

Fig. 1.— $\text{Nd}(\text{CF}_3\text{CO}_2)_3 \cdot 3\text{H}_2\text{O}$.

dioxide on Ascarite, passing the residual gas over hot copper oxide and again absorbing it on Ascarite. The water solution of the acid fluoride was titrated with standard base. 2.60 mmoles of $\text{Nd}(\text{CF}_3\text{CO}_2)_3$ yielded 4.04 mmoles of CF_3COF , 3.84 mmoles of CO_2 and 3.83 mmoles of CO . The

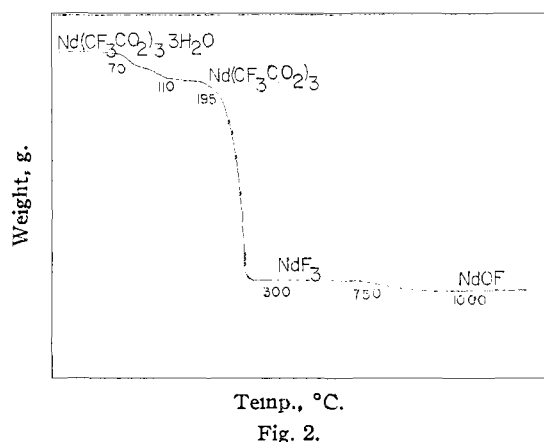
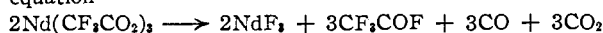


Fig. 2.

thermal decomposition is therefore represented by the equation



This is entirely analogous to the thermal decomposition of sodium trifluoroacetate as found by Swarts.⁴ The lanthanum salt behaved in exactly the same manner.

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(4) Swarts, *Bull. Classe Sci., Acad. Roy. Belg.*, **8**, 343 (1922).

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Compounds of Heptavalent Rhenium with the Perovskite Structure

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The compounds $\text{Ba}(\text{Na}_{0.5}\text{Re}_{0.5})\text{O}_3$ and $\text{Ba}(\text{Li}_{0.5}\text{Re}_{0.5})\text{O}_3$ have been prepared by interaction of rhenium metal with barium and alkali carbonates at 900° . They form a continuous series of solid solutions. The structure is shown to be of the ordered perovskite type in which the alkali metal ions and the rhenium(VII) ion are in sixfold coordination with oxygen.

Introduction

The recognition that multiple substitution of the B cations can be brought about in perovskite-type compounds (ABO_3) has led to the preparation of a multitude of phases.¹⁻⁴

When the A cation was barium or strontium, the B cations could be combinations of hexavalent and divalent cations—a typical example of which is $\text{Ba}(\text{Zn}_{0.5}\text{W}_{0.5})\text{O}_3$ (2) or combinations of pentavalent and trivalent cations leading to such compounds as $\text{Ba}(\text{Fe}_{0.5}^{\text{III}}\text{Ta}_{0.5})\text{O}_3$ (1). Both of these compounds have structures of the cubic perovskite type. In the latter, the arrangement of the iron and tantalum ions is random in the B-sites of the perovskite cell. The former, on the contrary, presents an ordered arrangement of the zinc and tungsten ions leading

to a unit cell whose edge is twice that of the simple perovskite unit. The arrangement of the B cations is thus face-centered cubic, each being surrounded by oxygen octahedra in which each oxygen is shared by the two different B cations. It appears that the tendency toward ordering is favored by the larger charge difference between the two types of B cations.

It therefore seemed possible that similar compounds could be prepared containing a combination of a heptavalent and a univalent cation except that octahedral coordination with oxygen has not been reported for heptavalent metal ions. This paper describes the preparation and properties of compounds of this type having the composition $\text{Ba}(\text{Na}_{0.5}\text{Re}_{0.5})\text{O}_3$ and $\text{Ba}(\text{Li}_{0.5}\text{Re}_{0.5})\text{O}_3$.

