$$H_2B[N(CH_3)_3]_2{}^+X^- \xrightarrow{120\text{–}200°} (CH_3)_3NBH_2X + N(CH_3)_3$$

Trimethylamine azidodihydroborane, $(CH_3)_3NBH_2N_3$, was prepared in 30–40% yield by slow heating of $H_2B[N(CH_3)_3]_2{}^+N_3{}^-$ to 120–150° under vacuum. The azide distilled from the pyrolysis flask as a mobile liquid which froze to a crystalline solid at 13°. On rapid heating the azidoborane detonates near 200°, but otherwise appears to be safe to handle. It is soluble in ethers, benzene, and chloroform and is sparingly soluble in water. On exposure to moist air for a day, partial hydrolysis takes place with formation of small amounts of a nonvolatile white solid.

The infrared spectrum of $(CH_3)_3NBH_2N_3$ shows the expected two BH stretching frequencies at 2400 and 2280 cm.$^{-1}$ and an azide stretching frequency at 2100 cm.$^{-1}$. It is reported in the literature[3] that crystalline $(CH_3)_3NBH_{3-n}(N_3)_n$ compositions, where $n$ = 1.5 and 1.9, result when trimethylamine is added to the reaction product of diborane and hydrazoic acid. It is quite apparent that these are gross mixtures, and $(CH_3)_3NBH_2N_3$ is probably not present in significant amounts since it is a liquid.

Trimethylamine azidodihydroborane adds one mole of boron trifluoride, apparently to form $(CH_3)_3NBH_2\text{-}N_3\text{-}BF_3$. The infrared spectrum of the adduct shows an azide stretching absorption shifted toward shorter wave length (2175 cm.$^{-1}$) and strong BF absorption at 1100–1200 cm.$^{-1}$. This type of adduct is not unknown in boron chemistry, as evidenced by the recently reported compound, $R_2NHBH_2CNBH_3$.[4]

Pyrolyses of other salts are being investigated. The chloride salt, $H_2B[N(CH_3)_3]_2{}^+Cl^-$, when heated to near 200°, gives pure $(CH_3)_3NBH_2Cl$; $H_2B[N(CH_3)_3]_2{}^+Br^-$ forms $(CH_3)_3NBH_2Br$; and the carbonate salt yields traces of a liquid which may have the structure $(CH_3)_3NBH_2OCO_2BH_2N(CH_3)_3$. The chlorine and bromine substituted adducts have been reported by Nöth and Beyer,[5] who prepared them by the reaction of trimethylamine borane and the corresponding hydrogen halide, but some difficulty was experienced by us in obtaining pure products by their procedure.

## Experimental

A 60-ml. portion of 2.3 $M$ $H_2B[N(CH_3)_3]_2OH$[2] was acidified with aqueous hydrazoic acid, and the water was evaporated *in vacuo* to leave about 26 g. of mushy solid. The residue was transferred to a short-path still equipped with a drip tip and take-off assembly.[6] The remainder of the water in the residue was removed by careful heating to 80° under high vacuum. On further heating, some gas evolution was observed at 100–120°. The solid changed to a liquid after several hours at this temperature, trimethylamine collected in the pump trap, and a clear mobile liquid distilled. Heating was continued for 3–4 hr. at 130–140° until a total of 5.2 g. (32%) of $(CH_3)_3NBH_2N_3$ had collected. The residue still contained some undecomposed $H_2B[N(CH_3)_3]_2{}^+N_3{}^-$.

*Anal.* Calcd. for $(CH_3)_3NBH_2N_3$: C, 31.6; H, 9.7; N, 49.2; B, 9.5. Found: C, 32.2; H, 9.9; N, 49.1; B, 9.5.

A 0.17-g. portion (1.5 mmoles) of $(CH_3)_3NBH_2N_3$ absorbed 1.27 mmoles of gaseous boron trifluoride from a total of 2.8 mmoles at room temperature to give a liquid adduct which was soluble in benzene without reaction.

