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Solid-solution effects, structural transitions and ferroelectricity in sodium–cadmium niobates.*

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The dielectric properties of some $NaNbO_3$–$Cd_2Nb_2O_7$ ceramics have been described by Wainer & Wentworth (1952). A detailed examination of structural and ferroelectric properties has recently been undertaken and is briefly reported here.

Sodium niobate dissolves cadmium niobate up to a certain limiting proportion to form solid solutions having the perovskite-type crystal structure. As the proportion of cadmium niobate increases the Curie temperature is lowered, the permittivity is increased and ferroelectric rather than antiferroelectric properties are observed. In view of the structural differences, solid solution between $NaNbO_3$ and $Cd_2Nb_2O_7$ is rather unexpected, but it is now apparent that the cadmium niobate enters the lattice as $CdNb_2O_6$. Valency requirements are satisfied and the perovskite-type structure is retained by the substitution of one Cd atom and one vacancy for a pair of Na atoms. Chemical analysis of fired ceramics shows that any excess CdO in the original mixture is easily lost. Any CdO that remains is detrimental, reducing the permittivity and density and the piezoelectric activity; excess Nb_2O_5 has no appreciable effect.

The limiting composition, beyond which $CdNb_2O_6$ or $Cd_2Nb_2O_7$ appears in addition to the perovskite-type phase, corresponds to the formula $6\,NaNbO_3.CdNb_2O_6$. This composition gives the highest permittivity and piezoelectric activity, and the lowest Curie temperature.

The compound $CdNb_2O_6$ has been prepared separately and is found to have an orthorhombic structure similar to the mineral columbite $(Fe, Mn)Nb_2O_6$, in agreement with a report by Jona, Shirane & Pepinsky (1955). The permittivity varies between 19 and 23 over the range −185° C. to 300° C.; no ferroelectric properties have been observed.

Structural examination of $NaNbO_3$ containing $CdNb_2O_6$ in solid solution shows that comparatively low concentrations of $CdNb_2O_6$ introduce a new tetragonal-phase region immediately below the Curie temperature; the orthorhombic region is displaced to lower temperatures. As the concentration of $CdNb_2O_6$ is increased, first the tetragonal and then the orthorhombic phase become ferroelectric. However, no evidence was found of a sharp transition from the antiferroelectric to the ferroelectric condition either with application of fields up to 30 kV.cm.$^{-1}$ or with variation of composition or temperature. This behaviour, which is similar to that reported by Shirane, Newnham & Pepinsky (1954) for $(Na, K)NbO_3$, is difficult to reconcile with conventional models of ferroelectric and antiferroelectric structures which differ in the positional arrangement of the atoms.

In solid solutions containing low concentration of $CdNb_2O_6$ the superlattice effects shown by X-ray examination are identical with those observed for $NaNbO_3$. The structure cell has monoclinic lattice parameters $2a_0$, $4b_0$, $2c_0$, and exhibits superlattice effects associated with the quadrupled b dimension which have been shown by Francombe (1956) to persist above the Curie temperature. Vousden (1951) has shown that displacements of the ions in the quadrupled-type cell result in a non-polar, antiferroelectric structure.

The structure of Cd-rich solid solutions below the Curie temperature is tetragonal, changing to orthorhombic near room temperature. In both forms the superlattice lines indicate a doubled rather than a quadrupled cell, and ferroelectric properties are observed. It appears that the antiparallel displacements, paired along the b axis, have been changed so as to halve the structure cell and make it polar. It is, perhaps, significant that the doubled structure cell contains eight simple cells, or one unit of the formula $6\,NaNbO_3.CdNb_2O_6$.

The intermediate compositions, which show weak ferroelectric properties, the two superlattice effects, corresponding to quadrupled and to doubled cells, coexist. The relative intensities of the superlattice lines alter with temperature and correspond to the observed changes in ferroelectric properties.

The conclusion is that within each crystallite of the ceramic, at any given temperature, the local cadmium concentration determines whether the structure is ferroelectric or antiferroelectric. Macroscopically, the ratio of the two modifications depends on the overall cadmium concentration and on the temperature.

