Crystal structure of novel high-pressure perovskite $K_{2/3}Th_{1/3}TiO_3$, a possible host for Th in the upper mantle

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ABSTRACT

The high-pressure perovskite $K_{2/3}Th_{1/3}TiO_3$ was synthesized at $P = 6$ GPa and $T = 1200$ °C. This compound does not form at ambient pressures, as both solid-state reaction and synthesis from the melt yield a mixture of thorianite ($ThO_2$) and jeppeite ($K_2Ti_6O_{13}$). $K_{2/3}Th_{1/3}TiO_3$ is a partially ordered derivative of the ideal perovskite structure, which crystallizes with tetragonal symmetry, in space group $P4/mmm$, $a = 3.9007(2)$, $c = 7.8099(7)$ Å, $V = 118.83(2)$ Å$^3$, $Z = 2$. The structure of this compound was refined by the Rietveld method from the X-ray diffraction powder data. The degree of disorder calculated from the refined cation occupancies of the 1a and 1b sites is 58%. The K$^{+}$ cations preferentially enter the 1a site, whereas most Th$^{4+}$ is accommodated in the comparatively smaller 1b site (polyhedral volumes are 53 and 46 Å$^3$, respectively). In response to this two-dimensional (planar) ordering, the Ti$^{4+}$ cations are displaced by about 0.1 Å toward the planes populated by the lower-charged cations. $K_{2/3}Th_{1/3}TiO_3$ and related structures may be a viable repository for Th in Ti-rich alkali metasomatites in the lithospheric upper mantle.

INTRODUCTION

It has been postulated that titanate minerals may serve as repositories for large-ion lithophile and high-field strength elements (including REE, Sr, Ba, Zr, and Nb) in the upper-mantle environment (Haggerty 1987, 1991). In this work, the term titanate is used in reference to complex Ti-dominant oxides whose structural framework is based on vertex- and edge-sharing TiO$\delta$ octahedra. Local enrichment of the upper-mantle rocks in these phases is believed to result from reaction of peridotite with metasomatic fluids/melts, and is a prerequisite for the generation of some alkaline magmas (e.g., lamproitic and basanitic) enriched in K, Ti, and “incompatible” elements (Wass and Rogers 1980; Mitchell and Bergman 1991). The occurrence of titanates in the upper-mantle metasomatic assemblages is supported by the recognition of these minerals in ultramafic xenoliths hosted by kimberlite, lamproite, and alkali basalt (e.g., Haggerty et al. 1989). Among the high-pressure titanates, crichtonite-, and magnetoplumbite-group minerals act as the principal hosts for Sr, Ba, and Zr, and may also incorporate significant proportions of light REE and Nb. An alternative host for the lanthanides, Sr, and Nb is perovskite-type phases, as indicated by the available experimental data and occurrence of Th-rich (up to 23 wt% ThO$2$) loparite in alkaline rocks (Mitchell and Chakhmouradian 1999a). In our previous studies (Mitchell and Chakhmouradian 1998a, 1999a), we showed that Th enters the A-site in naturally occurring loparite (ideally Na$^{1/2}$REE$^{1/2}$TiO$3$), defining solid solution series toward Na$^{2/3}$Th$^{1/3}$TiO$3$, Th$^{1/2}$Ti$^{1/2}$O$3$, and Th$^{1/4}$Nb$^{3/4}$O$3$. At high pressures, the solubility between loparite and the A-site deficient end-members is suppressed, whereas the solubility in the series (Na$^{1/2+}$REE$^{1/2}$Th$^{1/2}$TiO$3$) is limited to about 30 mol% Na$^{2/3}$Th$^{1/3}$TiO$3$ at $P = 6$ GPa (Mitchell and Chakhmouradian 1999a). As upper-mantle metasomatism is essentially potassic in character (Wass and Rogers 1980; Lloyd et al. 1987), it is important to examine the relative stability of K-bearing perovskite-type titanates under high pressures. Experimental investigation of the systems K$_2$La$_{1/2}$TiO$_3$-SrTiO$_3$ and K$_{12}$La$_{12}$TiO$_{24}$-LaCrO$_3$, by the authors of the present study, and of naturally occurring and synthetic K-La-Sr-Cr “loparite” by Burns et al. is currently underway. In the present work, we describe the synthesis conditions and crystal structure of a novel perovskite-type K-Th titanate, $K_{2/3}Th_{1/3}TiO_3$.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

Initially, we attempted to obtain $K_{2/3}Th_{1/3}TiO_3$ at atmospheric pressure using the conventional ceramic technique from stoichiometric amounts of K$_2$CO$_3$, ThO$_2$, and TiO$_2$ (high-purity...