An anhydrous sample of $H_2B[N(CH_3)_3]_2{}^+Cl^-$, 6.09 g. (36.6 mmoles), was heated in a vacuum sublimer to 200–250° over a period of 3 hr. The white sublimate was collected on a water jacket cooled to 0°. The pyrolysis gases were collected in a series of traps on a vacuum train. Repeated resublimation of the white sublimate yielded $(CH_3)_3NBH_2Cl$, 2.79 g. (71.2% yield). The pure product melts at 85–86°, lit.[5] 85°.

*Anal.* Calcd. for $(CH_3)_3NBH_2Cl$: C, 33.6; H, 10.3; N, 13.1; B, 10.1; Cl, 33.0. Found: C, 33.6; H, 10.3; N, 13.1; B, 10.3; Cl, 33.7.

The nonvolatile residue, 0.96 g., was identified by infrared analysis as $(CH_3)_3NH^+Cl^-$. The liquid nitrogen trap contained trimethylamine (83% yield) and a trace of chloroform which had been used in the drying of the original salt.

In the apparatus described above, 9.22 g. (43.6 mmoles) of anhydrous $H_2B[N(CH_3)_3]_2{}^+Br^-$ was decomposed at 200–250° to yield a gas, a sublimate, and a residue. The condensed gas, 2.47 g. (96% yield), was identified as trimethylamine by its infrared spectrum and vapor pressure. The sublimate was resublimed three times at 60–100° to yield a white crystalline product, 5.38 g. (88.4% yield), m.p. 74–75°, lit.[5] 67°.

*Anal.* Calcd. for $(CH_3)_3NBH_2Br$: C, 23.7; H, 7.30; N, 9.22; B, 7.12; Br, 52.6. Found: C, 24.2; H, 7.42; N, 9.34; B, 7.11; Br, 51.1.

A sample of $[H_2B[N(CH_3)_3]_2{}^+]_2CO_3{}^{-2}$ was prepared by treating one part of $H_2B[N(CH_3)_3]_2{}^+OH^-$ with carbon dioxide (from Dry Ice) until saturated, boiling to expel excess carbon dioxide, and adding one part of $H_2B[N(CH_3)_3]_2{}^+OH^-$. The solution was evaporated with careful mild heating until a white solid formed which decomposed with formation of hydrogen, carbon dioxide, trimethylamine, and a few drops of a clear mobile liquid. The infrared spectrum of the liquid had a $BH_2$ doublet absorption at 2400 and 2300 cm.$^{-1}$, a strong carbonyl absorption at 1700 cm.$^{-1}$, and bands in the long wave length region at 1180, 1250, and 850 cm.$^{-1}$, characteristic of $R_3NBH_2X$ derivatives. The product was not obtained in pure form.

*Anal.* Calcd. for $(CH_3)_3NBH_2OCO_2BH_2N(CH_3)_3$: C, 41.2; H, 10.9. Found: C, 38.4; H, 9.9.

This compound is quite sensitive to hydrolysis.

---

[2] N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

[3] E. Wiberg and H. Michaud, *Z. Naturforsch.*, **9b**, 497 (1954).

[4] V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).

[5] H. Nöth and H. Beyer, *Ber.*, **93**, 2251 (1960).

[6] R. J. McCarter, *Rev. Sci. Instr.*, **33**, 388 (1962).

---

CONTRIBUTION FROM THE PIGMENTS DEPARTMENT,
E. I. DU PONT DE NEMOURS AND CO.,
EXPERIMENTAL STATION, WILMINGTON, DELAWARE

# Preparation and Properties of the $Ln_2Ti_2O_7$-Type Rare Earth Titanates

BY L. H. BRIXNER

*Received April 22, 1964*

The mineral pyrochlorite $(CaNaNb_2O_6F)$[1] exists as a face-centered cubic structure which can be derived in principle from appropriate substitutions in a material of empirical formula $A_2B_2O_7$. Examples of a true $A_2B_2O_7$ compound are found in the synthetic structures

---

[1] O. Rosén and A. Westgren, *Geol. Foren. Stockholm For.*, **60**, 226 (1938).

