Monatsh Chem (2010) 141:495–499
DOI 10.1007/s00706-010-0289-1

ORIGINAL PAPER

Salt flux crystal growth of the titanyl arsenate NaTiO[AsO_4]

Hamdi Ben Yahia · Ute Ch. Rodewald ·
Rainer Pöttgen

Received: 10 December 2009 / Accepted: 25 February 2010 / Published online: 2 April 2010

Abstract The titanyl arsenate NaTiO[AsO_4] was synthesized in the form of colourless lath-shaped crystals from arsenic and titanium dioxide in a NaCl/KCl flux at 850 °C. NaTiO[AsO_4] crystallizes with the monoclinic low-temperature form LT-CaTiO[SiO_4], space group $P2_1/c$. The structure was refined from single crystal diffractometer data: $a = 6.7170(9)$, $b = 8.7707(12)$, $c = 7.2447(10)$ Å, $\beta = 114.77(1)°$, $wR2 = 0.0559$, 789 F^2 values, and 74 variables. NaTiO[AsO_4] is characterized by a topology common to a wide range of oxide structures of stoichiometry $AMOXO_4$. It consists of parallel chains of *trans*-corner-sharing TiO_6 octahedra, cross-linked by isolated AsO_4 tetrahedra.

Keywords Arsenate · Crystal chemistry · Titanyl compound

Introduction

Potassium titanyl phosphate, KTiO[PO_4] (KTP) [1], is one of a group of widely investigated non-centrosymmetric materials used industrially for non-linear optical materials [2–4]. In continuation of pioneering work on KTP, many isomorphous derivatives have been synthesized by standard solid-state reactions, hydrothermal crystal growth, ion exchange reactions, or different salt flux syntheses. An overview of these interesting materials is given in Refs. [4, 5].

By analogy with these phosphates, a series of arsenates ATiO[AsO_4] with the monovalent cations A = Li [6], K [7], Rb [7], Cs [8], and Tl [7] have been synthesized. Depending on the A cation, these compounds either crystallize in space group *Pnma* or the non-centrosymmetric subgroup $Pna2_1$. It is striking that so far, no purely sodium-containing analogue has been synthesized. Only a solid solution $K_{1-x}Na_xTiAsO_4$ has been reported. Those samples were prepared via ion-exchange reactions and an orthorhombic crystal of composition $Na_{0.87}K_{0.13}TiAsO_4$ was used for structure refinement [5].

During our recent attempts to synthesise arsenide oxides from salt fluxes [9, 10], we also obtained well shaped crystals of arsenite chlorides, e.g. $Ce_3OCl[AsO_3]_2$ [11] or $Pr_5O_4Cl[AsO_3]_2$ [12]. This proves that a salt flux: (1) favours crystal growth, but (2) can also lead to chloride incorporation into the materials.

Keeping the favourable crystal growth properties in mind we started a more systematic investigation of quaternary arsenite and arsenate phases. Herein we report on the salt flux synthesis of NaTiO[AsO_4] with an LT–CaTiO[SiO_4] type structure [13, 14], the missing link in the series of ATiO[AsO_4] titanyl arsenates.

Results and discussion

Structure refinement

Careful analyses of the diffractometer data set revealed a primitive monoclinic lattice, and the systematic extinctions observed for the NaTiO[AsO_4] crystal were compatible with the centrosymmetric space group $P2_1/c$. All atoms were localized by use of sir2004 software [15] and the structure was refined with Jana2006 [16].

H. Ben Yahia · U. Ch. Rodewald · R. Pöttgen (✉)
Institut für Anorganische und Analytische Chemie,
Westfälische Wilhelms-Universität Münster,
Corrensstrasse 30, 48149 Münster, Germany
e-mail: pottgen@uni-muenster.de

The difference-Fourier synthesis performed after the first refinement cycles did not reveal any significant residues. With anisotropic displacement parameters (ADP) for all positions, the residual factors converged to the values listed in Table 1. The refined atomic positions and ADPs are given in Tables 2 and 3. The $NaTiO[AsO_4]$ structure is isotypic with the low-temperature form of $CaTiO[SiO_4]$ [13, 14]. Refinement of the sodium occupancy parameter showed a value of 97(1)%, thus we observed no hint for potassium incorporation for the crystal investigated. Further information on the structure refinement is available (see "Experimental").

