CONTRIBUTION FROM THE UNITED AIRCRAFT CORPORATION
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Preparation of Single Crystals of Complex Perovskite Ferroelectric and Semiconducting Compounds

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Single crystals of ferroelectric perovskite-type compounds with the general formula $Pb(B'_{0.5}B''_{0.5})O_3$ where B′ is scandium or iron and B″ is niobium or tantalum and single crystals of some new semiconducting perovskite-type compounds with the general formula $La(B'_{0.5}B''_{0.5})O_3$ where B′ is a divalent ion and B″ is ruthenium or iridium were prepared from a flux and characterized by means of X-ray diffraction. Resistivity *vs.* temperature measurements made on crystals of two of the compounds, $La(Ni_{0.5}Ru_{0.5})O_3$ and $La(Mg_{0.5}Ru_{0.5})O_3$, showed that they exhibited typical semiconductor behavior with conduction activation energies of 0.120 and 0.046 e.v., respectively.

Introduction

Several years ago a large number of new complex compounds which contained two B elements of different valence states in the octahedrally coordinated position of the perovskite structure were prepared and studied by means of X-ray diffraction.[1,2] In ref. 1, these compounds were reported as a new group of structurally related materials with good potential electronic application. A recent survey of compounds of this type, however, has revealed that although over 200 of them have been prepared to date, the electrical properties of only a few compounds have been investigated. In addition, most of these studies were made on powder compacts whose properties often are dependent on the conditions of preparation. As a consequence, investigations were initiated at the United Aircraft Research Laboratories on the preparation of single crystals of complex perovskite-type compounds with two ions in the B position. The studies, which are reported in this paper, have resulted in the preparation of single crystals of complex ferroelectric compounds prepared previously as powders and also of single crystals of several new low-resistance complex perovskite-type compounds.

Experimental

Ferroelectric Perovskite Compounds.—The first investigations were directed toward the preparation of single crystals of four complex perovskite-type compounds whose compositions can be represented by the general formula $Pb(B'_{0.5}B''_{0.5})O_3$ where B′ is scandium or iron and B″ is niobium or tantalum. These compounds were of particular interest because they were reported as having ferroelectric properties. Their Curie temperatures, which were measured on powder compacts, are reported in Table I.

The techniques used for crystal growth were similar to either Remeika's lead oxide flux[3] or Nielsen's lead oxide–lead fluoride flux[4] methods. The flux and all the reactants, PbO, Sc_2O_3, Fe_2O_3, Nb_2O_5, and Ta_2O_5, used to grow single crystals of $Pb(B'_{0.5}B''_{0.5})O_3$-type compounds were all reagent grade chemicals. The perovskite samples were prepared as powders and fired for several hours at 800°, mixed with the flux, and then packed into platinum crucibles. Covers were put on firmly to prevent excess vaporization of the flux. The filled crucibles were placed in a platinum–13% rhodium wound furnace and held at a maximum temperature for 2 hr. Cooling was controlled by a Thermovolt electronic program controller.

TABLE I

CELL SIZES AND FERROELECTRIC DATA FOR $Pb(B'_{0.5}B''_{0.5})O_3$-TYPE COMPOUNDS

Compound	Cell size, Å.[a]	Curie temp., °C.
$Pb(Sc_{0.5}Nb_{0.5})O_3$	4.086	90[b]
$Pb(Sc_{0.5}Ta_{0.5})O_3$	4.080	26[b]
$Pb(Fe_{0.5}Nb_{0.5})O_3$	4.017	112[c]
$Pb(Fe_{0.5}Ta_{0.5})O_3$	4.011	−30[d]

[a] Pseudocubic cell size. [b] G. A. Smolenskii, V. A. Isupov, and A. I. Agranovskaya, *Soviet Phys. Solid State*, **1**, 150 (1959). [c] G. A. Smolenskii, A. I. Agranovskaya, S. N. Popov, and V. A. Isupov, *Soviet Phys. Tech. Phys.*, **3**, 1981 (1958). [d] G. A. Smolenskii, A. I. Agranovskaya, and V. A. Isupov, *Soviet Phys. Solid State*, **1**, 907 (1959).

$Pb(Sc_{0.5}Nb_{0.5})O_3$ crystals were prepared from a flux–sample mixture containing 86 wt. % lead oxide flux. The mixture was cooled from 1150 to 900° at 30°/hr.

