for the observations. The theoretical calculations of Basolo and Pearson[12] based on simple crystal-field theory predict a lower activation energy for dissociation of the octahedral complex to a square pyramidal one than for association to a pentagonal bipyramidal complex. With the available data no unambiguous conclusions can be reached about alternative mechanisms. It may be profitable in such a system of two rather similar substances such as $H_2O$ and $NH_3$ to try to study both the water exchange and ammonia exchange over the entire range of composition of a mixture of the two solvents. In this way some information might be obtained regarding possible competitive processes between $H_2O$ and $NH_3$ and thus a decision as to the role of water might be reached.

Some additional rate comparisons in aqueous solution may be of interest. Additional studies on the $Cu(NH_3)_x^{++}$–$NH_3$ exchange[4] show that only a lower limit to the exchange rate can be obtained. This lower limit is *ca.* a factor of ten faster than found for the nickel system. This result is consistent with the predictions of Basolo and Pearson.[12] It is possible, however, that, because of the Jahn–Teller effect, the ammonia molecules in the copper complex are not all equivalent, which would make the comparison less straightforward. The exchange reaction $Ni(NCS)_4^{-2} + NCS^- \rightleftharpoons$ also has been studied by n.m.r. methods.[13] The relevant rate constant $k_1$ is $1.6 \times 10^5$ sec.$^{-1}$ and $\Delta H^*$ is *ca.* 5 kcal./mole. The $NCS^-$ exchange thus is faster than the $NH_3$ exchange by about a factor of two. Garner and Bjerrum[14] report a value for the first-order rate constant for dissociation of the monoammine $Ni^{++}$ complex, at $-25°$ in *ca.* 3 *M* aqueous $Mg(NO_3)_2$ solution, of $1.1 \times 10^{-2}$ sec.$^{-1}$. Extrapolating our data to $-25°$ gives a $k_1$ for the hexaammine complex of *ca.* $2 \times 10^3$ sec.$^{-1}$. The media are quite different and the extrapolation rather a long one, but it appears that the monoammine complex is considerably less labile than the hexaammine species.

The results in liquid ammonia can be compared with the approximate $N^{15}$ tracer results.[3] The tracer data give a value for $k_1$ of 28 sec.$^{-1}$ at $-50°$. Our extrapolated value is 100 sec.$^{-1}$, which is probably as good agreement as can be expected considering the errors in both sets of data.

We hope to extend the work in liquid ammonia in order to get more detailed information. There are severe limitations on such a study, particularly because of the low solubility of most salts. Addition of water should be of interest as suggested earlier.

The number of aqueous ammonia complexes of paramagnetic ions suitable for study by n.m.r. is rather limited. One additional one which might be studied by the n.m.r. method is the $Co(NH_3)_6^{++}$ complex. We plan to investigate such complexes and also to try substituted ammonias as ligands.

---

(12) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958.

(13) H. W. Dodgen, F. Klanberg, and J. P. Hunt, reported at the Northwest Regional Meeting of the American Chemical Society, Pullman, Washington, June, 1962.

(14) C. S. Garner and J. Bjerrum, *Acta Chem. Scand.*, **15**, 2055 (1961).

---

CONTRIBUTION FROM THE UNITED AIRCRAFT CORPORATION
RESEARCH LABORATORIES, EAST HARTFORD, CONNECTICUT

# Ordering in Compounds of the $A(B'_{0.33}Ta_{0.67})O_3$ Type

BY FRANCIS GALASSO AND JANE PYLE

*Received November 24, 1962*

Several compounds with the general formula $A(B'^{II}_{0.33}Ta^{V}_{0.67})O_3$, where A is a barium or strontium ion and B′ is a divalent metal ion, were prepared and studied by means of X-ray diffraction techniques. Results of this investigation show not only that the difference in the charge of the B ions causes ordering, but also that the difference in the size of these ions is an important factor in influencing the degree of long-range ordering which exists in the structure of these compounds.

## Introduction

A well known structure adopted by many $ABO_3$-type compounds is the perovskite structure in which large A ions and oxygen ions form close-packed layers with small B ions in the octahedral holes. It was postulated from a study of several compounds that if more than one ion is present in the B position it is most probable that these B ions are ordered when a large difference exists in the size or charge of the ions.[1] The first quantitative study of this hypothesis was carried out at the United Aircraft Corporation Research Laboratories using compounds with the general formula $Ba(B'^{III}_{0.5}Nb^{V}_{0.5})O_3$ which, when ordered, adopt the $(NH_4)_3FeF_6$-type structure.[2,3]

Further investigation of this hypothesis was undertaken at the Research Laboratories using compounds with the general formula $A(B'_{0.33}B''_{0.67})O_3$, although relatively few compounds of this type have been previously shown to have an ordered perovskite-type structure. There are indications, however, that some of these compounds may adopt the $(NH_4)_3FeF_6$-type struc-

---

(1) F. Galasso, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **81**, 820 (1959).

