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Preparation of the Ordered Perovskite-Like Compounds $Ba_4M_3LiO_{12}$ (M = Ta,Nb): A Powder Neutron Diffraction Determination of the Structure of $Ba_4Ta_3LiO_{12}$

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The hexagonal ordered perovskite-like compounds $Ba_4Ta_3LiO_{12}$ and $Ba_4Nb_3LiO_{12}$ have been prepared. The structure of $Ba_4Ta_3LiO_{12}$ has been determined by profile analysis of a powder neutron diffraction pattern. The structure is based on an eight layer (*ccch*) stacking sequence of the BaO_3 layers (space group $P6_3/mmc$) with the lithium atoms confined to the face-shared octahedral sites. The relationship of this structure to that of $Ba_5Ta_4O_{15}$ is discussed.

Introduction

The structural chemistry of ABX_3 compounds of the perovskite type can be described in terms of close packing of the AX_3 layers, with the B cations in the centers of the X_6 octahedra. If the layers are cubic close packed, the octahedra form a three-dimensional array with only corner sharing to give the ideal cubic structure as found, for example, in $BaZrO_3$. Deviations from the perfect structure may be understood in terms of a tolerance factor (*1*) defined as

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)}$$

which, for perfect close packing, has a value $t = 1.0$. When $t < 1.0$, the BX_3 array can distort to rhombohedral or orthorhombic symmetry, but without change of the cubic AX_3 layer sequence. However, when $t > 1.0$, structures involving either mixed cubic and hexagonal or pure hexagonal close packing of the AX_3 layers are found (*1, 2*). If all of the layers are hexagonally close packed, the X_6 octahedra share faces to form chains parallel to the hexagonal *c*-axis. Since the chains are isolated from one another, relatively large A cations can be accommodated by adjustment of the *c*/*a* ratio, and the structure is competitive for $t > 1.0$.

Only three intermediate stacking sequences have been reported for stoichiometric ABX_3 compounds (see, for example, Goodenough and Longo (*1*)). These are: the six-layered (6*H*) *cchcch* stacking sequence of hexagonal $BaTiO_3$, the four-layered (4*H*) *chch* structure of $SrMnO_3$, and the nine-layered (9*R*) $BaRuO_3$ with sequence *chhchhchh*. Other structures have, however, been described for perovskites with B cation vacancies. The main types are exemplified by: 5-layered $Ba_5Ta_4O_{15}$, *ccchh* (*3*) 12-layered $Ba_4Re_2CoO_{12}$, *cchh*, and the 24-layered compound $Be_4Re_2BaO_{12}$, *ccch* (*4*). The structural relationships between all of the examples given above have been discussed in detail by Katz and Ward (*5*).

It should be noted that the perovskite structure may further be modified by the ordering of different B cations, when they differ sufficiently in charge and radius. It has been shown (*1, 5, 6*) that $A_2BB'O_6$ and $A_3B_2B'O_9$ perovskites order in either the fully cubic or the 6*H* structure. No compounds have previously been reported with other layer structures or with ordering ratios of the B cations other than 1:1 or 2:1.

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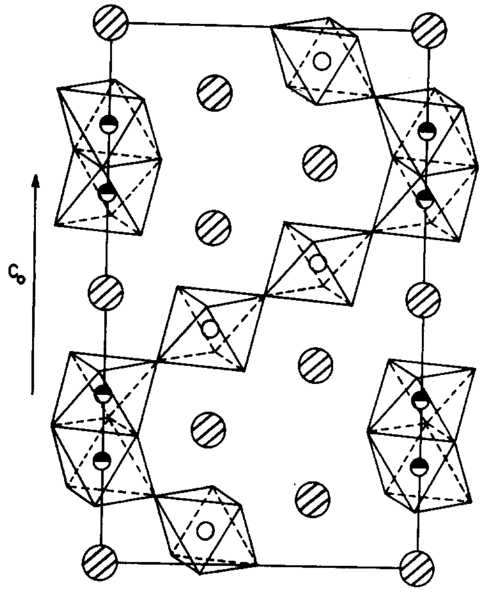

FIG. 1. Eight-layer $Ba_4Ta_3LiO_{12}$ structure. Striped circles are Ba, open circles are Ta, and half-shaded circles are Ta/Li. The ions shown lie in the (110) plane.