$Pb(Sc_{0.5}Ta_{0.5})O_3$ crystals were grown from a mixture containing 42.5 wt. % lead oxide and 42.5 wt. % lead fluoride flux. These samples were cooled from 1325 to 1025° at 25°/hr.

$Pb(Fe_{0.5}Nb_{0.5})O_3$ and $Pb(Fe_{0.5}Ta_{0.5})O_3$ crystals were prepared following Remeika's technique. These samples were cooled at 5°/hr. from 1230 to 900°. For growing crystals of $Pb(Fe_{0.5}Nb_{0.5})O_3$ and $Pb(Fe_{0.5}Ta_{0.5})O_3$, 64 wt. % lead oxide was mixed with the former compound and 54 wt. % lead oxide mixed with the latter, and the samples were cooled at 5°/hr. from 1230 to 800°.

The $Pb(Sc_{0.5}Nb_{0.5})O_3$, $Pb(Fe_{0.5}Ta_{0.5})O_3$, and $Pb(Sc_{0.5}Ta_{0.5})O_3$ crystals obtained using these procedures were small cubes about 1 mm. on edge, while the $Pb(Fe_{0.5}Nb_{0.5})O_3$ crystals were slightly larger and more irregular in shape. All $Pb(B'_{0.5}B''_{0.5})O_3$ crystals were dark brown in color except for crystals of $Pb(Sc_{0.5}Nb_{0.5})O_3$ which were dark blue to black. Crystal cubes of $Pb(Sc_{0.5}Ta_{0.5})O_3$ were joined together in flat sheets which seem to have grown in layers parallel to the bottom of the crucible.

X-Ray precession photographs were taken of a well-formed crystal of each compound to ensure that it was single. These photographs showed patterns which indicated that they had perovskite-type structures. Powder diffraction photographs of ground crystals taken using a 114.6-mm. Philips X-ray camera with copper Kα radiation confirmed the single crystal diffraction data and showed no evidence of ordering of the B ions in the structure of any of the compounds. It should be noted, however, that the back reflection lines in the X-ray powder pattern of $Pb(Sc_{0.5}Nb_{0.5})O_3$ were broad, which may mean that its unit cell is slightly distorted from the one found in the ideal cubic perovskite structure or that the crystal was not uniform in composition. The unit cell sizes for the $Pb(B'_{0.5}B''_{0.5})O_3$-type compounds are given in Table I. These must be presumed to be cell param-

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(3) J. P. Remeika, *ibid.*, **78**, 4259 (1956).
(4) J. W. Nielsen, *J. Appl. Phys.*, **31**, 51s (1960).

Table II

Crystal Growing Data for $La(B'_{0.5}B''_{0.5})O_3$-Type Compounds

Compound	Flux	Flux:sample ratio, wt. %	Temp. range, °C.	Cooling rate, °C./hr.	Crystal size, mm. edge
$La(Ni_{0.5}Ru_{0.5})O_3$	PbO	85:15	1300–850	30	0.5, max.
	$PbO-PbF_2$	85:15	1300–1000	30	2
$La(Ni_{0.5}Ir_{0.5})O_3$	$PbO-PbF_2$	85:15	1300–1000	30	0.5
$La(Mg_{0.5}Ru_{0.5})O_3$	$PbO-PbF_2$	85:15	1320–1000	30	1
$La(Zn_{0.5}Ru_{0.5})O_3$	PbO	80:20	1300–25	60	0.1

