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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-Tm AlO_3 at atmospheric pressure generally yields a mixture of phases, namely the rare earth orthoaluminate plus the rare earth aluminum garnet(1). More

(2). 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 $1200^\circ \pm 10^\circ\text{C}$, 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 parallelepiped-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 $\text{CuK}\alpha$ radiation ($\text{K}\alpha_1 = 1.5405 \text{ \AA}$ and $\text{K}\alpha_2 = 1.5443 \text{ \AA}$). 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 $\text{SmAlO}_3\text{-LuAlO}_3$. The standard deviations are less than 10^{-4} , except for those of EuAlO_3 and GdAlO_3 which are twice as large.

	$\underline{a, (\text{\AA})}$	$\underline{b, (\text{\AA})}$	$\underline{c, (\text{\AA})}$	$\underline{\text{Vol. \AA}^3}$
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

2:1. 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-LuAlO₃ are listed in Table 2.

Discussion

The lattice parameters of SmAlO₃-LuAlO₃ 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 REGaO₃ (10) compounds between Ce and Gd and the b parameter of the REFeO₃ 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 REAlO₃ compounds.

The entire series of REFeO₃ 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

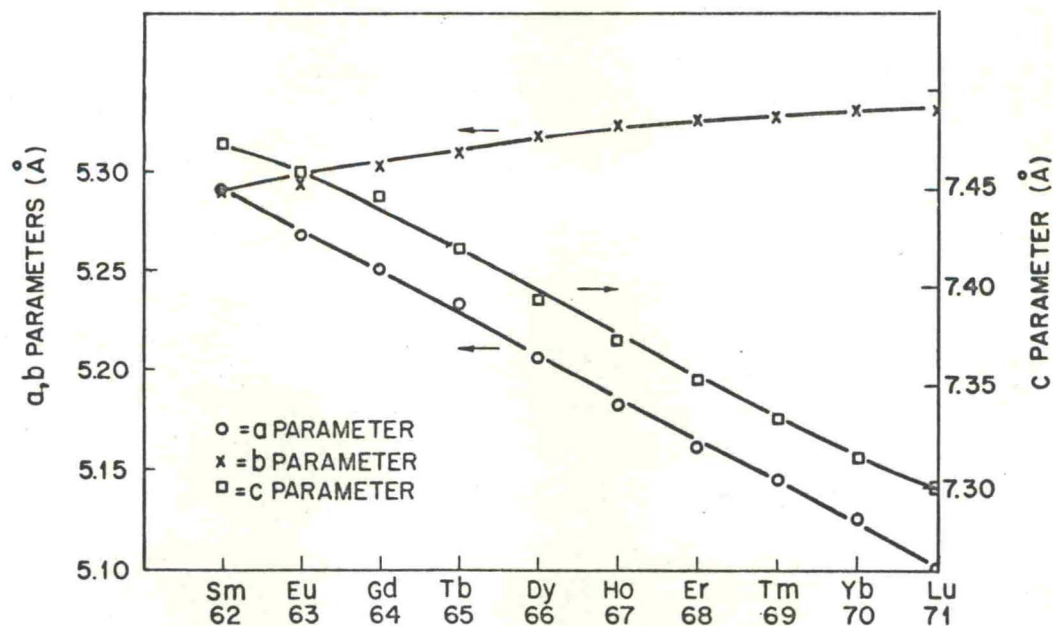


FIG. 1

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		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu			
	d _o	d _c	d _o	d _c	d _o	d _c	d _o	d _c	d _o	d _c	d _o	d _c	d _o	d _c	d _o	d _c	d _o	d _c		
101																				
110																				
002	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	4.215 vw	4.211	4.203 vw	4.197	4.180 vw	4.181		
111		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		
020	2.647 w	2.647	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		
112		2.639	2.651 w	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	2.662		
200	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		
021		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		
211			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		
103											2.214 w	2.214	2.208 w	2.209	2.202 w	2.202	2.194 w	2.194		
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		1.867	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 w	1.843		
004	1.865 wm	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 w	1.825		
023		1.812					1.808 w	1.810	1.805 wm	1.807	1.803 vw	1.804	1.802 wm	1.801	1.799 wm	1.799	1.797 w	1.797		
221	1.815 w	1.811					1.807	1.807	1.804	1.800 wm	1.800	1.797 m	1.797	1.795 wm	1.794	1.791 m	1.791	1.787 w	1.787	
222		1.669			1.665 wm	1.668	1.665 vw	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 w	1.645
114	1.668 w	1.668			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 w	1.636		
310					1.657 vw	1.657	1.649 vw	1.649	1.643 vw	1.643			1.637 m	1.637	1.636 m	1.636	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					1.632	1.632	1.635 m	1.636	1.635 w	1.636
311													1.593 w	1.593	1.589 vw	1.588				
132					1.527 w	1.527	1.528 w	1.528	1.528 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	1.515 wm	1.515			1.510 wm	1.510	1.508 wm	1.508	1.506 w	1.506		
204		1.522 w							1.502 w	1.502	1.497 wm	1.497	1.493 w	1.493	1.489 w	1.489	1.485 w	1.484		
312		1.521	1.518 wm	1.519	1.512 m	1.513	1.507 m	1.507	1.500 m	1.501	1.495 m	1.495	1.491 m	1.491	1.487 m	1.486	1.482 w	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 w	1.382		
115															1.360 vw	1.360				
041											1.310 w	1.310	1.310 vw	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						1.169 wm	1.170	1.168 wm	1.167			
043														1.167 w	1.167					
241														1.160 wm	1.161					
116	1.179 w	1.180														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.

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