(2) F. Galasso and W. Darby, *J. Phys. Chem.*, **66**, 131 (1962).

(3) R. W. G. Wyckoff, "The Structure of Crystals," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1931.

ture when $^1/_4$ of the B'' ions are randomly arranged with the B' ions in one position which is ordered with reference to the position occupied by the remaining B'' ions, *i.e.*, $A((B'_{0.33}B''_{0.17})(B''_{0.5}))O_3$.[4,5] While this arrangement allows partial ordering, complete ordering is theoretically possible in the $Ba(Sr_{0.33}Ta_{0.67})O_3$-type structure, which can be described by a hexagonal unit cell containing three close-packed $BaO_3$ layers with B ions in an ordered arrangement in the octahedral holes (see Fig. 1).[6] When the compound $Ba(Ca_{0.33}Ta_{0.67})O_3$, with a smaller difference in the radii of the B ions than in $Ba(Sr_{0.33}Ta_{0.67})O_3$, also was found to have this structure, additional studies were undertaken to investigate the effect that systematic variation of the size of the B' ions has on ordering.[7]

## Experimental Procedure

The compounds prepared can be represented by the general formula $A(B'_{0.33}Ta_{0.67})O_3$, where A is a barium or strontium ion and B' is a divalent ion. The divalent ions were selected so as to obtain compounds with differences ranging from 0.01 to 0.52 in the radii of the B' and Ta ions. The reagents were mixed according to the equation

$$ACO_3 + {}^1/_3B'O + {}^1/_3Ta_2O_5 \longrightarrow A(B'_{0.33}Ta_{0.67})O_3 + CO_2$$

and heated in combax boats, which are primarily composed of zircon, at 1400° for 24 hr. $Ba(Cd_{0.33}Ta_{0.67})O_3$ was heated at 1000° and $Ba(Pb_{0.33}Ta_{0.67})O_3$ at 700° because there was X-ray evidence of decomposition to $Ba_5Ta_4O_{15}$ at higher temperatures. When compounds containing the divalent cobalt ion were prepared, barium or strontium oxide was used in place of the carbonate. The mixtures were then pressed into pellets, sealed in evacuated silica capsules, and heated at 1000°. No evidence of reaction with the silica capsules was found.

X-Ray powder photographs of these compounds were taken using a 57.3-mm. radius Philips X-ray powder camera and high intensity copper K$\alpha$ radiation with settings of 40 kv., 30 ma. for 3.5 hr. High-temperature X-ray diffractometer tracings were made of $Ba(Ca_{0.33}Ta_{0.67})O_3$ to 1000° using a Norelco diffractometer with an attached Tem-Pres heater.

## Results

Table I presents the cell sizes, ionic radii of the divalent ions, and the difference in the ionic radii of the B ions for the compounds studied, with $Ba(Sr_{0.33}Ta_{0.67})O_3$ being the only compound not prepared at the Research Laboratories. Some of these compounds were reported previously in other papers, but their X-ray patterns were indexed on the basis of cubic perovskite pseudocells.[1,6-8] The other compounds in the table were prepared to provide a range of differences in the ionic radii of the B ions so that the effect of these differences on ordering could be determined.

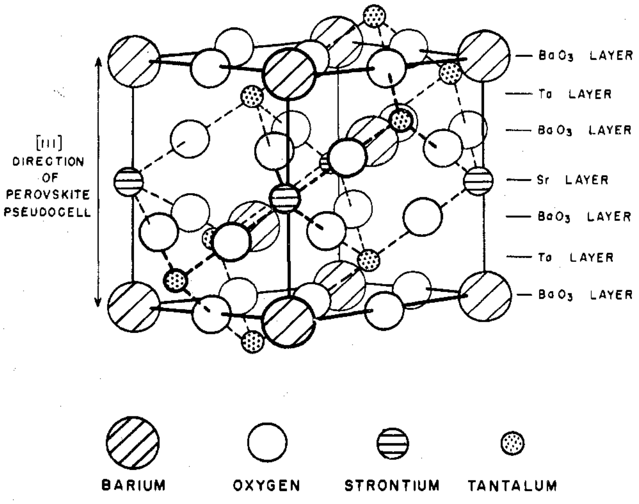

Fig. 1.—$Ba(Sr_{0.33}Ta_{0.67})O_3$.

