HIGH PRESSURE SYNTHESIS AND CRYSTAL DATA
OF THE RARE EARTH ORTHOALUMINATES

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ABSTRACT

Single crystals of the rare earth orthoaluminates, $REAlO_3$, with RE = Dy - Lu, have been synthesized at high pressure in the presence of a flux. Lattice parameters for the orthorhombic members of the series, Sm-Lu, are reported. The a and c lattice parameters decrease smoothly in the direction Sm to Lu but the b parameter increases asymptotically to a maximum value at Lu. The anomalous behavior of the b parameter is similar to the variation of this parameter in the isostructural $REFeO_3$ series between La and Gd. For these latter compounds the variation has been explained in terms of a gradual change in the coordination number of the rare earth cation. A similar mechanism appears to be the cause in the case of the rare earth orthoaluminates.

Introduction

Unlike the ABO_3 perovskite-like compounds where A = rare earth and B = Fe, Ga, V, Cr, Rh, Sc and In, the rare earth orthoaluminates are not isostructural across the entire series. From La through Nd the orthoaluminates have a trigonal distortion of the ideal perovskite structure whereas from Sm through Lu they have the orthorhombic distortion found in the rare earth orthoferrites. The series is also unusual in that the synthesis of the members Dy-$TmAlO_3$ at atmospheric pressure generally yields a mixture of phases, namely the rare earth orthoaluminate plus the rare earth aluminum garnet[1]. More

recently Garton and Wanklyn have reported the synthesis of single crystals of Dy-YbAlO$_3$ using an equimolar mixture of oxides in PbO flux and a cooling rate from 1260°C of 50°C/hr (2). However, the Tm and Yb runs contained mixtures of orthoaluminate and garnet, while LuAlO$_3$ could not be synthesized under these conditions.

From recent structural refinements of NdAlO$_3$ and SmAlO$_3$, it has been shown that the coordination number of Nd^{3+} is twelve, and very nearly twelve for Sm^{3+} (3). In contrast to this the coordination number of the rare earth ions in the (RE)FeO$_3$ series is considerably less and varies from a maximum of approximately nine for LaFeO$_3$ to a minimum of about eight for LuFeO$_3$ (4,5). It appears that in general the coordination numbers of the rare earth ions in the (RE)AlO$_3$ series are larger than their iron counterparts. As a consequence of this it has been suggested that high pressures would favor the synthesis of the smaller rare earth orthoaluminates, especially LuAlO$_3$ (3).

This paper reports the synthesis of single crystals of REAlO$_3$, where RE = Dy - Lu, via direct combination of equi-molar mixtures of the oxides at high pressure in the presence of a flux. Also reported are the lattice parameters and X-ray powder patterns for the orthorhombic members of the series Sm-LuAlO$_3$.

Experimental

High pressures were generated in a piston-cylinder device. An 0.5 inch diameter tungsten carbide piston was forced by means of an oil-driven hydraulic ram into a supported tungsten carbide pressure vessel. The pressure-transmitting medium in our pressure vessel was a talc cylinder with a carbon resistance heater. This apparatus has been more thoroughly described elsewhere (6). Equimolar mixtures of aluminum and rare earth oxides were ball-milled in ethanol for approximately 12 hours, filtered, and dried. The resulting powders were then mixed with crushed NaOH pellets in a mole weight ratio of roughly 2:1. Previously it was found that NaOH does not react to any appreciable extent with the rare earth oxides, rare earth

gallium garnets and Ga_2O_3(7),and for this reason was chosen as a
flux for the orthoaluminates. Sample volumes of approximately
0.054 cc. each were packed into separate platinum containers.
During all runs, two materials were pressed simultaneously at
32.5 kilobars and 1200°±10°C, for a period of four hours. After
quenching, the apparatus was allowed to cool over night, the
pressure released, and the subsequent recovery of the sample
containers effected. Each platinum cell was then broken open
and immersed in distilled water. The NaOH rapidly dissolved
leaving small, rectangular parallelpiped-shaped, transparent
crystals. The crystals of the Ho, Er, and Tm compounds were
colored pale yellow, pale pink, and pale green respectively,
while those of Dy, Yb and Lu aluminate were colorless. All the
crystals were strongly birefringent.