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The δ phase found in the U–Zr alloys.

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The δ phase, as shown by Saller & Rough (1955), in the U–Zr binary diagram appears to be a cubic phase with an a_0 of approximately 10·69 Å. This phase appears over a range in composition—approximately 60–80 atomic%

Zr—and its a_0 varies somewhat according to the ratio of uranium to zirconium.

A single crystal of this phase was positioned so that one of its major axes was parallel to the main axis of a goniometer. Laue back-reflection photograms were then obtained at each 45° rotation about this axis in order to check for symmetry. Fourfold symmetry was observed at the 0°, 90°, 180° and 270° positions and twofold symmetry was noted at the 45°, 135°, 225° and 315° positions. This same symmetry was observed with several different crystals.

The Laue patterns also showed fourfold symmetry after moving the crystal 90° to the above described rotation axis. In addition, the crystal was positioned so that the (111) plane was perpendicular to the X-ray beam. The resulting Laue photograph showed threefold symmetry.

Rotation and equi-inclination Weissenberg photographs for seven layer lines from these crystals were indexed according to a body-centered cubic unit cell with a_0 approximately 10·69 Å.

Powder photographs of specimens of the same composition could also be indexed according to this cubic cell, except a few of the high-angle lines, which appear to be displaced in a regular way such that this displacement would indicate an increase in a_0 of approximately 1 part in 500.

The a_0 of the δ phase, as shown in Table 1, is slightly less than three times the a_0 of the parent γ phase from which the δ was formed. The γ phase, which is body-centered cubic, is a high-temperature solid-solution phase between γ uranium and β zirconium. Density measurements of the δ phase indicate that there are 54 atoms per unit cell.

Table 1. *Lattice parameters of the γ and δ phases of the same composition* U–Zr *alloy*

Phase	a_0 (Å)
γ	3·575
(3 times γ)	(10·725)
δ	10·688

A transformation has also been made from a single crystal of γ to a single crystal of δ in which the (100) cube face of the small γ cubic cell became the (100) cube face of the δ phase.

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Unit cell and space group of sodium pyrophosphate.

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Sodium pyrophosphate decahydrate, $Na_4P_2O_7.10H_2O$, crystallizes in the monoclinic holohedral class (Groth, 1906–19). Holohedral symmetry has been confirmed by the present writers from morphological study, and the absence of optical activity supports the same conclusion. When crystallized from aqueous solution, the crystal very often grows along the b axis with $\{\bar{1}01\}$, $\{101\}$ and $\{001\}$ as the most prominent faces. From Groth, we get the following crystallographic data:

$$a:b:c = 1{\cdot}2873:1:1{\cdot}8954;\quad \beta = 98^\circ\ 16'\ .$$

To conform to the space group $C2/c$, to which the crystal was found to belong on analysis, the a axis and the shorter diagonal of Groth's cell are taken as the a and c axes respectively in the present investigation. Rotation pictures about the b axis yielded $b = 6{\cdot}97$ Å. Weissenberg pictures of the zero, first, second and the third layers, taken with b as the rotation axis, showed that the cell is C face centered with the following systematic absences:

Reflexions	Absences
hkl	$h+k$ odd
$h0l$	(h odd) l odd

The space group is thus $C2/c$.

The monoclinic angle β with the axes chosen as above was found to be 118° 30′, as measured from Weissenberg pictures. This is in very close agreement with Groth's data, which yield $\beta = 118^\circ\ 25'$. Rotation pictures about the present a and c axes gave $a = 17{\cdot}92$, $c = 14{\cdot}9$ Å. These values have been confirmed by calculations using high-angle reflexions on Weissenberg pictures. It is seen that the actual a axial identity period is twice the corresponding Groth axis, and the calculated values of a and c axes using Groth's data are $a = 17{\cdot}94$, $c = 14{\cdot}89$ Å, which show close agreement with the values obtained from the X-ray data.

Using the above data and the known density $\varrho = 1{\cdot}815$ g.cm.$^{-3}$, the number of molecules per unit cell comes out as four. Complete investigation of the structure is in progress.

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