Table 1 Crystallographic data and structure refinement for $NaTiO[AsO_4]$

Formula	$NaTiO[AsO_4]$
Crystal colour	Colourless
MW ($g\ mol^{-1}$)	225.80
Crystal system	Monoclinic
Space group	$P2_1/c$
Lattice parameters	$a = 6.7170(9)$ Å
	$b = 8.7707(12)$ Å
	$c = 7.2447(10)$ Å
	$\beta = 114.77(1)°$
Cell volume (Å^3)	$V = 387.55\ (10)$
Z	4
Density calc. ($g\ cm^{-3}$)	3.87
Crystal shape	block
Temperature (K)	293 (1)
Diffractometer	Stoe IPDS II
Monochromator	Oriented graphite
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Scan mode	Multiscan
$h\ k\ l$ range	±9; ±12; ±10
θ_{min}, θ_{max} (°)	3.3/31.9
Linear absorption coeff. (mm^{-1})	10.7
Absorption correction	Gaussian
T_{min}/T_{max}	0.595/0.812
No. of reflections	4,625
R_{int}	0.061
No of independent reflections	1,211
Reflections used [$I \geq 2\sigma(I)$]	789
Refinement technique	F^2
$F(000)$ (e)	424
R factors $R(F)/wR(F^2)$	0.0324/0.0559
No. of refined parameters	74
G.o.f.	0.96
Weighting scheme	$w = 1/(\sigma^2(I) + 0.0009I^2)$
Diff. Fourier residues (e^-, Å^3)	–0.67, +0.59

Table 2 Atom positions and isotopic displacement parameters (Å^2) for $NaTiO[AsO_4]$

Atom	x	y	z	U_{eq}
Na	0.7506(12)	0.4221(2)	0.7594(10)	0.0222(8)
Ti	0.2521(2)	0.24138(16)	0.97853(13)	0.0070(2)
As	0.7507(2)	0.06672(4)	0.75206(17)	0.0040(1)
O1	0.9445(10)	0.1829(5)	0.9184(6)	0.0106(18)
O2	0.5636(10)	0.1850(5)	0.5874(6)	0.0085(17)
O3	0.8495(9)	0.9586(5)	0.6170(5)	0.0070(16)
O4	0.6429(10)	0.9599(5)	0.8809(6)	0.0092(19)
O5	0.2512(12)	0.1835(3)	0.7531(6)	0.0074(8)

All atoms are on Wyckoff sites 4*e* of space group $P2_1/c$

Crystal chemistry

The new titanyl arsenate $NaTiO[AsO_4]$ belongs to a large number of compounds with the monoclinic $CaTiO[SiO_4]$ type structure, space group $P2_1/c$ [17–23]. So far only partially substituted samples of the solid solution $K_{1-x}Na_xTiAsO_4$ have been prepared by ion exchange [5]. Now salt flux synthesis has enabled the growth of $NaTiO[AsO_4]$ crystals. Besides the arsenide oxide $Na_2Ti_2As_2O$, with a totally different structure and bonding pattern [24, 25], and $Na_4TiAs_2O_9$ [26], $NaTiO[AsO_4]$ is the third compound in the quaternary system Na–Ti–As–O.

The structure is characterized by a topology common to a wide range of oxide structures of stoichiometry $AMOXO_4$. It consists of parallel chains of *trans* corner sharing MO_6:TiO_6 octahedra, cross-linked by isolated XO_4:AsO_4 tetrahedra (Fig. 1). Within this three-dimensional network, the sodium atoms are connected to seven oxygen atoms forming a highly distorted capped prism (Fig. 2) with one short, four normal, and two stretched Na–O distances (Table 4). The average value of 2.498 Å is close to the value expected for a seven-coordinated sodium atom (2.520 Å).

The TiO_6 octahedra show a broad range of Ti–O distances from 1.707 to 2.098 Å, indicating substantial distortion. The average Ti–O distance of 1.977 Å is in good agreement with the sum of the ionic radii of 2.005 Å. The shorter Ti–O distance of 1.707 Å is a direct consequence of the titanyl-type $[O{=}Ti{-}O_5]$ coordination observed in many related compounds [4, 5, 22]. For a more detailed discussion of these titanyl species we refer the reader to review articles [4, 5].