Table I

Lattice Parameters and Densities of the $A^{III}_2B^{IV}_2O_7$-Type Rare Earth Titanates

| Compn. | Lattice parameters, Å. | X-Ray density, g. ml.$^{-1}$ | Pycn. density, g. ml.$^{-1}$ |
|---|---|---|---|
| $Sc_2Ti_2O_7$ | 9.801 | 4.117 | 3.98 |
| $Y_2Ti_2O_7$ | 10.080 | 5.041 | 5.01 |
| $La_2Ti_2O_7$ | ... | ... | ... |
| $Ce_2Ti_2O_7$ | ... | ... | ... |
| $Pr_2Ti_2O_7$ | ... | ... | ... |
| $Nd_2Ti_2O_7$ | ... | ... | ... |
| $Sm_2Ti_2O_7$ | 10.211 | 6.478 | 6.40 |
| $Eu_2Ti_2O_7$ | 10.192 | 6.544 | 6.51 |
| $Gd_2Ti_2O_7$ | 10.171 | 6.706 | 6.66 |
| $Tb_2Ti_2O_7$ | 10.148 | 6.779 | 6.70 |
| $Dy_2Ti_2O_7$ | 10.119 | 6.912 | 6.87 |
| $Ho_2Ti_2O_7$ | 10.095 | 7.008 | 6.94 |
| $Er_2Ti_2O_7$ | 10.069 | 7.105 | 7.00 |
| $Tm_2Ti_2O_7$ | 10.050 | 7.152 | 7.01 |
| $Yb_2Ti_2O_7$ | 10.028 | 7.316 | 7.31 |
| $Lu_2Ti_2O_7$ | 10.011 | 7.392 | 7.29 |

Table II

Resistivities, Dielectric Constants, and Dissipation Factors of the $A_2B_2O_7$-Type Rare Earth Titanates

| Compn. | Resistivity at 25°, ohm cm. | Dielectric constant | Dissipation factor, % |
|---|---|---|---|
| $Sc_2Ti_2O_7$ | $6.9 \times 10^{12}$ | 30.0 | 1.1 |
| $Y_2Ti_2O_7$ | $3.1 \times 10^{12}$ | 34.6 | 0.9 |
| $La_2Ti_2O_7$ | $1.9 \times 10^{13}$ | 36.9 | 1.0 |
| $Ce_2Ti_2O_7$ | $1.1 \times 10^{11}$ | 40.0 | 3.2 |
| $Pr_2Ti_2O_7$ | $2.3 \times 10^{11}$ | 37.3 | 4.1 |
| $Nd_2Ti_2O_7$ | $3.2 \times 10^{12}$ | 32.7 | 1.1 |
| $Sm_2Ti_2O_7$ | $1.8 \times 10^{12}$ | 35.1 | 1.2 |
| $Eu_2Ti_2O_7$ | $3.2 \times 10^{12}$ | 31.7 | 0.9 |
| $Gd_2Ti_2O_7$ | $2.0 \times 10^{12}$ | 32.6 | 1.0 |
| $Tb_2Ti_2O_7$ | $9.3 \times 10^{10}$ | 40.2 | 3.7 |
| $Dy_2Ti_2O_7$ | $3.7 \times 10^{12}$ | 30.6 | 0.9 |
| $Ho_2Ti_2O_7$ | $8.1 \times 10^{11}$ | 30.9 | 1.4 |
| $Er_2Ti_2O_7$ | $7.0 \times 10^{11}$ | 33.7 | 0.9 |
| $Tm_2Ti_2O_7$ | $1.9 \times 10^{12}$ | 37.3 | 1.6 |
| $Yb_2Ti_2O_7$ | $6.2 \times 10^{12}$ | 32.2 | 0.9 |
| $Lu_2Ti_2O_7$ | $5.3 \times 10^{12}$ | 29.6 | 0.8 |