In this work we have explored an alternative way of introducing a mixed stacking sequence in perovskite-like compounds by 3:1 ordering of tantalum or niobium with lithium. The resulting eight-layer structure ($Ba_4M_3LiO_{12}$, Fig. 1) has stacking sequence *ccch*, similar to $Ba_4Re_2BaO_{12}$. Several compounds with similar stoichiometries have been prepared previously, but have been reported as having disordered cubic structures (*7–9*). The lattice parameters for the disordered phases given in the literature are summarized in Table I.

TABLE I

LATTICE PARAMETERS FOR $A_4B_3B'O_{12}$ COMPOUNDS[a]

A=	Ba		Sr	
B'=	Na	Li	Na	Li
B = Nb	4.107 (*7*)	4.095 (*7*)	—	3.998 (*8*)
B = Ta	4.137 (*9*)	—	4.055(*9*)	3.990 (*8*)

[a] Lattice parameters are in Å, and the numbers in parentheses are the references.

Preparation and Characterization of Samples

All of the starting materials were obtained from Johnson–Matthey 'Specpure' Chemicals Ltd. The $BaCO_3$ and Li_2CO_3 were prefired for 48 hr in CO_2 at 1000°C and 500°C, respectively; the Ta_2O_5 and Nb_2O_5 were fired for 48 hr in pure O_2 at 900°C. Stoichiometric mixtures of the starting materials were weighed on an analytical balance and hand mixed in an agate mortar for 0.5 hr. Sintered-alumina crucibles were used for the preparations and there was no evidence for any reaction with the samples.

$Ba_4Ta_3LiO_{12}$

A small sample (approximately 1 g) was prepared by firing the starting mixture at 600°C (12 hr), 800°C (12 hr), 1000°C (24 hr), 1200°C (48 hr), and 1300°C (12 hr) in air. The products all of which were white, were reground between each firing. The compositions $Ba_4Ta_3LiO_{12.02\pm0.05}$ and $Ba_4Ta_3LiO_{11.90\pm0.08}$ were found from the weight loss on reaction for the 1000 and 1200°C products, respectively. X-ray photographs of the two compounds were taken with a Debye–Scherrer camera (diam. 11.46 cm) using Cu *Kα* radiation. All the lines of the product obtained at 1000°C were indexed on the simple perovskite unit cell. A least-squares analysis of the high-angle X-ray reflections gave a lattice parameter of 4.106 ± 0.001 Å. However, the sample made at 1200°C showed extra lines which could only be indexed on the basis of a *hexagonal* unit cell with a *c*-axis of approximately 19 Å.

The development of long-range order in a 20-g sample was followed by examining the intermediate products with a Philips X-ray diffractometer. Two of the reflections are particularly sensitive to the degree of order, viz. the (200) reflection of the disordered cubic compound and the (205) of the ordered hexagonal phase. The intensities of these reflections (in arbitrary units), together with the firing times and temperatures, are given in Table II. For the final product, the stoichiometry was calculated from the weight change to be $Ba_4Ta_3LiO_{11.98\pm0.02}$. The positions of 87 reflections were measured from the diffractometer profile in the range $5° < 2\theta <$

TABLE II

PREPARATIVE CONDITIONS FOR $Ba_4Ta_3LiO_{12}$, AND SUMMARIZED X-RAY DATA FOR THE INTERMEDIATE PRODUCTS

Temp. (°C)	Time (hr)	I(obs) 200 cubic	I(obs) 205 hex.
700	24	—	—
1000	24	35	0
1000	48	31	3
1130	24	30	4
1235	24	22	13
1300	4	15	18
1300	72	1	33
1300	96	0	34

140°. The lattice parameters were obtained by a least-squares refinement of 60 clearly resolved lines and found to be: $a_0 = 5.7980 \pm 0.0006$ Å and $c_0 = 19.059 \pm 0.006$ Å.

$Ba_4Nb_3LiO_{12}$

The starting mixture was fired in air at 470°C (24 hr), 1000°C (48 hr), 1150°C (24 hr), 1250°C (48 hr), and 1300°C (96 hr). The general behavior was similar to that observed for the tantalum compound. X-ray diffractometer traces were taken of the 1000 and 1300°C products, and they were found to be completely analogous to the corresponding tantalum phases. The lattice parameters obtained were 4.105 ± 0.001 Å (cubic phase) and $a_0 = 5.797 \pm 0.001$ Å and $c_0 = 19.06 \pm 0.01$ Å (hexagonal phase).

