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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 %