TABLE I

STRUCTURE DATA FOR $A(B'_{0.33}Ta_{0.67})O_3$ COMPOUNDS

| Compound | Cell size, Å.[d] | Ionic radii of B' ion, Å.[e] | Diff. in ionic radii of B ions, Å.[e] |
|---|---|---|---|
| $Ba(Mg_{0.33}Ta_{0.67})O_3$ | $a = 5.782$ | 0.67 | 0.01 |
| | $c = 7.067$ | | |
| $Ba(Ni_{0.33}Ta_{0.67})O_3$[a] | $a = 5.758$ | .69 | .01 |
| | $c = 7.052$ | | |
| $Ba(Co_{0.33}Ta_{0.67})O_3$[a] | $a = 5.776$ | .73 | .05 |
| | $c = 7.082$ | | |
| $Ba(Zn_{0.33}Ta_{0.67})O_3$[b] | $a = 5.782$ | .74 | .06 |
| | $c = 7.097$ | | |
| $Ba(Mn_{0.33}Ta_{0.67})O_3$ | $a = 5.819$ | .80 | .12 |
| | $c = 7.127$ | | |
| $Ba(Cd_{0.33}Ta_{0.67})O_3$ | $a = 4.167$ | .97 | .29 |
| $Ba(Ca_{0.33}Ta_{0.67})O_3$[f] | $a = 5.895$ | .99 | .31 |
| | $c = 7.284$ | | |
| $Ba(Sr_{0.33}Ta_{0.67})O_3$[c] | $a = 5.95$ | 1.12 | .44 |
| | $c = 7.47$ | | |
| $Ba(Pb_{0.33}Ta_{0.67})O_3$ | $a = 4.250$ | 1.20 | .52 |
| $Sr(Mg_{0.33}Ta_{0.67})O_3$[a] | $a = 5.652$ | 0.67 | .01 |
| | $c = 6.951$ | | |
| $Sr(Ni_{0.33}Ta_{0.67})O_3$[b] | $a = 5.607$ | .69 | .01 |
| | $c = 6.923$ | | |
| $Sr(Co_{0.33}Ta_{0.67})O_3$[b] | $a = 5.630$ | .73 | .05 |
| | $c = 6.937$ | | |
| $Sr(Zn_{0.33}Ta_{0.67})O_3$[b] | $a = 5.664$ | .74 | .06 |
| | $c = 6.951$ | | |
| $Sr(Ca_{0.33}Ta_{0.67})O_3$ | $a = 5.764$ | .99 | .31 |
| | $c = 7.096$ | | |

[a] Reported in paper by Roy, indexed on cubic pseudo-cell.[8] [b] Reported in paper by Galasso, Katz, and Ward, indexed on cubic pseudo-cell.[1] [c] Not prepared at Research Laboratories; data taken from paper by Galasso, Barrante, and Katz.[6] [d] Indexed on hexagonal system when "*a*" and "*c*" are given; cubic system when "*a*" is given. [e] Ahrens ionic radii values used. [f] Data taken from paper by Galasso and Pyle.[7]

The X-ray patterns of all compounds in the $Ba(B'_{0.33}Ta_{0.67})O_3$ and $Sr(B'_{0.33}Ta_{0.67})O_3$ series which could be heated to 1400° without decomposing showed sharp ordering lines. The X-ray patterns of $Ba(Cd_{0.33}Ta_{0.67})O_3$ and $Ba(Pb_{0.33}Ta_{0.67})O_3$, which were prepared at 1000°, were indexed on the basis of a small cubic cell since no evidence of ordering was found in these patterns. It is believed that had firing at a higher temperature been possible without decomposition of the perovskite phase and the appearance of $Ba_5Ta_4O_{15}$, evidence of ordering might appear because of the large difference in the size of the B ions.

For most of the remaining compounds, the reflections

---

(4) E. J. Fresia, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **81**, 4783 (1959).

(5) A. W. Sleight, J. Longo, and R. Ward, *Inorg. Chem.*, **1**, 245 (1962).

(6) F. Galasso, J. R. Barrante, and L. Katz, *J. Am. Chem. Soc.*, **83**, 2830 (1961).

(7) F. Galasso and J. Pyle, *J. Phys. Chem.*, **67**, 533 (1963).

(8) R. Roy, *J. Am. Ceram. Soc.*, **37**, 581 (1954).