Lithium Analysis

Because of the possibility of lithium volatilization, the compounds were dissolved in a mixture of HNO_3, $HClO_4$, and HF and chemically analyzed for lithium by atomic absorption. The results were 0.55 ± 0.01 wt% (theoretical = 0.537 wt%) and 0.69 ± 0.01 wt% (0.676 wt%) for the tantalum and niobium compounds, respectively. These results are confirmed by the weight loss and by the neutron occupation numbers (see below).

Neutron Diffraction Measurements and Refinements

Neutron diffraction measurements were made at liquid-helium temperature (4.2°K) on a diffractometer at the reactor PLUTO, A.E.R.E., Harwell. The sample was continued in a thin-walled vanadium can. A wavelength of 1.540 Å from the (511) planes of a germanium monochromator with a takeoff angle of 90° was used. The counter was stepped every 0.02° and counts accumulated every 0.1° interval. The complete range of data obtained ($7° < 2\theta < 102°$) was used in the refinement. Absorption and extinction effects were small and no corrections were considered necessary.

The structural parameters were refined by a full-matrix least-squares analysis of the powder diffraction profile (*10*). In this method, the Bragg reflections are assumed to be Gaussian in shape. For each 2θ point in the neutron pattern, the computer program calculates the contribution from all of the reflections in the vicinity and the weighted difference between the observed and calculated profiles is minimized by least-squares. As a consequence, the lattice parameters, diffractometer zero-point error, and the half-width (HW) parameters from the function

$$(\mathrm{HW})^2 = U \tan^2\theta + V \tan\theta + W$$

are refined simultaneously with the atomic positional and thermal parameters. The contribution to the profile of the background was estimated by hand. All R indices quoted in this work refer to the function

$$R_{\text{profile}} = \frac{100 \sum |y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc})|}{\sum |y_i(\text{obs})|}$$

(where y_i is the intensity at position $2\theta_i$ and c is the scale factor).

Space group $P6_3/mmc$ (No. 194) was chosen initially (*11*). The starting parameters were taken as those corresponding to ideal close packing of the AX_3 layers with sequence *ccch*. Four Ta were placed in position 4(*f*), and two Li and two Ta were placed in 4(*e*). All of the lithiums are consequently in octahedra which are face shared (see Fig. 1). Since the data was collected at 4.2°K, the difference between

TABLE III

ATOM PARAMETERS FOR $Ba_4Ta_3LiO_{12}$. (x, y, z ARE FRACTIONS OF THE UNIT CELL EDGES. THE ERRORS REFER TO ONE STANDARD DEVIATION)

$Ba_4Ta_3LiO_{12}$ ($P6_3/mmc$)

Atom	Position	x	y	z
Ba(1)	2(*a*)	0	0	0
Ba(2)	2(*c*)	1/3	2/3	1/4
Ba(3)	4(*f*)	1/3	2/3	0.8600(4)
Ta	4(*f*)	1/3	2/3	0.0630(3)
Ta/Li	4(*e*)	0	0	0.1906(6)
O(1)	6(*g*)	1/2	0	0
O(2)	6(*h*)	0.8410(6)	0.6820(6)	1/4
O(3)	12(*j*)	0.8287(5)	0.6574(5)	0.8805(1)

Overall Temperature Factor B = 0.30(4) Å2
$R_{\text{profile}} = 11.1\,\%$ (this corresponds to a conventional R index of 5.4%).

Occupation Numbers

Atom	Position	Tantalum	Lithium
Ta	4(*f*)	3.86(4)	0.14(4)
Ta/Li	4(*e*)	2.22(6)	1.78(6)
Total Occupation		6.08(7)	1.92(7)

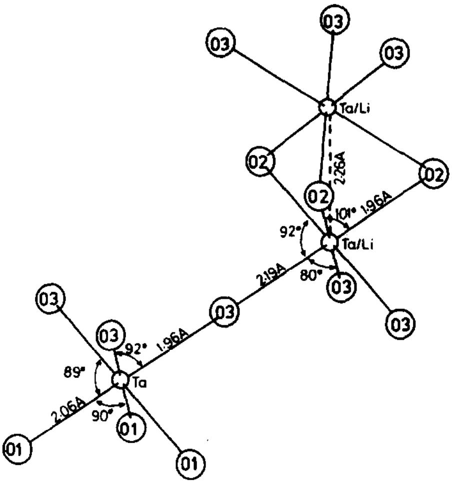

FIG. 2. The B cation environment in $Ba_4Ta_3LiO_{12}$.