The arsenic atoms are four-coordinated to the oxygen atoms. The $[AsO_4]$ tetrahedra are quite regular with an average As–O distance of 1.686 Å, which is slightly lower than the value 1.715 Å estimated from the effective ionic radii of four-coordinated As^{5+} and O^{2-} [27].

Table 3 Anisotropic displacement parameters (Å^2) for NaTiO[AsO_4]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	0.0133(9)	0.0093(8)	0.0392(14)	0.0010(18)	0.0064(9)	−0.0005(17)
Ti	0.0061(3)	0.0030(4)	0.0106(3)	−0.0003(2)	0.0023(3)	0.0005(3)
As	0.00367(18)	0.00329(16)	0.00491(16)	0.0001(3)	0.00172(12)	0.0005(3)
O1	0.011(4)	0.010(2)	0.0087(15)	−0.0062(19)	0.0014(16)	−0.0061(13)
O2	0.004(3)	0.010(2)	0.0102(15)	0.0016(17)	0.0014(15)	0.0039(13)
O3	0.004(3)	0.009(2)	0.0092(15)	−0.0007(18)	0.0049(16)	−0.0027(13)
O4	0.015(4)	0.0029(19)	0.0130(16)	0.0011(18)	0.0093(19)	0.0043(13)
O5	0.0112(14)	0.0070(11)	0.0045(10)	−0.002(2)	0.0039(9)	0.0001(15)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \ldots + 2hka^*b^*U_{12}]$

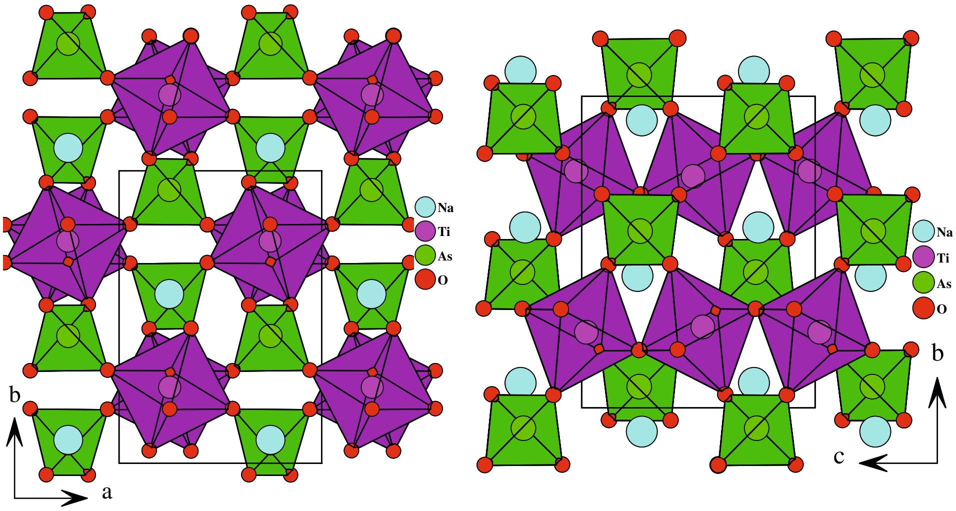

Fig. 1 View of the NaTiO[AsO_4] structure along [001] (**a**) and [100] (**b**)

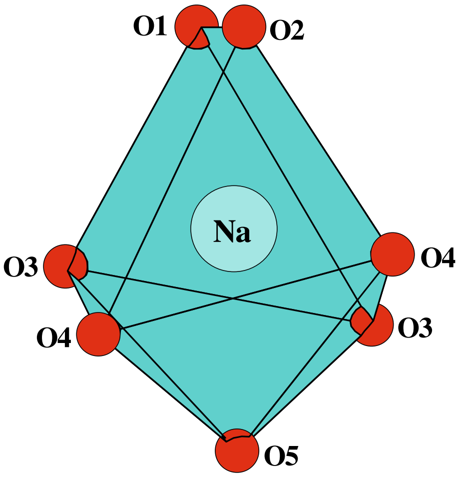

Fig. 2 Perspective view of environment of the sodium atoms in NaTiO[AsO_4]

The calculated BVS values of 1.13, 4.14, and 4.97 are in good agreement with the expected values for Na^+, Ti^{4+}, and As^{5+}, respectively [28, 29].