Experimental

Reagents.—The carbonates of lithium, sodium, strontium and barium were C.P. or reagent grade. Rhenium metal (99.99%) was procured from the Chase Brass and Copper

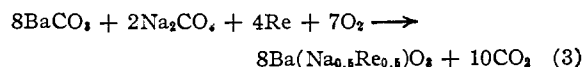
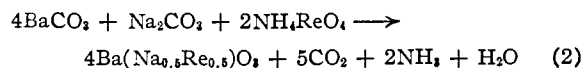
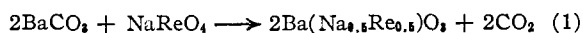
(1) Francis Galasso, Lewis Katz and Roland Ward, *This Journal*, **81**, 820 (1959).

(2) E. J. Frescia, Lewis Katz and Roland Ward, *ibid.*, **81**, 4783 (1959).

(3) L. H. Brixner, *ibid.*, **80**, 3214 (1958).

(4) L. H. Brixner, *J. Phys. Chem.*, **64**, 165 (1960).

Company. Perrhenic acid, sodium perrhenate and ammonium perrhenate were made from the rhenium metal by standard procedures.



Preparation of samples was brought about by three methods represented by equations 1 to 3. The reagents were intimately mixed, placed in a zircon boat and heated in air at 900°. The quality of the product was estimated by microscopic and X-ray analysis.

It was found that the most satisfactory preparations came from the third method in which about 2% excess of rhenium metal was used. The mixture (approximately 0.4 g.) was heated for about ten minutes, removed from the furnace for regrinding and again heated for about half an hour. Longer heating periods were required for larger samples. The lithium compounds and phases in the series $\text{Ba}(\text{Na}_{0.5-x}\text{Li}_x\text{Re}_{0.5})\text{O}_3$ were prepared by this method.

TABLE I

LATTICE CONSTANTS IN THE SYSTEM $\text{Ba}(\text{Li}_{0.5-x}\text{Na}_x\text{Re}_{0.5})\text{O}_3$

X	a_s , Å.
0	8.1183 ± 0.0003A
1/8	8.156 ± .001
1/4	8.204 ± .001
3/8	8.251 ± .001
1/2	8.2963 ± .0009

The sodium compound invariably contained small amounts of barium mesoperrhenate $\text{Ba}_3(\text{ReO}_6)_2$ which is readily formed by heating a mixture of barium carbonate and rhenium in air at 900°. The lithium compound did not contain enough of this impurity to be detected by X-ray analysis. The products were red when hot but changed to yellow when cold. The compounds undergo some decomposition on prolonged heating (12 hr. or more) at 900°. They are hydrolyzed by water and slowly attacked by moist air. X-Ray diffraction data were obtained from powder photographs using copper $K\alpha$ radiation with a Philips camera of radius 57.3 mm. Exposures of 6 hr. were taken. A General Electric XRD-5 Diffractometer was used especially for intensity data.

All of the reflections observed, with the exception of those attributable to the two strongest reflections of barium mesoperrhenate in the sodium compounds, could be interpreted on the basis of a face-centered cubic cell. The lattice constants for the series $\text{Ba}(\text{Na}_{0.5-x}\text{Li}_x\text{Re}_{0.5})\text{O}_3$ are given in Table I. They were calculated from the last five back reflection lines. The precision indicates the mean deviation. The back reflection lines of the solid solutions were somewhat more diffuse than those of the end members.

