

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

ANTON R. CHAKHMOURADIAN* AND ROGER H. MITCHELL

Department of Geology, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada

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 jepeite ($K_2Ti_6O_{13}$). $K_{2/3}Th_{1/3}TiO_3$ 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, $V = 118.83(2)$ Å³, $Z = 2$. 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^{1+} cations preferentially enter the 1a site, whereas most Th^{4+} is accommodated in the comparatively smaller 1b site (polyhedral volumes are 53 and 46 Å³, 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_6 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, although only two occurrences of mantle-derived titanate perovskite (sensu lato) have been described thus far (Haggerty 1987; Kopylova et al. 1997). The character of the upper-mantle repository for Th and U remains uncertain, primarily due to the paucity of data on the stability of Th and U phases under high pressures, and distribution of these elements in xenolithic mineral assemblages. The incorporation of Th and U in

crichtonite- and magnetoplumbite-group minerals is probably inhibited by their small ionic radii in comparison with K, Sr, and Ba. O'Reilly et al. (1997) suggested that apatite serves as a major host for the actinides in metasomatized peridotites, and determined that up to 640 ppm Th and 140 ppm U occur in apatite from French and Alaskan xenoliths. Alternatively, the actinides may be effectively sequestered in 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 $Na_{2/3}Th_{1/3}TiO_3$, $Th_{1/2}\square_{1/2}TiO_3$ and $Th_{1/4}\square_{3/4}NbO_3$. At high pressures, the solubility between loparite and the A-site deficient end-members is suppressed, whereas the solubility in the series $(Na_{1/2+x}REE_{1/2-3x}Th_{2x})TiO_3$ 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 $K_{1/2}La_{1/2}TiO_3$ - $SrTiO_3$ and $K_{1/2}La_{1/2}TiO_3$ - $LaCrO_3$ 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_2CO_3 , ThO_2 , and TiO_2 (high-purity

* Present address: Department of Geological Sciences, University of Manitoba, Winnipeg, MB R3T 2N2, Canada. E-mail chakhmou@ms.umanitoba.ca

grade). The reagents dried at 150° C were mixed, ground in an agate mortar, and calcined in air for 24 h at 1000 °C to avoid the loss of K. After regrinding, the sample was heated in air for 48 h at 1200 °C. This synthesis yielded minute crystals of cubic ThO₂ (thorianite) enclosed in prismatic crystals of K₂Ti₆O₁₃ (jeppite). Synthesis from the melt ($T = 1300\text{ }^{\circ}\text{C}$) also led to the crystallization of thorianite plus jeppite. Hence, we conclude that K_{2/3}Th_{1/3}TiO₃ does not form under ambient pressures.

High-pressure experiments were undertaken using the MA6/8 2000-ton uniaxial split-sphere multi-anvil apparatus (Luth 1993), located at the University of Alberta (Edmonton). The calcined samples were placed in 2 mm Pt capsules, sealed, and loaded into a furnace assembly consisting of a stepped graphite heater contained within a semi-sintered MgO-Cr₂O₃ (5%) octahedron of 18 mm edge length. The octahedron was placed in the cavity formed by truncating the corners of eight WC anvils. The truncation edge length was 11 mm. The temperature was monitored with a W₉₅Re₅-W₇₄Re₂₆ thermocouple. The samples were run at 6 GPa and 1200 °C for 5 h. One of the samples (no. 1) was mounted in epoxy, carbon-coated, and examined by scanning electron microscopy (SEM) and energy-dispersion spectrometry (EDS) using a Hitachi 570 instrument located at Lakehead University (Ontario). The composition of this sample was obtained using a LINK ISIS analytical system incorporating a Super ATW Light Element Detector (133 eV FWHM MnK α). Raw EDS spectra were acquired for 130 seconds (live time) with an accelerating voltage of 20 kV and beam current of 0.86 nA. X-ray spectra were collected and processed with the LINK ISIS-SEMQUANT software package. Full ZAF corrections were applied to the raw X-ray data. The following well-characterized standards were employed for the analysis: orthoclase (K), perovskite (Ti) and metallic Th. The accuracy of this method was cross-checked by wave-length-dispersive electron-microprobe analysis on an automated CAMECA SX-50 microprobe at Purdue University (Indiana) using a zoned crystal of perovskite from the Hills Pond lamproite (Mitchell and Chakhmouradian 1999b). The second sample was examined by X-ray powder diffraction (CoK α ₁ radiation) using a Rigaku Geigerflex diffractometer. The XRD pattern was measured in the 2 θ range 10–120° with a $\Delta 2\theta$ step of 0.02°, and an exposure time of 2 s per step. The pattern was then analyzed by the Rietveld method (Rietveld 1969), using the FULLPROF program (Rodriguez-Carvajal 1990). Unfortunately, the small volume of experimental charges and difficulties associated with sample preparation did not allow the *same* sample to be examined by both SEM-EDS and XRD.