X-ray powder films were taken of Eu-$LuAlO_3$ crushed
crystals with a Guinier camera using KCl as internal standard
and Cu$K\alpha$ radiation ($K\alpha_1$ = 1.5405 Å and $K\alpha_2$ = 1.5443 Å). None of
the powder films showed any trace of garnet lines after 24 hrs.
exposure. They were all indexed on the basis of the orthorhombic
cell, space group Pbnm, with lattice constants given in Table 1.

TABLE 1

Orthorhombic Cell Data for the Series $SmAlO_3$-$LuAlO_3$. The
standard deviations are less than 10^{-4}, except for those of
$EuAlO_3$ and $GdAlO_3$ which are twice as large.

	a,(Å)	b,(Å)	c,(Å)	Vol. Å
$SmAlO_3$	5.2912	5.2904	7.4740	209.22
$EuAlO_3$	5.267	5.294	7.459	208.0
$GdAlO_3$	5.250	5.302	7.447	207.3
$TbAlO_3$	5.2317	5.3097	7.4196	206.11
$DyAlO_3$	5.2053	5.3172	7.3950	204.68
$HoAlO_3$	5.1811	5.3229	7.3741	203.37
$ErAlO_3$	5.1595	5.3271	7.3539	202.12
$TmAlO_3$	5.1435	5.3277	7.3335	200.96
$YbAlO_3$	5.1251	5.3310	7.3146	199.85
$LuAlO_3$	5.1012	5.3317	7.3000	198.55

The lattice parameters were refined from values of 2θ which
were $\leq 2\theta(224)$, excluding overlapped lines. The lattice
parameters for $SmAlO_3$ were determined by a simplified version

of Bond's method (8, 9). The powder patterns for Eu-LuAlO$_3$ are listed in Table 2.

Discussion

The lattice parameters of SmAlO$_3$-LuAlO$_3$ are plotted against atomic number in Fig. 1. Atomic numbers rather than ionic radii were chosen as abscissae since the variation in coordination number across the series is not known. One can see that while the a and c parameters decrease in a nearly linear fashion from Sm-Lu, b increases asymptotically to the Lu value. The behavior of the b parameter resembles that of REGaO$_3$ (10) compounds between Ce and Gd and the b parameter of the REFeO$_3$ series between La and Gd (11). However, in the case of the two latter series, the b values eventually decrease for smaller rare earth ions, but no decrease occurs for the REAlO$_3$ compounds.

The entire series of REFeO$_3$ structures have been refined from single crystal data in order to fully understand the mechanism underlying this anomalous behavior (4). It is now clear that the oxygen polyhedron around the rare earth ion is distorted and this distortion varies drastically across the series. The rare earth ion has approximately an eight fold
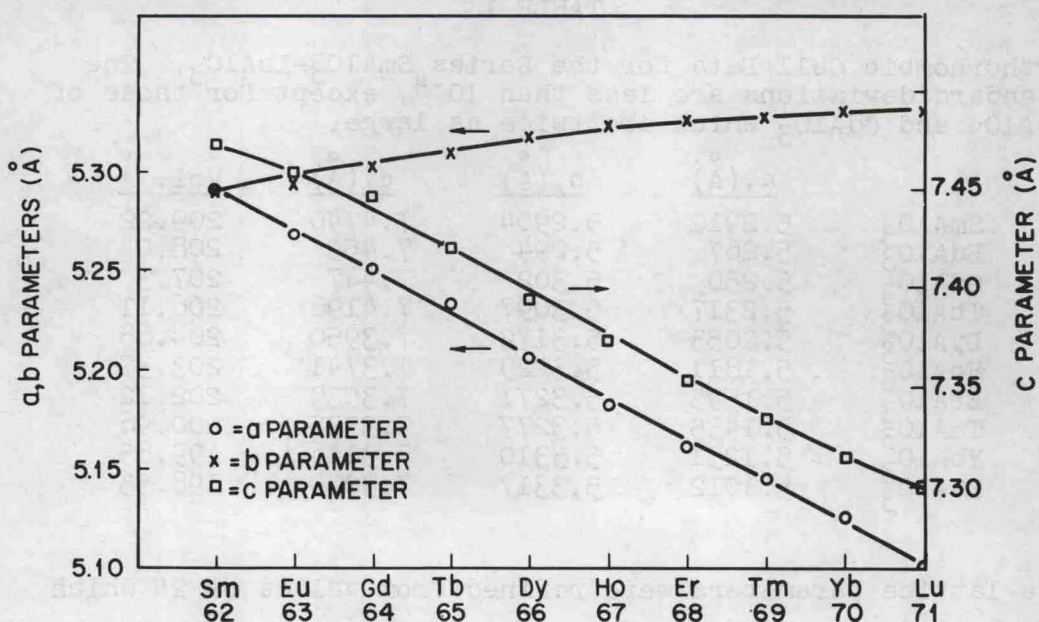

FIG. 1

Lattice parameters a, b, and c versus atomic number for the rare earth orthoaluminates.