individual-atom temperature factors are small and an overall value was used. The scattering lengths were: $b_{Ba} = 0.52$, $b_{Ta} = 0.70$, $b_{Li} = -0.194$, and $b_O = 0.577$ (10^{-12} cm) (*12*). The data were refined until all parameter shifts were less than 0.3 standard deviations. The experimental atom positions are given in Table III, and from these values some of the important interatomic distances and bond angles have been calculated; see Table IV

TABLE IV

BOND DISTANCES AND ANGLES IN $Ba_4Ta_3LiO_{12}$[a]

Bond Distances

Ba(1)–O(1)	2.899(1) Å	Ta/Li–O(2)	1.961(11) Å
Ba(1)–O(3)	2.886(2)	Ta/Li–O(3)	2.190(11)
Ba(2)–O(2)	2.900(3)	Ta–O(1)	2.057(6)
Ba(2)–O(3)	2.971(2)	Ta–O(3)	1.955(6)
Ba(3)–O(1)	3.132(8)	O(1)–O(1)	2.899(1)
Ba(3)–O(2)	2.744(8)	O(1)–O(3)	2.815(2)
Ba(3)–O(3)	2.923(8)	O(2)–O(2)	3.022)4)
Ta/Li–Ta/Li	2.258(15)	O(2)–O(3)	2.991(4)
	O(3)–O(3)	2.818(3)	

Angles

O(1)–Ta–O(1)	89.6(0.4)°	O(2)–Ta/Li–O(2)	100.8(1.0)°
O(1)–Ta–O(3)	89.1(0.4)	O(2)–Ta/Li–O(3)	92.0(0.8)
O(3)–Ta–O(3)	92.2(0.5)	O(3)–Ta/Li–O(3)	80.1(0.6)
	Ta/Li–O(2)–Ta/Li	70.3(1.0)	

[a] Errors refer to one standard deviation.

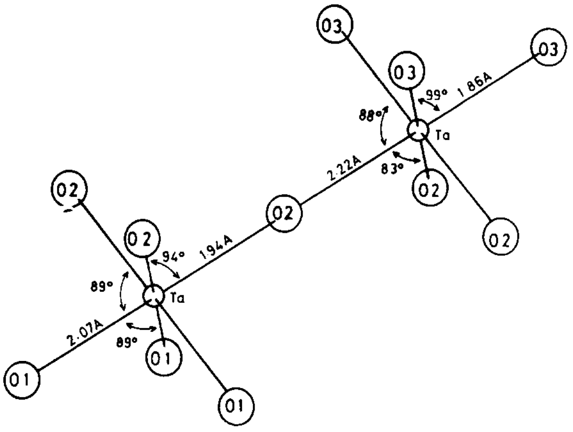

FIG. 3. The B cation environment in $Ba_5Ta_4O_{15}$.

and Fig. 2. The tantalum and lithium occupation numbers for the two B cation sites are also given in Table III. These were obtained by refining the occupation numbers with an average scattering length of 0.253 (10^{-12} cm). Assuming a total occupancy of four atoms for each site, the individual Ta and Li occupancies were calculated. There is evidence for a small amount of residual disorder between the two sites. However, the lithium can be seen to contribute far more to the scattering from the face-shared position. The total Ta and Li occupation numbers are seen to be in excellent agreement with the values expected for ideal stoichiometry. The experimental and calculated profiles, a difference plot, and the positions of the Bragg reflections are shown in Fig. 4.

The possibility that the true space group is $P6_3mc$ (No. 186) was considered. However, no statistically significant improvement was obtained in either the R index (10.9%) or the positional parameters. Also, the Ta/Li distribution was found to be essentially the same.