RESULTS

Synthetic sample no. 1 consists of approximately equal proportions of unreacted thorianite and rutile (TiO₂) enclosed in a matrix of K-Th titanate. The crystals of thorianite are never in direct contact with rutile, being separated by bands of microgranular K-Th titanate. Further away from the rutile inclusions, the titanate phase becomes coarser-grained (up to 25 mm across), indicating that the reaction front moved across the capsule and was followed by recrystallization of the reaction product. Nowhere in the sample did we find any evidence of exsolution. From these observations, we infer that the K-Th

titanate is an equilibrium phase in our experiments, and the presence of impurities in the sample simply results from a low reaction rate and, possibly, some loss of K during calcination. Our more recent synthesis experiments involving high-pressure K-Ti perovskites indicate that run durations close to 10 h are normally required for the starting materials to fully react (authors' unpublished data). The K-Th titanate obtained in this study shows relatively minor variation in K, Th and Ti contents, approaching the ideal composition K_{2/3}Th_{1/3}TiO₃. Some deficiency in K content and excess of Th over the expected value (Table 1) probably reflect the presence of minor vacancies in the crystal structure of this compound [<0.05 atoms per formula unit (apfu) relative to 3 atoms of oxygen]. However, the content of the A-site deficient end-member component (Th_{1/2}□_{1/2}TiO₃) in the compound synthesized does not exceed 10 mol%.

The XRD pattern of sample no. 2 contains well-resolved diffraction lines corresponding to thorianite [$a = 5.5967(1)\text{ \AA}$], rutile [$a = 4.5926(2)$, $c = 2.9588(2)\text{ \AA}$] and a perovskite-type structure. The lines belonging to the individual phases show very little overlapping within the 2 θ range measured. The diffraction pattern of K_{2/3}Th_{1/3}TiO₃ shows two distinct sets of peaks. The most intensive of these can be indexed on a simple perovskite cell with $a_o \approx 3.90\text{ \AA}$, whereas comparatively weaker superlattice peaks can only be indexed on a doubled perovskite cell with $a = b \approx 2a_o$ and $c \approx 2a_o$ (Table 2, marked with asterisks). As polyhedral rotation, the most common type of structural distortions in perovskites, inevitably results in doubling of unit-cell parameters along at least two axes of the pseudocubic cell, the superlattice reflections hkl with l odd clearly indicate planar ordering of K and Th along [001], i.e., splitting of the A-site into two non-equivalent sites. Such ordering reduces the symmetry to tetragonal (space group $P4/mmm$), as initially determined by Trunov and Kovba (1966). Careful examination of the XRD pattern of K_{2/3}Th_{1/3}TiO₃ revealed no splitting of the superlattice reflections (Fig. 1), that could indicate further reduction in symmetry due to cation ordering within the (001) planes and/or rotation of TiO₆ octahedra. In K_{2/3}Th_{1/3}TiO₃, the K/Th ratio does not allow for complete 1:1 ordering, and at least one third of the "thorium" positions must be occupied by K. Hence, in the most ordered state, the relative degree of disorder (D) would still be about 33%.

The full-profile refinement of the XRD data was carried out in a three-component mode, with thorianite and rutile included as impurity phases. In the initial structural model for

TABLE 1. Composition of K_{2/3}Th_{1/3}TiO₃

Oxide	Synthetic sample			Ideal composition
	Mean (wt%)*	Range (wt%)	Standard deviation	
K ₂ O	14.16	13.32–14.87	0.50	15.75
ThO ₂	46.02	44.62–47.13	0.85	44.14
TiO ₂	39.81	38.20–41.51	1.14	40.11
Total	99.99			100.00
Structural formulae calculated on the basis of 3 O atoms				
K	0.603	0.667		
Th	0.350	0.333		
Ti	1.000	1.000		

* Mean of 11 electron-microprobe analyses.