In Table II is given a comparison of the observed intensities of the reflections and the intensities calculated on the basis of the cubic ordered perovskite. It can be seen that the agreement is excellent. Chemical analysis of the compounds gave Ba, 47.0; Na, 3.6; Re, 32.2, compared to Ba, 47.4; Na, 4.0; Re, 32.1, calcd. for $\text{Ba}(\text{Na}_{0.5}\text{Re}_{0.5})\text{O}_3$, and Ba, 48.2; Re, 32.5, compared to Ba, 48.7, and Re, 33.0, calcd. for $\text{Ba}(\text{Li}_{0.5}\text{Re}_{0.5})\text{O}_3$. The barium was determined as sulfate and the sodium by means of the flame photometer. A colorimetric procedure using a thiocyanate complex was followed for the rhenium determination. The standardization of the reference solution was made by electrodeposition of the rhenium. Similar phases were prepared with strontium in the A position. It was apparent from the X-ray powder patterns that these compounds were distorted from cubic symmetry. The forward reflections in the pattern of the lithium compound $\text{Sr}(\text{Li}_{0.5}\text{Re}_{0.5})\text{O}_3$ corresponded to the

cubic perovskite type but for larger angles some line splitting was observed. Much greater distortion occurred in the case of the corresponding sodium compound.

TABLE II

COMPARISON OF THE CALCULATED AND OBSERVED INTENSITIES OF REFLECTIONS FOR $\text{Ba}(\text{Na}_{0.5}\text{Re}_{0.5})\text{O}_3$

hkl	I (calcd.)	I (obsd.)
111	25.2	25.0
200	0.5	0.5
220	100.0	97.3
311	16.5	18.8
222	4.9	6.5
400	30.8	36.4
331	7.8	7.8
420	0.3	0.2
422	41.8	44.2
511	5.6	7.8
333
440	19.1	21.4
531	5.8	8.1
600	0.2	0.2
422
620	18.1	18.8
533	2.1	2.0
622	1.1	1.6
444	6.3	5.8
711	3.4	3.5
551
640	0.1	0.0
642	21.6	20.8
731	4.3	3.5
553
800	3.2	2.5
733	1.3	0.7
820	0.2	0.0
644
822	13.3	12.3
660
751	2.8	2.7
555
662	0.6	0.2
840	12.1	13.6
911	3.9	4.2
753
842	0.2	0.2
664	9.5	11.0
931	2.9	3.6
844	14.8	13.0
933	5.3	4.6
771
755
10.00	0.2	0.0
860
10.20	43.3	35.7
862

Attempts to introduce other univalent B cations such as potassium and silver did not lead to recognizable phases. The products contained a considerable amount of barium mesoperrhenate.

Discussion

There would seem to be little doubt that the compounds $\text{Ba}(\text{Ml}_{0.5}\text{Re}_{0.5})\text{O}_3$ contain heptavalent rhenium.

nium in six-fold coordination with oxygen. The high lattice energy of the perovskite arrangement permits the formation of these crystalline phases at a temperature several hundred degrees above the decomposition temperature of the perhenates. It has been shown that the latter contain the tetrahedral ion ReO_4^{-1} .⁵ The Re-O distance in KReO_4 was found to be 1.77 Å., considerably less than the sum of the ionic radii.

The X-ray data available for the compounds $\text{Ba}(\text{M}_{0.5}\text{Re}_{0.5})\text{O}_3$ do not permit the determination of the oxygen parameters.

If the oxygen did not lie on the edges of the unit cell, the symmetry would no longer be face-centered cubic and additional reflections would be possible although the intensities might be very low because of the relatively low atomic scattering factor for

the oxygen atoms compared with barium and rhenium. None of these reflections was detected. Upon the assumption that the oxygens do lie on the edges of the unit cell, we may take the Re-O distance as 1.78 Å. in the case of the sodium compound and 1.98 Å. in the lithium compound using Ahrens values—Na = 0.97, Li = 0.68, O = 1.40.⁶ The marked difference in these values indicates either that the oxygens are displaced from the edge positions or that the polarization of the oxide ions by the alkali metal ion affects the Re-O length.

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(5) J. C. Morrow, *Acta Cryst.*, **13**, 443 (1960).

(6) L. H. Ahrens, *Geochim. Cosmochim. Acta*, **2**, 155 (1952).