$Cd_2Nb_2O_7$[2] and $Ca_2Ta_2O_7$.[2] Earlier work in other laboratories[3–6] indicated that the divalent metal ion, A, in $A_2B_2O_7$ can be replaced by a trivalent rare earth ion if the pentavalent Nb or Ta ion, B, is replaced by tetravalent Ti. Compounds of the general formula $M_2Ti_2O_7$ have thus been reported where M is $Y^{+3}$, $La^{+3}$, $Pr^{+3}$, $Nd^{+3}$, $Sm^{+3}$, $Gd^{+3}$, $Dy^{+3}$, and $Yb^{+3}$.

In this study $M_2Ti_2O_7$ compounds of Sc and Y as well as of all of the trivalent rare earth ions except Pm have been prepared. Lattice parameters of each compound have been obtained from X-ray powder diffraction data and the resistivity and dielectric constant values of each compound have been determined on sintered compacts.

## Experimental

Oxides of the rare earths and yttrium were obtained in 99.9% purity from Lindsay Chemical Co. Scandium oxide was prepared from resublimed $ScCl_3$, which in turn was obtained by chlorination of thortveitite from Norsk Feldspat, Norway. High purity $TiO_2$ was prepared by careful hydrolysis of redistilled water-clear $TiCl_4$ and subsequent sintering between 900 and 1000° under oxygen. Some of the rare earth oxides, such as those of Ce, Pr, and Tb, were obtained in oxidation states higher than III, and the corresponding sesquioxides were prepared by hydrogen reduction at 1200°. In order to eliminate the possibility of reoxidation during the subsequent reaction of these oxides with $TiO_2$, all preparations involving these oxides were carried out under argon gettered with Zr–Ti alloy turnings. All other rare earth titanates were prepared either in air or under oxygen. The weighed samples of oxide were mixed in stoichiometric amounts in a mechanical agate ball mill under acetone. During a first firing step, the dried mixtures were fired at 1050° for 10–14 hr. and furnace cooled. In order to homogenize this primary reaction product, it was again wet ball milled and 1-in. diameter pellets were pressed under 20,000–40,000 p.s.i. These pellets were then refired at 1200–1350° for another 10–14 hr., and after this procedure, homogeneous final reaction products were obtained which did not give any X-ray patterns of the constituent components. Since the measured weight losses during the different firing operations were always less than 0.1% for 10-g. charges, analysis was not considered useful.

**X-Ray Study.**—Lattice parameters were determined in the previously described fashion.[7] Parameters can be considered accurate to ±0.001 Å. The densities were determined on powdered specimens of −200 mesh, by weighing 1–2-g. samples into a 5-ml. pycnometer and distilling pure $CCl_4$ onto the compound under vacuum. While the $CCl_4$ was frozen out with liquid nitrogen, it was possible to pump the system to $10^{-5}$ mm. or better. Table I summarizes the structural parameters together with the X-ray and pycnometrically determined densities. The parameters of the compounds previously reported in the literature are in good agreement with those given in Table I.

**Electrical Properties.**—In view of the fact that Cook and Jaffé[8] discovered the ferroelectric modification of $Cd_2Nb_2O_7$ below room temperature, it was of particular interest to determine the dielectric constants of the prepared compositions and check them as a function of temperature. Since 12 of the 16 compounds were truly cubic, one would not expect these to be ferroelectric at room temperature, but there was a possibility that the noncubic materials might exhibit ferroelectric behavior. Unfortunately, lacking single crystals, the structure of the La, Ce, Pr, and Nd compounds is not known at this moment. MacChesney[6] had already demonstrated that $La_2Ti_2O_7$ is not ferroelectric between 25 and 500°.