$K_{2/3}Th_{1/3}TiO_3$, we adopted the atomic coordinates refined for the low-pressure $Na_{2/3}Th_{1/3}TiO_3$ by Mitchell and Chakhmouradian (1998b). In contrast to low-pressure $Na_{2/3}Th_{1/3}TiO_3$, we did not observe any domain-induced broadening of the superlattice peaks relative to the “lattice” reflections (hkl , l even) on the XRD pattern of $K_{2/3}Th_{1/3}TiO_3$ (Fig. 1). Hence, both sets of peaks were refined as a single phase, using the same set of line-width parameters. In the final

TABLE 2. X-ray powder diffraction data for $K_{2/3}Th_{1/3}TiO_3$

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (Å)	<i>I</i> _{calc}	<i>I</i> _{obs}	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (Å)	<i>I</i> _{calc}	<i>I</i> _{obs}
0	0	1	7.81*	12	14	2	1	4	1.302	3	3
0	0	2	3.91	5	5	2	2	2	1.301	2	1
1	0	1	3.49*	9	7	3	0	0	1.301	1	1
1	0	2	2.76	100	100	3	0	1	1.284*	1	1
1	1	0	2.76	50	50	1	0	6	1.235	13	12
0	0	3	2.61*	1	1	3	0	2	1.234	13	12
1	1	1	2.60*	4	6	3	1	0	1.233	13	12
1	1	2	2.255	31	29	2	0	5	1.219*	2	2
1	0	3	2.167*	3	2	2	2	3	1.219*	1	1
0	0	4	1.954	20	25	3	1	1	1.218*	2	2
2	0	0	1.952	40	43	1	1	6	1.177	5	5
1	1	3	1.894*	3	4	3	1	2	1.176	10	9
2	0	1	1.894*	3	3	2	1	5	1.164*	2	2
1	0	4	1.747	2	2	3	0	3	1.163*	1	1
2	0	2	1.746	2	2	2	2	4	1.126	19	19
2	1	0	1.746	2	2	3	1	3	1.114*	3	2
2	1	1	1.703*	4	5	2	0	6	1.083	2	2
1	1	4	1.595	22	22	3	0	4	1.082	2	2
2	1	2	1.594	44	42	3	2	0	1.082	2	2
2	0	3	1.562*	1	1	1	0	7	1.073*	1	2
1	0	5	1.452*	1	1	3	2	1	1.072*	2	4
2	1	3	1.450*	3	3	2	1	6	1.043	27	25
2	0	4	1.381	27	27	3	1	4	1.043	27	25
2	2	0	1.380	14	13	3	2	2	1.042	27	25
1	1	5	1.360*	1	1	1	1	7	1.034*	2	1
2	2	1	1.359*	1	1	2	2	5	1.034*	1	1

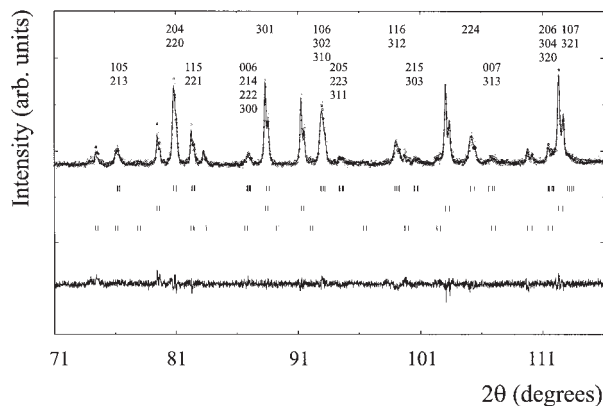


FIGURE 1. Observed (dots) and calculated (line) XRD patterns (high-angle region) and a difference spectrum (bottom) from the profile refinement of sample no. 2 consisting of perovskite-type $K_{2/3}Th_{1/3}TiO_3$ (upper row of tick marks), ThO_2 (thorianite, middle row) and TiO_2 (rutile, lower row). Peaks corresponding to $K_{2/3}Th_{1/3}TiO_3$ are indexed on a $P4/mmm$ cell. Note that the 301 reflection is not split as in low-symmetry ordered perovskites.

cycles, 51 variables were refined simultaneously, including the unit-cell dimensions, atomic coordinates and occupancies of the 1a and 1b sites in the structure of $K_{2/3}Th_{1/3}TiO_3$. The results of the refinement are summarized in Table 3.

