After purification by fractional codistillation, the yield of chlorodifluoramine isolated was 66%.

That part of the mixture of chlorine and difluoramine which was not contacted with the potassium fluoride was largely unchanged after 18 hr. in the dark at ambient temperature. The infrared spectrum showed strong difluoramine absorptions and only weak absorptions due to chlorodifluoramine.

**Reaction of Chlorine and Difluoramine in the Presence of Rubidium Fluoride.**—Chlorine (3.9 mmoles) and difluoramine (1.0 mmole) were condensed[7] at −196° into a 220-ml. Pyrex glass reactor which contained 5.0 g. of rubidium fluoride. The reactor was allowed to warm to room temperature and then allowed to stand at room temperature for approximately 2 hr. An infrared spectrum then showed that all of the difluoramine had reacted and that chlorodifluoramine was a major product.

The product was purified by a method similar to that used by Petry.[2a] The yield of purified material was 63%, but small amounts of impurities were present.

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## Preparation of $Ba(Na_{0.25}Ta_{0.75})O_3$ and $Sr(Na_{0.25}Ta_{0.75})O_3$ with the Perovskite Structure

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The perovskite structure, when it is adopted by oxides with the general formula $ABO_3$, can be described by a cubic unit cell with a large A cation at the center, a smaller B cation at the corner, and oxygen ions at the edges. In recent years, a large number of new compounds which contain two B elements with different valence states in the octahedrally coordinated cation position of the perovskite structure have been prepared, *i.e.*, $Ba(M^{II}{}_{0.33}Ta^{V}{}_{0.67})O_3$[1] and $Ba(M^{III}{}_{0.5}Nb^{V}{}_{0.5})O_3$[2] where M represents various divalent and trivalent ions. In each of the examples, the average valence for the B ions has to be 4+ because of the necessity for electrostatic balance. A search for new compounds of this type has resulted in the preparation of $Ba(Na_{0.25}Ta_{0.75})O_3$ and $Sr(Na_{0.25}Ta_{0.75})O_3$, which also have the perovskite structure.

### Experimental

Reagent grade $BaCO_3$ or $SrCO_3$, $Na_2CO_3$, and $Ta_2O_5$ were mixed in the proper proportions according to the equation

$$ACO_3 + {}^1/_8Na_2CO_3 + {}^3/_8Ta_2O_5 \longrightarrow A(Na_{0.25}Ta_{0.75})O_3 + {}^9/_8CO_2 \ (A = \text{Ba or Sr})$$

The compound $Ba(Na_{0.25}Ta_{0.75})O_3$ was prepared by firing the mixture in air in a combax boat, composed mainly of zircon, at 900° for 15 hr., 1100° for 6 hr., and then 1250° for 1 hr. The samples were ground in an agate mortar after each firing. The compound $Sr(Na_{0.25}Ta_{0.75})O_3$ was prepared by a single firing of the appropriate reactants in air at 900° for 2.5 hr. Prolonged heating of these compounds at temperatures higher than those reported above resulted in decomposition of the perovskite compounds with the subsequent formation of $Ba_5Ta_4O_{15}$ or $Sr_5Ta_4O_{15}$.[3]

TABLE I

COMPARISON OF OBSERVED AND CALCULATED INTENSITIES AND *d* VALUES FOR $Ba(Na_{0.25}Ta_{0.75})O_3$

| *hkl* | *d* Obsd. | *d* Calcd. | Obsd. intensities | Calcd. intensities |
|---|---|---|---|---|
| 100 | 4.14 | 4.13 | $w^{=}$ | <1 |
| 110 | 2.92 | 2.92 | s | 100 |
| 111 | 2.386 | 2.385 | $w^{=}$ | <1 |
| 200 | 2.064 | 2.066 | $m^{+}$ | 23 |
| 211 | 1.685 | 1.686 | $s^{-}$ | 40 |
| 220 | 1.460 | 1.460 | $m^{-}$ | 14 |
| 310 | 1.307 | 1.307 | m | 17 |
| 222 | 1.192 | 1.192 | w | 4 |
| 321 | 1.105 | 1.105 | m | 15 |
| 400 | 1.033 | 1.034 | $w^{-}$ | 2 |
| 411, 330 | 0.974 | 0.975 | $w^{+}$ | 9 |
| 420 | 0.924 | 0.924 | w | 6 |
| 332 | 0.881 | 0.882 | w | 7 |
| 422 | 0.844 | 0.844 | $w^{+}$ | 9 |
| 510, 431 | 0.811 | 0.811 | $s^{-}$ | 30 |

X-Ray powder diffraction photographs of the compounds were taken with a Philips 114.6-mm. diameter camera and high intensity copper $K\alpha$ radiation with a setting of 50 kv. and 40 ma. for 8 hr. The X-ray patterns were indexed on the basis of a simple cubic cell of $a_0 = 4.137$ Å. for $Ba(Na_{0.25}Ta_{0.75})O_3$ and $a_0 = 4.055$ Å. for $Sr(Na_{0.25}Ta_{0.75})O_3$. It should be noted, however, that if the structure of the strontium compound was distorted slightly it could not be detected because the back reflections of the X-ray pattern were poor. The relative intensities were calculated for $Ba(Na_{0.25}Ta_{0.75})O_3$ by assuming that the barium ion was in the A position and the sodium and tantalum ions were randomly distributed in the B position of the perovskite structure. Structure amplitudes were determined using atomic scattering factors for sodium and oxygen ions from a paper by Berghuis, *et al.*,[4] and those for tantalum and barium ions from a paper by Thomas and Umeda.[5] The agreement between the observed and calculated intensities given in Table I indicates that the positions of the atoms selected were probably correct.

### Discussion

The compounds $Ba(Na_{0.25}Ta_{0.75})O_3$ and $Sr(Na_{0.25}Ta_{0.75})O_3$ contain a different ratio of B ions than has been reported previously in $A(B'_xB''_y)O_3$ type compounds, where B′ and B″ represent two elements having different valence states and $x$ and $y$ are fractions whose sum is equal to 1. However, it should be pointed out that while the existence of these compounds was not surprising, the fact that they did not have an ordered perovskite structure, in spite of the large differences in the radii (0.26 Å.) and charges of the sodium and tantalum ions, was not expected. A study of $Ba(B'_{0.5}Nb_{0.5})O_3$-type compounds, for example, showed that the B ions ordered if their radii differed by more than 15%,[2] and a comparable investigation of $Ba(B'_{0.33}Ta_{0.67})O_3$-type compounds pointed out that the B ions would order even when the size difference was smaller than 15% if the charge difference was large.[6] It may well be, however, that much of the previous knowledge of ordering in $A(B'_xB''_y)O_3$-type compounds cannot be applied to these new compounds where the ratio of the two B ions is 3.

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