta_2O_7$ or $Y_2Ti_2O_7$ between 20°C and -180°C. The dielectric constants of these pyrochlore types are relatively high in general, which fact renders them worth examining. Hulm⁴ reported no anomaly in $Cd_2Ta_2O_7$, $Pb_2Ta_2O_7$, $In_2Ti_2O_7$, or $In_2Zr_2O_7$. The structure of the last two compounds is unknown.

To date, no rules are known according to which one can judge whether or not a compound of constitution $A_2B_2O_7$ is likely to have a pyrochlore structure. However, the following may be said upon consideration of the ionic radii of the involved ions. It does seem that a pyrochlore structure can be realized for only a narrow range of ionic radii: 0.95 to 1.15 Å for ion A and 0.60 to 0.70 Å for ion B . (It should of course be possible to include small amounts of other ions in the network, thus accounting for the large number of mineral

varieties in this species.) $Cd_2Nb_2O_7$ has the smallest A ion and the largest B ion in this range, and this might be related to the fact that the Curie temperature of $Cd_2Nb_2O_7$ is always shifted downward upon replacement of Cd or Nb by other ions. This critical condition on ion size is in contrast with the case of the perovskite-type structure of composition ABO_3 . A large number of crystals have been reported as members of this group, with a relatively wide range of ionic radii for A and B ; and several of the members have been found to be ferroelectric. A good number of other types of multiple oxides containing Nb, Ta, and/or Ti deserve examination, and some of them are under study in our laboratory.

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Model for Luminescence and Photoconductivity in the Sulfides

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A model for sulfides activated by monovalent metals is discussed which differs in several important respects from that usually employed. Because of the net negative charge of the lattice volume surrounding the activator there is a large cross section for trapping of holes which may be accompanied by release of a large amount of energy. This is presumed to be the transition leading to luminescence. A subsequent trapping of an electron returns the center to its original condition. For the electron trapping there is no Coulomb field and both the capture cross section and energy released would be expected to be small compared with the case of hole trapping. On the basis of this model, there is a simple explanation of the fast luminescence decay associated with hole capture and the slow conductivity decay associated with that of free electrons. Other well-known phenomena in the sulfides are examined on the basis of this model. In addition, predictions of this model concerning the infrared photoconductivity and infrared stimulation of luminescence have been verified by experiment on silver-activated cadmium sulfide.

I. INTRODUCTION

THERE exists an extensive literature on both the luminescence and conductivity properties of the sulfide phosphors. Impurity-activated sulfides have been among the earliest materials studied, and in recent years have been the subjects of intensive investigations, stimulated in part by their many practical applications. A recent paper by Klasens¹ summarizes much of the current theory of luminescence for sulfides. Similarly a large amount of work has been done on the conductivity of sulfides, particularly on cadmium sulfide which can be prepared in the form of fairly large crystals by the method of Frerichs,² and

which is of special practical interest because of its unusually high photosensitivity. An introduction to the literature on the conductivity of cadmium sulfide may be found in a paper by Rose.³ Schön⁴ and Klasens and his associates⁵ have proposed a "hole migration" theory of luminescence of sulfides activated with monovalent impurities such as Ag^+ . This theory is illustrated in Fig. 1 for the case where excitation of luminescence is by absorption of light in the fundamental band of the host lattice. The sequence of events is as follows:

³ A. Rose, RCA Rev. **12**, 362 (1951).

⁴ M. Schön, Z. Physik **119**, 463 (1942).

⁵ H. A. Klasens, Nature **158**, 306 (1946); Klasens, Ramsen, and Quantie, J. Opt. Soc. Am. **38**, 60 (1948).

¹ H. A. Klasens, J. Electrochem. Soc. **100**, 72 (1953).

² R. Frerichs, Naturwiss. **33**, 381 (1946).