DISCUSSION

The crystal structure of $K_{2/3}Th_{1/3}TiO_3$ (Fig. 2) consists of vertex-sharing TiO_6 octahedra forming a three-dimensional framework characteristic of perovskite-type compounds. “Voids” in this framework accommodate the K^{1+} and Th^{4+} cations ordered into successive (001) planes. The independently

TABLE 3. $K_{2/3}Th_{1/3}TiO_3$: Crystallographic characteristics

Atom	Site	S.o.f.	x	y	z	<i>B</i> (Å ²)‡
K1	1a	0.90(2)	0	0	0	0.60(9)
K2	1b	0.48(2)	0	0	1/2	0.60(9)
Th1	1a	0.10(2)	0	0	0	0.60(9)
Th2	1b	0.52(2)	0	0	1/2	0.60(9)
Ti	2h	1	1/2	1/2	0.249(1)	1.0(2)
O1	1c	1	1/2	1/2	0	0.6(2)
O2	1d	1	1/2	1/2	1/2	0.6(2)
O3	4i	1	0	1/2	0.267(2)	0.6(2)

Selected interatomic distances and bond angles

4 × K-O1	2.758(1) Å	O1-Ti-O3	94.1(7)°
8 × K-O3	2.86(1) Å	O2-Ti-O3	85.9(7)°
4 × Th-O2	2.758(1) Å	O3-Ti-O3	172(1)°
8 × Th-O3	2.67(1) Å		
1 × Ti-O1	1.945(8) Å		
1 × Ti-O2	1.960(7) Å		
4 × Ti-O3	1.955(1) Å		

Note: Final agreement factors and cell parameters: $R_p = 10.1\%$, $R_{wp} = 12.8\%$, $R_f = 5.2\%$, $\chi^2 = 1.51$, $DW = 1.37$. $a = 3.9007(2)$, $c = 7.8099(7)$ Å, $V = 118.83(2)$ Å³, $D_{calc} = 5.57(1)$ g/cm³.

‡ *B* factors are kept at the same values for all O atoms.

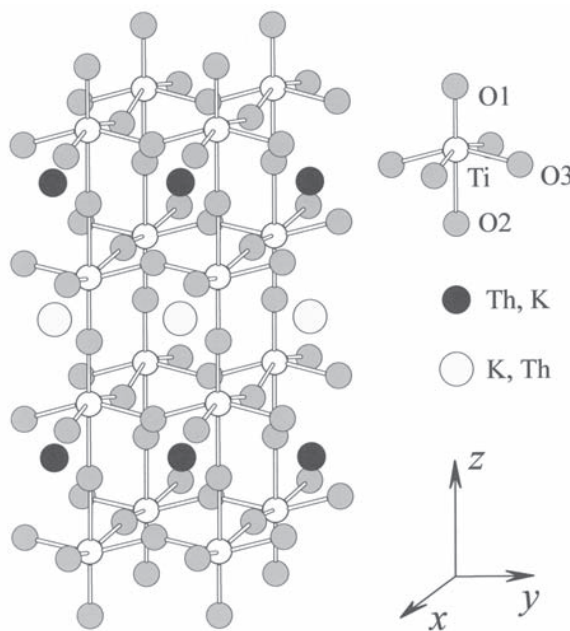


FIGURE 2. Crystal structure of $K_{2/3}Th_{1/3}TiO_3$. Displacement of Ti^{4+} cations is exaggerated for clarity. For the occupancies of “potassium” and “thorium” sites see Table 3.

refined occupancies of the 1a and 1b sites correspond to a K/Th ratio of 2.23, approaching the ideal value of 2. Attempts to assign a small number of vacancies to one of the sites, in accordance with the microprobe analytical data, were unsuccessful. It is possible that the samples studied by EDS and XRD have slightly different compositions due to some loss of K from sample 1 during its calcination (see above).

As expected, the structure of $K_{2/3}Th_{1/3}TiO_3$ shows only partial ordering of K and Th over the "A-sites". Note that in our case, the degree of disorder (D) cannot be quantified from the conventional equation $D = 2x|M_p - 50|$, where M_p is the percent amount of K or Th in the corresponding sites (Woodward et al. 1994). For example, for a fully disordered structure with the $(K_{2/3}Th_{1/3})$ occupancy in each of the sites, the above equation gives $D \approx 33\%$. Assuming that the amount of Th in the 1b site varies from 1/3 in a fully disordered structure ($D = 100\%$) to 2/3 in the structure with the maximum order possible ($D \approx 33\%$, see Results), the intermediate degrees of disorder should satisfy the equation $D = 200 - (M_K + M_{Th})$, where the M values signify the percentage of K or Th in the 1a and 1b sites, respectively. For the high-pressure $K_{2/3}Th_{1/3}TiO_3$ synthesized in the present study, $D = 58\%$ (cf. $D = 57\%$ for isostructural $Na_{2/3}Th_{1/3}TiO_3$; Mitchell and Chakhmouradian 1998b). At present, we cannot explain this similarity in the degree of disorder. From appreciable size differences between K^{1+} and Na^{1+} , as well as distinctive growth histories of the two compounds, we expect that the observed similarity in D is merely a coincidence.