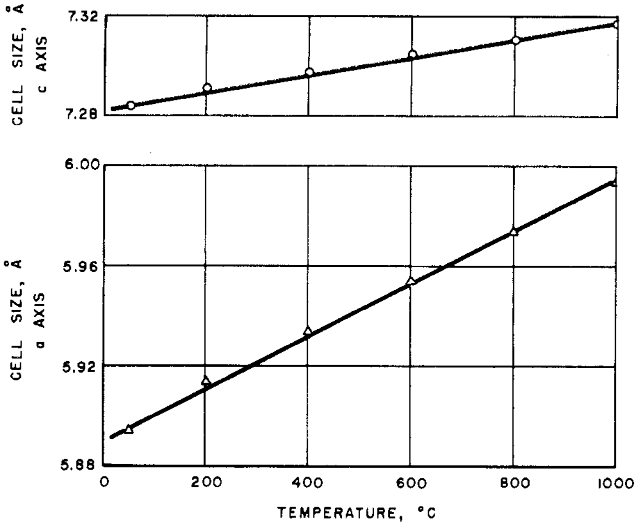

Fig. 2.—Thermal expansion data for $Ba(Ca_{0.33}Ta_{0.67})O_3$.

due to ordering were diffuse and hardly visible when prepared at 1000°, but the X-ray patterns of a few compounds did show sharp ordering lines even at 1000°. When ordering lines were sharp in the X-ray patterns of the compounds, however, heating to higher temperatures did not seem to change their intensities with relation to the remaining lines. From these observations, it was felt that the diffuseness of the ordering lines at 1000° probably was due to the presence of small ordering domains which increased in size when the compounds were heated to higher temperatures, causing the ordering lines to become sharper.

For the compounds in this study, there does not appear to be a critical difference in the ionic radii of the B ions which will cause ordering as was found in the $Ba(B'^{III}_{0.5}Nb^{V}_{0.5})O_3$ compounds. It appears, however, from an examination of the X-ray patterns that the degree of ordering is less for compounds with small differences in the ionic radii of the B ions. More specifically, while the agreement between the observed and calculated intensities for $Ba(Sr_{0.33}Ta_{0.67})O_3$ and $Ba(Ca_{0.33}Ta_{0.67})O_3$ was good, it can be seen from the data presented in Table II for $Sr(Mg_{0.33}Ta_{0.67})O_3$ that the intensities of lines due to ordering are weaker than those calculated on the basis of complete ordering of the magnesium and tantalum ions.

High-temperature X-ray diffraction tracings were made using $Ba(Ca_{0.33}Ta_{0.67})O_3$ powder to see if any order–disorder transformation involving the B ions existed, but none could be found up to 1000° (see Fig. 2).

Table II

Comparison of Observed and Calculated Intensities and $\sin^2\theta$ Values for $Sr(Mg_{0.33}Ta_{0.67})O_3$

| | $\sin^2\theta$ | | Intensities | |
|---|---|---|---|---|
| *hkl* | Obsd. | Calcd. | Obsd. | Calcd. |
| 001[a] | 0.0124 | 0.0123 | $w^-$ | 9 |
| 100[a] | .0249 | .0248 | $w^+$ | 12 |
| 101, 011 | .0371 | .0371 | m | 18 |
| 002[a] | .0495 | .0492 | $w^{-2}$ | 2 |
| 102, 012 | .0745 | .0740 | $s^{++}$ | 100 |
| 110 | | .0744 | | |
| 111[a] | .0861 | .0867 | $w^{-2}$ | 5 |
| 200[a] | .1002 | .0992 | $w^{-2}$ | 2 |
| 201, 021 | .1114 | .1115 | $w^-$ | 2 |
| 003 | | .1107 | | |
| 112[a] | .1233 | .1236 | $w^{-2}$ | 3 |
| 103, 013[a] | .1353 | .1355 | $w^{-2}$ | 3 |
| 202, 022 | .1488 | .1484 | s | 31 |
| 211, 121 | .1861 | .1859 | $m^-$ | 5 |
| 113 | | .1851 | | |
| 212, 122 | .2230 | .2228 | $s^+$ | 32 |
| 300 | | .2232 | | |
| 220 | .2970 | .2976 | m | 18 |
| 204, 024 | | .2960 | | |
| 303, 033 | .3344 | .3339 | w | 2 |
| 311, 131 | | .3347 | | |
| 312, 132 | .3713 | .3716 | m | 18 |
| 214, 124 | | .3704 | | |
| 402, 042 | .4462 | .4460 | $m^-$ | 5 |

[a] Reflections caused by ordering of the B ions.

## Discussion

If the compounds which decompose at temperatures above 1000° are excluded from consideration, it can be stated that all of the compounds in this study have the ordered $Ba(Sr_{0.33}Ta_{0.67})O_3$-type structure. This result is not entirely unexpected since the charge difference of the B ions in these compounds is greater than that of the B ions in the $Ba(B'^{III}_{0.5}Nb^{V}_{0.5})O_3$-type compounds. In addition, however, it appears that the degree of long-range ordering is less for compounds in which the difference in the radii of the B ions is small.

The results of this study tend to confirm the hypothesis that differences in size and charge of the B ions are important factors in causing ordering in those compounds which contain more than one ion in the B position of the perovskite octahedrally coördinated position.