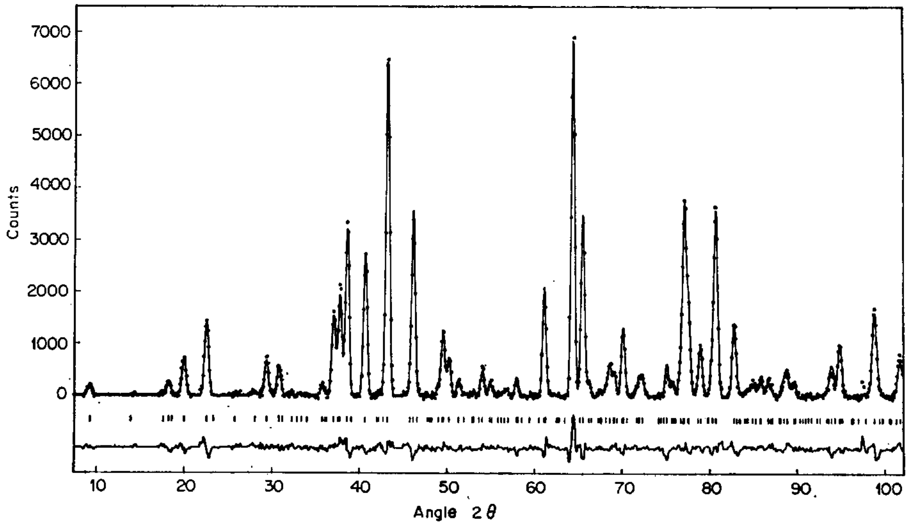

FIG. 4. Powder neutron diffraction profile for $Ba_4Ta_3LiO_{12}$. Small circles are the experimental points, and the continuous line passes through the calculated points. The small vertical lines are the calculated *hkl* positions and the bottom trace is a difference plot.

The presence of small amounts of the disordered phase may be responsible for the small discrepancy between the (220) observed and calculated intensities (Fig. 4) All other disordered cubic lines are expected to be much weaker than the (220).

Discussion

Ordering of B cations has not been observed before in compounds of similar stoichiometry, probably because prolonged heating times at high temperature are required. In the case of the sodium compounds, the larger size of this atom may prevent such ordering, and favor the formation of a multiphase mixture (*9*). Thus when $Ba_4Ta_3NaO_{12}$ is fired above 1250°C $Ba_5Ta_4O_{15}$ is formed. It is possible that the ordering is restricted to lithium compounds, i.e., to the smallest Group IA cation.

In ABO_3 compounds, where the B cation has high charge, the introduction of hexagonal close-packed layers increases B cation repulsions and results in a loss of considerable Madelung energy. The electrostatic repulsive forces can be reduced in structures containing two or three face-shared octahedra by B cation displacements along the *c*-axis, and by contraction of the distances between the B cations and the oxygen in the face.

In $Ba_4Ta_3LiO_{12}$, the introduction of the monovalent ion stabilizes the hexagonal structure by reducing the B cation repulsions when the lithiums are confined to the face-sharing octahedra. The Ta/Li–O(2) distance (see Fig. 2) is short (1.96 Å) as would be expected and there is considerable distortion of the octahedron. Also, the Ta/Li–O(3) bond is long (2.19 Å) and is compensated by a shortening of the Ta–O(3) distance. There is close similarity between atomic displacements found here and those in $Ba_5Ta_4O_{15}$ when the same element of structure is compared (see Figs. 2 and 3). However, it can be seen by comparing the metal to face-shared oxygen distances for the two compounds that the distortion is not quite as marked in $Ba_4Ta_3LiO_{12}$. This can be accounted for by the Ta/Li–Ta/Li electrostatic repulsions. Accurate atomic positions are not available for either the 12- or 24-layer compounds (*4*), though both are thought to contain Re^{7+} ions in the face-sharing octahedra adjacent to vacancies, and similar distortions might be expected.

The behavior found for $Ba_4Ta_3LiO_{12}$ may be contrasted with that of the 6*H* structures of $Ba_3Ru_2MgO_9$ and $Ba_3Ru_2NiO_9$ (*13*) where the divalent ions order into the corner-sharing octahedra. However, in this case, the Ru^{5+} ions (t_{2g}^3) have *d* electrons available and the hexagonal structure may be stabilized by Ru–Ru bonding.

We are further investigating the effects of ordering lithium with other highly charged cations on B sites in perovskite-type compounds. We have prepared the compound $Ba_5W_3Li_2O_{15}$ with an X-ray pattern which can be completely indexed on a hexagonal unit cell with lattice parameters $a_0 = 5.7559 \pm 0.0006$ Å and $c_0 = 23.719 \pm 0.003$ Å. These were determined from a least-squares refinement of 98 nonoverlapping reflections The *c*/*a* ratio is consistent with a unit cell. containing ten BaO_3 layers.

Note added in proof. Eight and ten layer ordering in lithium compounds has also been reported by T. Negas, R. S. Roth, H. S. Parker, and W. S. Brower in *Journal of Solid State Chemistry* **8**, 1–13 (1973).

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