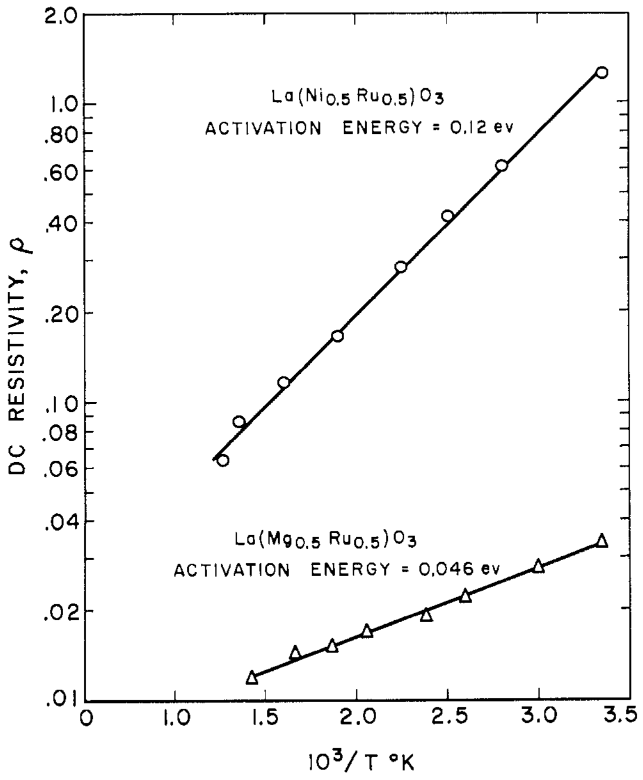

Figure 1.—Log resistivity *vs.* $1000/T$ for $La(Ni_{0.5}Ru_{0.5})O_3$ and $La(Mg_{0.5}Ru_{0.5})O_3$.

eters of the cubic pseudocells, even though the splitting of back reflection lines could not be detected because ferroelectric crystals cannot be perfectly cubic.

Semiconducting Perovskite Compounds.—Attempts also were made to prepare a number of new perovskite-type compounds with the general formula $La(B'_{0.5}B''_{0.5})O_3$ where B′ is a divalent ion and B″ is Ru or Ir in a single crystal form. These black compounds were produced initially as powders by mixing reagent grade La_2O_3, a divalent metal oxide, and RuO or IrO in a 1:1:1 molar ratio and firing the mixture in air at 1150° for 24 hr. These materials were of interest because of their low electrical resistances and stability in air.

Single crystals of four of the $La(B'_{0.5}B''_{0.5})O_3$-type compounds were prepared using either a lead oxide or a lead oxide–lead fluoride flux with enough La_2O_3, divalent metal oxide, and RuO_2 or IrO_2 to form the desired compound.[3,4] The flux techniques employed were similar to those used to grow the $Pb(B'_{0.5}B''_{0.5})O_3$-type crystals. The amount and composition of the fluxes, firing conditions, and cooling rates are given in Table II. The resulting black crystals were cubic in shape.

X-Ray powder diffraction photographs, taken of the powders and ground crystals, showed the typical perovskite pattern with extra lines. However, the entire diffraction pattern of these compounds still could be indexed on the basis of a cubic unit cell with an edge twice the length of the simple perovskite cell *a* axis. A typical indexing, in this case, for $La(Ni_{0.5}Ru_{0.5})O_3$, is given in Table III and the unit cell sizes for all of the $La(B'_{0.5}B''_{0.5})O_3$-type compounds prepared in this study are given in Table IV. The cell sizes observed indicate that magnesium and zinc both have larger effective ionic radii than nickel. The fact that the magnesium ions appear to be larger than the nickel ions is consistent with the results obtained for ordered $A(B_{0.33}Nb_{0.67})O_3$ perovskite-type compounds.[5] The much smaller cell size found for compounds which contain manganese, however, probably means that the manganese is in the trivalent state. It should be noted that the lattice type for these compounds is simple cubic and not face-centered cubic as it is for the ordered $Ba(B'_{0.5}Nb_{0.5})O_3$ perovskite-type compounds prepared in a previous study.[6] Precession X-ray photographs of the single crystals showed diffraction symmetry to be m3m and a syste-

Table III

X-Ray Data for $La(Ni_{0.5}Ru_{0.5})O_3$

hkl	I/I_0	Obsd. *d*	Calcd. *d*
111	10	4.55	4.56
200	40	3.91	3.95
210	10	3.52	3.53
220	100	2.78	2.78
221	10	2.62	2.63
311	10	2.37	2.38
222	50	2.27	2.28
320	10	2.18	2.19
400	80	1.970	1.975
410	30	1.915	1.916
420	40	1.765	1.767
421	40	1.722	1.724
422	90	1.611	1.613
430	<10	1.578	1.580
432,520	20	1.465	1.467
440	60	1.395	1.397
522,441	<10	1.374	1.375
531	<10	1.335	1.336
600,442	<10	1.317	1.317
610	<10	1.298	1.299
620	70	1.248	1.249
621,540	20	1.233	1.234
622	10	1.191	1.191
630	20	1.178	1.178
444	50	1.140	1.140
632	10	1.129	1.130
642	80	1.055	1.056
650	10	1.012	1.012

Table IV

Lattice Parameters for $La(B'_{0.5}B''_{0.5})O_3$-Type Compounds

Compound	Cell size, Å.
$La(Ni_{0.5}Ru_{0.5})O_3$	7.90[a]
$La(Ni_{0.5}Ir_{0.5})O_3$	7.90[a]
$La(Mn_{0.5}Ru_{0.5})O_3$	7.84[b]
$La(Mn_{0.5}Ir_{0.5})O_3$	7.86[b]
$La(Mg_{0.5}Ru_{0.5})O_3$	7.91[a]
$La(Mg_{0.5}Ir_{0.5})O_3$	7.92[b]
$La(Zn_{0.5}Ru_{0.5})O_3$	7.97[c]

[a] From X-ray data for ground single crystals. [b] From X-ray data for powder samples. [c] From single crystal X-ray data.