The resistivities and dielectric constants were determined on 1-in. diameter pellets, 1–2 mm. thick. These disks were fired up to 1650° and the resulting densities were about 80–85% of theoretical. All reported data are characteristic of this condition, since no extrapolation to 100% density was attempted. The fired disks were polished with abrasive paper (No. 400 and 600) and silver-coated on both sides with No. 6320 Du Pont silver paint, baked on at 800°. Leads were then soldered on these adherent contacts. The capacitance and loss measurements were carried out with a General Radio Type 650-A impedance bridge, using a Hewlett–Packard Model 201B oscillator-amplifier as a source of 20 kc. current. The resistivities were determined with a 610A Keithley electrometer and can be considered accurate to ±0.50 ohm. cm. The electrical properties are summarized in Table II. It is apparent from these data that at least at room temperature none of the compositions (including the ones not cubic) exhibited an exceptionally high dielectric constant. The value 36.9 for $La_2Ti_2O_7$ is in good agreement with 37.5 determined by MacChesney.[6]

Practically all of the other compounds had a dielectric constant

---

(2) A. Byström, *Arkiv Kemi*, **18A**, No. 21 (1945).

(3) A. L. H. Ahrens, *Geochim. Cosmochim. Acta*, **2**, 115 (1954).

(4) D. Giusca and I. Popescu, *Bull. Soc. Roumaine Phys.*, **40**, 13 (1939).

(5) R. S. Roth, *J. Res. Natl. Bur. Std.*, **56**, 17 (1956).

(6) J. B. MacChesney and H. A. Sauer, *J. Am. Ceram. Soc.*, **45**, 416 (1962).

(7) L. H. Brixner, *Inorg. Chem.*, **2**, 992 (1963).

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

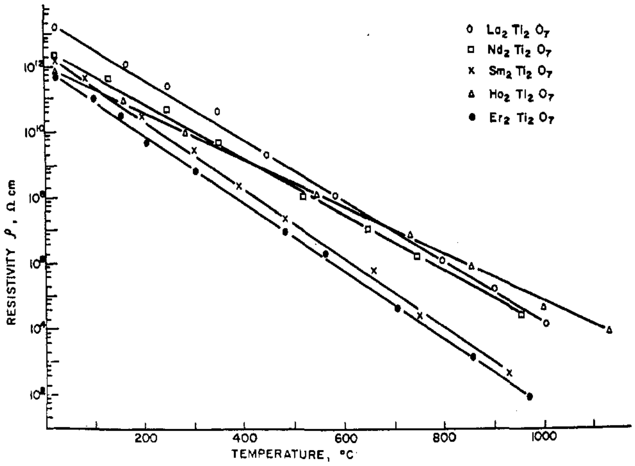

Fig. 1.—Electrical resistivities as a function of temperature for some rare earth titanates.

of about the same magnitude, and the reason for the somewhat lower resistivity (and high dissipation factor) for the Ce, Pr, and Tb compounds is probably a slight oxygen deficiency which came about during the firing of these compositions in an inert atmosphere. With the exception of these particular compounds, the dielectric constants of all other compositions were measured up to 300°. In each case, the dielectric constant stayed relatively constant up to this temperature. At higher temperatures, both the apparent dielectric constant and the dissipation factor increased, not because of any ferroelectric behavior but rather due to the exponential decrease of the electrical resistivity as demonstrated for $La_2Ti_2O_7$, $Nd_2Ti_2O_7$, $Sm_2Ti_2O_7$, $Ho_2Ti_2O_7$, and $Er_2Ti_2O_7$ in Fig. 1. All these compounds exhibited p-type semiconduction at elevated temperatures.

