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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-$TmAlO_3$ 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 equimolar 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