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matic absence of $h00$ reflections when h is odd. Therefore, the crystals probably belong to the space group $P4_232$.

Although the low resistances of all of these compounds were confirmed by single measurements, only the single crystals of two of them, $La(Ni_{0.5}Ru_{0.5})O_3$ and $La(Mg_{0.5}Ru_{0.5})O_3$, were found to be sufficiently large and well-shaped so that platinum paste electrodes could be applied to the faces and extensive electrical resistivity measurements made. The former cubic crystals were 2 mm. on an edge while the latter were 1 mm. on an edge. A constant current was applied and the voltage drop was measured across a standard resistor in series with the crystal. The plots of log resistivity *vs.* $1000/T$ for $La(Ni_{0.5}Ru_{0.5})O_3$ and $La(Mg_{0.5}Ru_{0.5})O_3$ shown in Figure 1 are typical of semiconductors. Calculations from these plots show that the conduction activation energies for these compounds are 0.120 and 0.046 e.v., respectively.

Conclusions

The growth of single crystals of several complex perovskite-type compounds, although the crystals are not large, is a step toward obtaining many of these materials in a suitable form for good electrical measurements. Crystals of $La(Ni_{0.5}Ru_{0.5})O_3$ and $La(Mg_{0.5}Ru_{0.5})O_3$, for instance, were large enough to make meaningful resistivity measurements. It is realized that other techniques of crystal growing besides the flux technique may produce larger crystals of complex perovskite-type compounds. In this connection, investigations of growing these crystals by the Czochralski and Verneuil techniques are presently being conducted at the Research Laboratories.

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Solid State Studies of Tungsten Trioxide Single Crystals below Room Temperature[1]

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The Hall voltage, electrical resistivity, and thermoelectric power have been measured as a function of temperature on single crystals of WO_3 in the range 140–300°K. Discontinuities appear on cooling at approximately +10 and −40°, corresponding, respectively, to a monoclinic-to-triclinic (γ-to-β) and a piezoelectric-to-ferroelectric (β-to-α) transition. The γ-to-β transition is strongly dependent on the domain characteristics and the impurity concentrations of the individual crystals. Introduction of oxygen vacancies leads to disappearance of the discontinuities at +10 and −40°.

Introduction

Tungstic oxide is the host structure for the "tungsten bronzes," M_xWO_3 ($0 < x < 1$). The solid state properties of WO_3 are of interest, since the metallic properties of the tungsten bronzes can be interpreted in terms of a quasi-free-electron model in which a d-orbital conduction band of the host WO_3 is populated by electrons from donor atoms M.[2] In the case of the alkali tungsten bronzes with $x > 0.25$, the donor ionization energy is apparently very small and may even be zero,[3] but in the copper tungsten bronzes[4] the donor ionization energy seems to be large enough compared to the thermal energy to produce semiconducting behavior below about 220°K. Single crystal studies of Cu_xWO_3 by electrical conductivity, Hall voltage, and thermoelectric power measurements disclose, however, anomalously low carrier densities. Also, there are marked changes in specific resistivity which have been assigned to major changes in carrier mobility brought about by phase changes in the host structure. Similar resistivity behavior has been observed in single crystals of Ag_xWO_3.[5] The present investigation was undertaken to elucidate the carrier characteristics in the conduction band of the WO_3 host structure. This paper reports the results obtained below room temperature. Results obtained above room temperature have been reported previously.[6]

WO_3 can exist in antiferroelectric[7] as well as ferroelectric modifications[8] and shows several other transitions at which changes occur in domain structure,[9–11] optical indices of refraction,[12] dielectric constant,[8,9] "thermal transition of transparency,"[13] optical absorption edge,[14] specific heat,[10] coefficient of expansion,[15] and electrical conductivity.[9,16] Figure 1 summarizes the relations of the four phases that have been defined, including the hysteresis effects noted.

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