Finally, we checked all of the compounds prepared for luminescence in the visible by irradiating them with both a 2537 Å. and a 3660 Å. ultraviolet source. None of the compounds fluoresced in the visible. This is somewhat surprising since most of the rare earths, at least in the configuration of their sesquioxides, absorb ultraviolet light in the region of the stated excitation. We could possibly have a case of concentration quenching or else the particular coordination of the cubic pyrochlore structure does not provide an appropriate host lattice for the excitation of the trivalent rare earths. Finally, the fact that $TiO_2$ is known to absorb ultraviolet light strongly, without re-emitting in the visible, could also be the cause for the nonluminescence of these rare earth titanates. Since it is established that there actually exists a photochemical interaction between ultraviolet light and $TiO_2$, this would also rule out the possibility of the excitation of fluorescent emission by energy transfer from the host structure because all incident energy would be dissipated through chemical reaction.

**Acknowledgment.**—The author gratefully acknowledges the assistance of Mr. A. T. Weinmann in obtaining the lattice parameters.

# Correspondence

## Divergence in the Relative Shielding of Ring and Side-Chain Protons in Substituted Metallocenes

*Sir:*

We have recently examined the proton nuclear magnetic resonance spectra of several mono- and diacyl derivatives of the ferrocene–ruthenocene–osmocene triad and have observed that there is a gradual deshielding of all the corresponding ring protons proceeding from the iron to the ruthenium to the osmium analogs.[1] We have subsequently noted a gradual *shielding of the methyl protons* of acetylmetallocenes in this same series. In order to test the generality of this phenomenon, two series of substituted metallocenes with hydrogen atoms $\alpha$ and $\beta$ to the ring have been synthesized and analyzed by proton n.m.r.

Ethylruthenocene [*Anal.* Calcd. for $C_{12}H_{14}Ru$: C, 55.85; H, 5.44; Ru, 38.98; mol. wt., 259. Found: C, 55.80; H, 5.53; Ru, 39.20; mol. wt., 258], m.p. 12–12.5°, and ethylosmocene [*Anal.* Calcd. for $C_{12}H_{14}Os$: C, 41.37; H, 4.05; Os, 54.59; mol. wt., 348. Found: C, 41.67; H, 4.21; Os, 52.54; mol. wt., 356], m.p. 33–33.5°, were both prepared in 88% yield by reduction of the appropriate acetylmetallocene with $LiAlH_4 + AlCl_3$ in ethyl ether.[2] Benzylruthenocene [*Anal.* Calcd. for $C_{17}H_{16}Ru$: C, 63.53; H, 5.02; Ru, 31.44; mol. wt., 321. Found: C, 63.68; H, 5.31; Ru, 31.25; mol. wt., 323], m.p. 86–87°, and benzylosmocene [*Anal.* Calcd. for $C_{17}H_{16}Os$: C, 49.74; H, 3.93; Os, 46.33; mol. wt., 410. Found: C, 50.00; H, 4.13; Os, 46.38; mol. wt., 409], m.p. 100–101°, were prepared in 87–90% yield by similar reduction of the corresponding benzoylmetallocenes. These alkylmetallocenes as well as ethylferrocene[3] and benzylferrocene[4] were purified by chromatography on activated alumina and subsequent recrystallization from methanol.

The proton n.m.r. spectra of the ethyl- and benzylmetallocenes, together with pertinent n.m.r. spectra for monoacetyl- and 1,1′-diacetylmetallocenes, are abstracted in Table I. It is apparent that the introduction of an ethyl or benzyl substituent generally effects shielding of the ring protons with respect to the parent unsubstituted metallocene. As in the case of the various acylmetallocene series, both the ethyl- and benzylmetallocenes show a gradual deshielding of all the corresponding ring protons proceeding from the

---

(1) M. D. Rausch and V. Mark, *J. Org. Chem.*, **28**, 3225 (1963).

(2) K. L. Rinehart, Jr., A. F. Ellis, C. J. Michejda, and P. A. Kittle, *J. Am. Chem. Soc.*, **82**, 4112 (1960); K. Schlogl, A. Mohar, and M. Peterlik, *Monatsh.*, **92**, 921 (1961).

(3) F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955); M. Rosenblum and R. B. Woodward, *ibid.*, **80**, 5443 (1958).

(4) M. D. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957).