Experimental

Synthesis

The title compound was prepared, by solid-state reaction, from a mixture of arsenic (Sigma–Aldrich, 99.999%), titanium dioxide (Chempur, >99.99%), and an NaCl (Merck, >99.5%)/KCl (Chempur, 99.9%) salt flux (1:1 molar ratio) in 2:3:10 molar ratio, respectively. The arsenic was purified by fractional sublimation [9] under vacuum before use. The mixture was placed in a silica tube which was sealed under vacuum (a precisely calculated amount of $KClO_4$ was placed in the bottom of the tube to ensure a partial pressure of oxygen upon decomposition). The tube was heated at 500 °C for 12 h and at 850 °C for 48 h. By reducing the temperature at a rate of 20 °C/h to room temperature we obtained colourless crystals of NaTiO[AsO_4] and KTiO[AsO_4] besides the new phase $NaTi_2[AsO_4]_3$ [30] with the so-called NASICON-type structure. NaTiO[AsO_4] was then synthesised successfully starting from a stoichiometric mixture of Na_2CO_3, $NH_4H_2AsO_4$, and TiO_2. The mixture

Table 4 Interatomic distances (Å) and bond valence sums (BVS) for NaTiO[AsO_4]

	Distance	BV
Na–O5	2.295(3)	0.265
Na–O4	2.425(10)	0.186
Na–O3	2.471(10)	0.164
Na–O2	2.479(6)	0.161
Na–O1	2.483(6)	0.159
Na–O3	2.609(8)	0.113
Na–O4	2.730(8)	0.082
	<2.498>	1.129
Ti–O5	1.707(6)	1.339
Ti–O1	1.992(7)	0.620
Ti–O2	2.009(6)	0.592
Ti–O4	2.012(4)	0.587
Ti–O3	2.044(5)	0.539
Ti–O5	2.098(6)	0.465
	<1.977>	4.142
As–O2	1.680(4)	1.265
As–O4	1.685(6)	1.248
As–O3	1.686(6)	1.245
As–O1	1.695(5)	1.215
	<1.686>	4.973

Average distance values are given in parentheses

BV = $e^{(r0-r)/b}$ with the following parameters: $b = 0.37$, r_0 (Na^I–O) = 1.803, r_0 (As^V–O) = 1.767, and r_0 (Ti^{IV}–O) = 1.815 [27, 28]

was fired at 400 °C for 12 h, at 600 °C for 24 h, and at 750 °C for 24 h with intermediate grinding.

Scanning electron microscopy

Semiquantitative EDX analyses of many crystals, including that investigated on the diffractometer (Fig. 3), were carried out with a Leica 420i scanning electron microscope with Ti, InAs, and the mineral Albite (for Na) as standards. The experimentally observed compositions were close to the ideal one. A few traces of KTiO[AsO_4] were observed on the surface of some crystals. There was no hint of incorporation of potassium into the crystals, in agreement with the single crystal X-ray data.

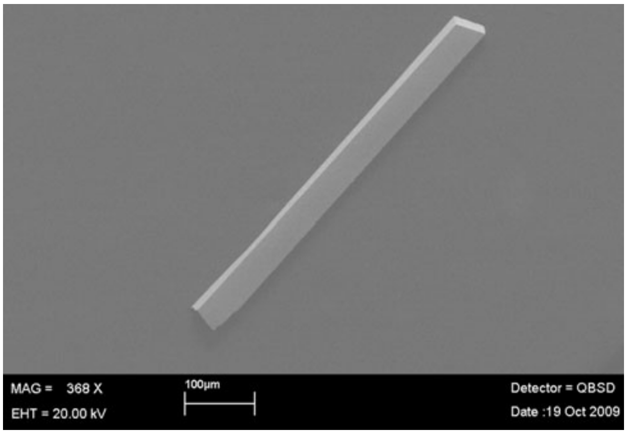

Fig. 3 Scanning electron micrograph of the NaTiO[AsO_4] single crystal used for X-ray data collection

X-ray data collection

The NaTiO[AsO_4] sample was studied by a Guinier powder pattern (imaging plate technique, Fujifilm BAS-1800) using Cu Kα_1 radiation and α-quartz ($a = 491.30$ and $c = 540.46$ pm) as an internal standard. Full pattern-matching refinement was performed with the Jana2006 software package [16]. The background was estimated by use of a Legendre function, and the peak shapes were described by use of a pseudo-Voigt function. This allowed us to confirm the formation of NaTiO[AsO_4] as a major phase, besides few very weak reflections of $NaTi_2[AsO_4]_3$. The refined lattice parameters are $a = 6.7361(3)$, $b = 8.7965(3)$, $c = 7.2511(3)$ Å, $\beta = 114.811(3)°$.