As expected from the very different ionic radii of K^{1+} and Th^{4+} (1.64 and 1.21 Å; Shannon 1976), the "thorium" site is significantly smaller than the "potassium" site (Table 3), although in both cases, the 12-fold coordination of the central cation is retained. Volumes of the KO_{12} and ThO_{12} polyhedra calculated using IVTON software (Balić Žunić and Vicković 1996) are 53 and 46 Å³, respectively. The TiO_6 polyhedra are relatively regular, with a mean Ti-O distance of 1.955 Å; this value being in excellent agreement with the sum of ionic radii of Ti^{4+} and O^{2-} (1.955 Å; Shannon 1976). In common with other ordered perovskites incorporating highly charged rare-earth or actinide cations in one of the sites (Fourquet et al. 1996, Mitchell and Chakhmouradian 1998b), Ti^{4+} in the structure of $K_{2/3}Th_{1/3}TiO_3$ is displaced from the centers of octahedra away from O2, i.e., toward the planes populated by the lower-charged cations. The magnitude of this offset estimated from the interatomic distances and O3-Ti-O3 angle (Table 3) is about 0.1 Å.

To the best of our knowledge, the structure of $K_{2/3}Th_{1/3}TiO_3$ is the first proven example of high-pressure perovskite with a planar (two-dimensional) ordering of A-site cations. Most previously described high-pressure perovskites with large cations of different size and charge adopt the $Im\bar{3}$ structure with a three-dimensional arrangement of symmetrically non-equivalent sites (e.g., $CaFe^{2+}_3Ti_4O_{12}$; Leinenweber et al. 1995). An unusual, one-dimensional ordering pattern (in rods parallel to [001]) has been observed in $CaFe^{2+}_2Ti_2O_6$, the only known member of perovskite family with the $P4_2/nmc$ symmetry (Leinenweber and Parise 1995). In contrast to $K_{2/3}Th_{1/3}TiO_3$, the comparatively smaller sites in both $Im\bar{3}$ and $P4_2/nmc$ -type structures are most suitable for cations favoring a fourfold coordination environ-

ment (Leinenweber et al. 1995; Woodward 1997). A two-dimensional ordering pattern is very common among perovskites with two types of B-site cations, including such high-pressure compounds as Ca_2TiSiO_6 (Leinenweber and Parise 1997). However, in these structures, planes occupied by individual types of cations alternate along [111], rather than [001], and are much less densely populated.

As the perovskite structure is essentially a cubic close-packing of anions and large cations in a 3:1 ratio, it should be expected (Hazen and Navrotsky 1996) that the A-site ordering in perovskites is promoted by elevated pressures, and results in a small positive value of volume of disordering (ΔV_{dis}). Our estimations show that a hypothetical cubic structure ($Pm\bar{3}m$) with the K^{1+} and Th^{4+} cations disordered over the twelve-coordinated positions has a molar volume of 36.01 cm³/mol; hence, $\Delta V_{dis} = 36.01 - 35.79 = 0.22$ cm³/mol. This value is similar to the volumes of disordering observed for other close-packed structures (Hazen and Navrotsky 1996, their Table 1). For $K_{2/3}Th_{1/3}TiO_3$, the partial ordering observed is accompanied by a density increase of approximately 0.6%.

CONCLUSIONS

The data obtained in this study demonstrate that a high-pressure crystallization environment is favorable for crystallization of the partially ordered K-Th perovskite, whereas the assemblage of thorianite (ThO_2) and jeppeite ($K_2Ti_6O_{13}$) is stable at ambient pressures. These results are consistent with the occurrence mode of jeppeite in lamproites as a groundmass phase and mantles on priderite (Haggerty 1987; Mitchell and Bergman 1991). The high-pressure K-Th perovskite contains 44–46 wt% ThO_2 , depending on the number of A-site vacancies tolerated by the perovskite structure at a particular pressure. Hence, $K_{2/3}Th_{1/3}TiO_3$ and related structures, e.g., members of the series $K_{1/2+x}REE_{1/2-3x}Th_{2x}TiO_3$, may be a viable repository for Th in Ti-rich alkali metasomatites in the lithospheric upper mantle.

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