TABLE 2

Guinier Diffraction Data for Some Rare Earth Orthoaluminates.

hkℓ	Eu d_o	Eu d_c	Gd d_o	Gd d_c	Tb d_o	Tb d_c	Dy d_o	Dy d_c	Ho d_o	Ho d_c	Er d_o	Er d_c	Tm d_o	Tm d_c	Yb d_o	Yb d_c	Lu d_o	Lu d_c
101													4.215 vw	4.211	4.203 vw	4.197	4.180 vw	4.181
110	3.735 m	3.734	3.731 m	3.731	3.729 m	3.727	3.722 m	3.720	3.714 s	3.713	3.709 m	3.706	3.700 ms	3.700	3.696 s	3.695	3.685 ms	3.686
002		3.731	3.726 w	3.723	3.711 wm	3.710	3.699 m	3.698	3.688 ms	3.687	3.679 m	3.677	3.667 m	3.667	3.655 ms	3.657	3.651 wm	3.650
111			3.337 w	3.335	3.330 w	3.330	3.325 wm	3.323	3.316 m	3.316	3.310 m	3.310	3.303 m	3.304	3.298 m	3.298	3.291 m	3.290
020	2.647 w	2.647	2.651 s	2.651	2.653 w	2.655	2.659 wm	2.659	2.662 wm	2.661	2.663 wm	2.664	2.663 m	2.664	2.665 m	2.666	2.665 wm	2.666
112	2.639 s	2.639	2.635 s	2.635	2.628 s	2.629	2.622 vs	2.622	2.617 vs	2.616	2.611 s	2.610	2.603 s	2.605	2.598 vs	2.599	2.593 vs	2.594
200		2.634	2.626 w	2.625	2.616 w	2.616	2.603 wm	2.603	2.591 m	2.591	2.579 wm	2.580	2.572 m	2.572	2.562 m	2.563	2.550 wm	2.551
021			2.499 vvw	2.497	2.500 vw	2.500	2.502 wm	2.502	2.503 wm	2.503	2.505 m	2.504	2.503 m	2.504	2.503 m	2.504	2.503 m	2.504
211											2.214 w	2.214	2.208 w	2.209	2.202 w	2.202	2.194 w	2.194
103												2.214						
022	2.158 wm	2.159	2.159 w	2.159	2.159 w	2.159	2.158 m	2.159	2.159 m	2.158	2.158 wm	2.157	2.154 m	2.155	2.154 m	2.154	2.153 m	2.153
202	2.151 wm	2.151	2.145 w	2.145	2.138 w	2.138	2.128 m	2.128	2.120 m	2.120	2.113 wm	2.112	2.104 m	2.105	2.098 ms	2.099	2.091 m	2.091
113					2.060 vw	2.061	2.055 vw	2.055	2.050 w	2.050	2.044 w	2.045	2.039 wm	2.040	2.035 m	2.035	2.030 m	2.031
122									1.992 vw	1.992					1.986 vw	1.986		
220	1.865 wm	1.867	1.865 wm	1.865	1.864 wm	1.863	1.860 m	1.860	1.856 m	1.856	1.854 wm	1.853	1.850 m	1.850	1.848 m	1.847	1.843 m	1.843
004		1.865			1.855 w	1.855	1.849 m	1.849	1.843 m	1.844	1.839 wm	1.838	1.833 wm	1.833	1.828 m	1.829	1.824 wm	1.825
023	1.815 w	1.812			1.808 w	1.810			1.805 w	1.806	1.803 vw	1.804	1.802 wm	1.801	1.799 wm	1.799	1.797 wm	1.797
221		1.811				1.807	1.805 wm	1.804	1.800 wm	1.800	1.797 m	1.797	1.795 wm	1.794	1.791 m	1.791	1.787 m	1.787
222	1.668 w	1.669	1.665 wm	1.668	1.665 vv	1.665	1.661 vw	1.661	1.658 w	1.658	1.654 wm	1.655	1.652 w	1.652	1.649 w	1.649	1.645 m	1.645
114		1.668		1.666	1.661 vw	1.661	1.655 w	1.656	1.652 wm	1.651	1.647 wm	1.647	1.643 wm	1.643	1.639 wm	1.639	1.635 m	1.636
310					1.657 vw	1.657	1.649 vw	1.649	1.643 vw	1.643					1.628 w	1.627	1.620 w	1.620
131			1.634 w	1.634	1.635 vw	1.635	1.636 wm	1.636	1.636 wm	1.637	1.637 m	1.637	1.636 m	1.636	1.636 m	1.636	1.635 m	1.636
311														1.632	1.589 vw	1.588		
													1.593 w	1.593				
132			1.527 w	1.527	1.528 w	1.528	1.528 wm	1.528	1.527 wm	1.528	1.527 wm	1.527	1.527 wm	1.526	1.526 wm	1.526	1.526 w	1.525
024			1.520 w	1.521	1.518 wm	1.518	1.518 wm	1.518	1.515 wm	1.515			1.510 wm	1.510	1.508 wm	1.508	1.506 wm	1.506
204	1.522 w	1.522	1.518 wm	1.519	1.512 m	1.513	1.507 m	1.507	1.502 w	1.502	1.497 wm	1.497	1.493 w	1.493	1.489 w	1.489	1.485 wm	1.484
312		1.521		1.518		1.513		1.506	1.500 m	1.501	1.495 m	1.495	1.491 wm	1.491	1.487 m	1.486	1.482 m	1.481
223											1.478 w	1.478	1.476 wm	1.475	1.473 wm	1.472	1.470 w	1.469
133							1.387 w	1.387	1.386 wm	1.386	1.384 m	1.385	1.384 m	1.384	1.383 wm	1.383	1.382 wm	1.382
115															1.360 vw	1.360		
041											1.310 w	1.310	1.310 vv	1.310	1.312 w	1.311		
224	1.320 w	1.319			1.315 w	1.315	1.311 m	1.311	1.308 m	1.308	1.305 m	1.305	1.302 wm	1.302	1.300 wm	1.300	1.297 m	1.297
314															1.215 wm	1.215		
331									1.220 w	1.221								
332							1.178 m	1.176						1.170	1.168 wm	1.167		
043													1.169 wm	1.169				
241													1.167 w	1.167				
116	1.179 w	1.180											1.160 wm	1.161	1.158 w	1.158		
420		1.179																
225													1.149 w	1.149	1.148 w	1.147		
135														1.104				
422													1.105 wm	1.104				
206														1.104				