Lath-shaped single crystals of NaTiO[AsO_4] were selected on the basis of the size and sharpness of the diffraction spots in Laue photographs obtained on a Buerger camera (using white Mo radiation), equipped with the same Fujifilm, BAS-1800 imaging plate technique. Intensity data were collected on a Stoe IPDS II diffractometer (graphite monochromatic Mo Kα radiation; oscillation mode). Data processing and all refinements were performed with the Jana2006 software package [16]. A Gaussian-type absorption correction was applied, and the shape of the crystal was determined with the video microscope of the Stoe CCD camera. All relevant details concerning data collection and evaluation are listed in Table 1.

Further information on the structure refinement may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-421302.

Acknowledgments This work was financially supported by the Deutsche Forschungsgemeinschaft. H. B. Y. is indebted to the Alexander von Humboldt Foundation for a postdoc stipend.

References

1. Tordjman I, Masse R, Guitel JC (1974) Z Kristallogr 139:103
2. Zumsteg FC, Bierlein JD, Gier TE (1976) J Appl Phys 47:4980
3. Bierlein JD, Vanherzeele H (1989) J Opt Soc Am 6:622
4. Stucky GD, Phillips MLF, Gier TE (1989) Chem Mater 1:492
5. Phillips MLF, Harrison WTA, Stucky GD, McCarron EM III, Calabrese JC, Gier TE (1992) Chem Mater 4:222
6. Robertson A, Fletcher JG, Skakle JMS, West AR (1994) J Solid State Chem 109:53
7. El Brahimi M, Durand J (1986) Rev Chim Miner 23:146

8. Protas J, Marnier G, Boulanger B, Menaert B (1989) Acta Crystallogr C45:1123
9. Lincke H, Glaum R, Dittrich V, Möller MH, Pöttgen R (2009) Z Anorg Allg Chem 635:936
10. Pöttgen R, Johrendt D (2008) Z Naturforsch 63b:1135
11. Ben Yahia H, Rodewald UCh, Pöttgen R (2009) Z Naturforsch 64b:896
12. Ben Yahia H, Rodewald UCh, Schleid T, Pöttgen R (2010) Z Naturforsch (in press)
13. Robbins CR (1968) Mater Res Bull 3:693
14. Taylor M, Brown GE (1976) Am Mineral 61:435
15. Burla MC, Camalli M, Carrozzini B, Cascarano G, Giacovazzo C, Polidori G, Spagna R (2003) J Appl Crystallogr 36:1103
16. Petricek V, Dusek M, Palatinus L (2006) Structure determination software programs. Institute of Physics, University of Prague, Prague (Czech Republic)
17. Malcherek T, Bosenick A, Cemič L, Fechtelkord M, Guttzeit A (2004) J Solid State Chem 177:3254
18. Liferovich RP, Mitchell RH (2005) Min Petrol 83:271
19. Ellemann-Olesen R, Malcherek T (2005) Phys Chem Miner 32:531
20. Lii KH, Li CH, Chen TM, Wang SL (1991) Z Kristallogr 197:67
21. Mill' BV, Belokoneva EL, Butashin AV (1990) Sov Phys Crystallogr 35:176
22. Nagornyi PG, Kapshuk AA, Stus' NV, Slobodyanik NS (1989) Russ J Inorg Chem 34:1731
23. Haddad A, Jouini T, Piffard Y (1992) Eur J Solid State Inorg Chem 29:57
24. Adam A, Schuster H-U (1990) Z Anorg Allg Chem 584:150
25. Ozawa TC, Kauzlarich SM, Bieringer M, Greedan J (2001) Chem Mater 13:1804
26. Yaakoubi A, Jouini T (1998) Acta Crystallogr C 54:1200
27. Shannon RD (1976) Acta Crystallogr A 32:751
28. Brown ID, Altermatt D (1985) Acta Crystallogr B 41:244
29. Brese NE, O'Keefe M (1991) Acta Crystallogr B 47:192
30. Ben Yahia H, Rodewald UCh, Pöttgen R (2010) Z Naturforsch (in press)