coordination between $TbFeO_3$ and $NdFeO_3$. At the extremities of the series this approximation breaks down. For $LuFeO_3$ the seventh and eighth nearest oxygen atoms are becoming second nearest neighbors, while for $LaFeO_3$ the ninth nearest oxygen is too close to be considered a next nearest-neighbor. This change in coordination number governs the behavior of the b parameter.

It seems likely that a similar mechanism applies in the case of the $REAlO_3$ series. However, it is important to note that the orthorhombic series begins with $SmAlO_3$ where the coordination number of Sm^{3+} is very nearly twelve, compared to eight for its iron counterpart. Also, the non-linear variation of the c parameter and the significant change in slope of the b parameter between Sm and Tb in Fig. 1 suggest a rapid decrease in the coordination numbers of the rare earth ions. Between $DyAlO_3$ and $LuAlO_3$ the coordination number does not appear to decrease as drastically. However, without a detailed knowledge of the structure of at least several more $REAlO_3$ members, it is difficult to ascertain how the rare earth polyhedron varies across the series.

Another interesting point is that starting with Ho one needs high pressures to synthesize single phase rare earth orthoaluminates. $LuAlO_3$ was easily formed at 32 kbar but no attempt was made to find the minimum pressure necessary for this synthesis. We suspect that 32 kbar exceeds the minimum considerably. It is a logical step to attempt to synthesize under pressure $MAlO_3$, where M is of smaller ionic radius than Lu^{3+}. We believe In^{3+} and possibly Sc^{3+} are likely M-cations and expect to proceed with these experiments in the near future.

Acknowledgements

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