Crystal Structure of the Arsenate(V) $NaTi_2[AsO_4]_3$

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The arsenate(V) $NaTi_2[AsO_4]_3$ has been synthesized by a solid-state reaction route using a salt flux. Its structure has been solved and refined from single-crystal X-ray data: NASICON-type, $R\bar{3}c$, a = 8.8057(5), c = 22.2406(15) Å, Z = 6, $wR(F^2)$ = 0.0617 for 576 unique reflections and 30 variables. The $NaTi_2[AsO_4]_3$ structure consists of a three-dimensional framework of corner-sharing AsO_4 tetrahedra and TiO_6 octahedra. The negatively charged $[Ti_2As_3O_{12}]$ framework gives rise to two different interstices. The Na^+ cation is located on the 6*b* position with a trigonal antiprismatic coordination and enhanced anisotropic displacement parameters.

Key words: Crystal Structure, Nasicon, Arsenate(V), Single Crystal Diffraction, Salt Flux Synthesis

Introduction

In the last three decades, complex oxides with the general formula $AA'_3B_2[XO_4]_3$, where A are monovalent (alkali, Cu^+, Ag^+,...), divalent (alkaline earth, Mn^{2+}, Cu^{2+}, Zn^{2+},...) or trivalent (rare earth) cations, B trivalent (Fe^{3+}, Er^{3+},...), tetravalent (Ti^{4+}, Sn^{4+}, Ge^{4+},...) or even pentavalent (Nb^{5+}, Sb^{5+},...) cations, and X = As, Ge, Mo, P, Si have been widely studied. Besides the rich structural chemistry, the interest in these materials mainly concerns the remarkable electrochemical properties of selected oxides with potential application as solid electrolytes, gas sensors, or battery materials [1 – 8].

The NASICON structure of $Na_4Zr_2[SiO_4]_3$ was first reported by Sizova *et al*. [9]. It is characterized by a three-dimensional framework of BO_6 octahedra, sharing corners with XO_4 tetrahedra and forming tunnels which may be vacant ($\square_4NbTi[PO_4]_3$) [10], partially filled ($\square_1Na_3Fe_2[PO_4]_3$ [11], $Ag\square_3Ge_2[PO_4]_3$ [12], $Sr_{0.5}\square_{0.5}\square_3Zr_2[AsO_4]_3$ [13], $Ca\square_3TiFe[PO_4]_3$ [14], $Pr_{0.33}\square_{0.67}\square_3Zr_2[PO_4]_3$ [15]), or fully occupied by A and A' ions ($Na_4Zr_2[SiO_4]_3$ [9]). The A ions are sandwiched between two BO_6 octahedra along the c axis giving rise to a trigonal antiprismatic coordination whereas the A' ions are 6- or (6+2)-coordinated to the oxygen atoms depending on the composition [9, 11]. These few examples underline the rich crystal chemistry of NASICON-related materials.

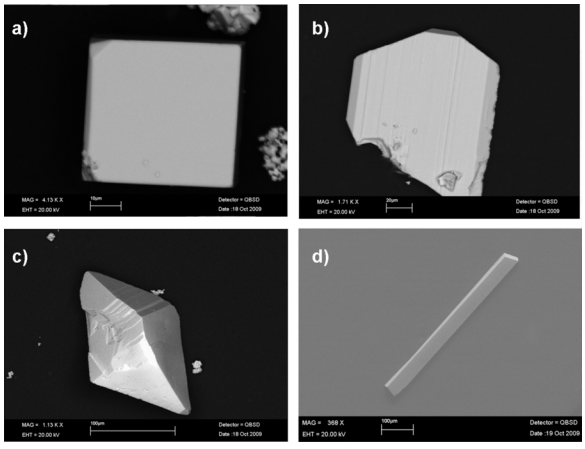

Fig. 1. Scanning electron micrograph of (a) the $NaTi_2[AsO_4]_3$ single crystal used for the XR data collection, (b) $KTiO[AsO_4]$ and (c, d) $NaTiO[AsO_4]$ single crystals.

During our recent salt flux synthesis of arsenide oxides [16, 17] we obtained $NaTiO[AsO_4]$ [18] with LT-$CaTiO[SiO_4]$-type structure as a by-product. During the bulk synthesis of $NaTiO[AsO_4]$ a new arsenate(V), $NaTi_2[AsO_4]_3$, was discovered. Its crystal structure is reported herein.

Experimental Section

Synthesis

$NaTi_2[AsO_4]_3$ was prepared by solid-state reaction from a mixture of arsenic (Sigma-Aldrich, 99.999 %), titanium dioxide (Chempur, > 99.99 %) and a NaCl (Merck, > 99.5 %) / KCl (Chempur, 99.9 %) salt flux (1 : 1 molar ratio) with a 2 : 3 : 10 molar ratio. The arsenic was purified by fractional sublimation [16]. The mixture was put in an alumina tube which was sealed under vacuum in a silica tube. The tube was heated at 500 °C for 12 h and at 850 °C for 48 h under controlled partial pressure of oxygen ($KClO_4$). By decreasing the temperature at a rate of 20 °C/h to r. t. we obtained few colorless crystals of $NaTi_2[AsO_4]_3$ (cubes),

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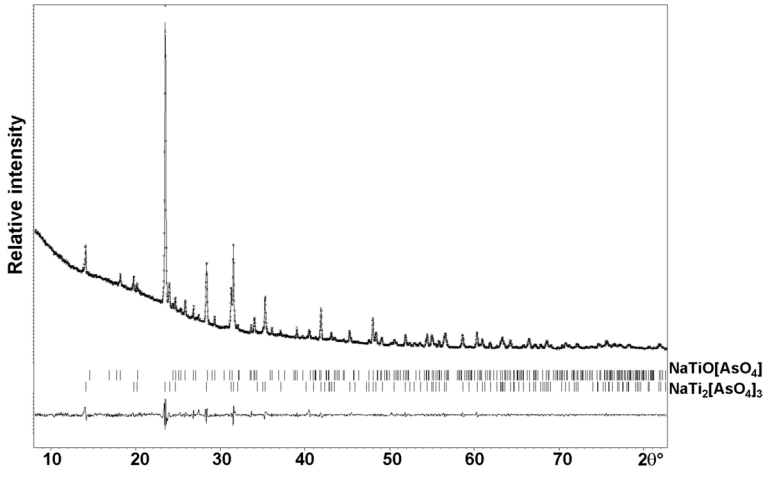

Fig. 2. Observed, calculated and difference plots for the XRPD profile refinement of the $NaTi_2[AsO_4]_3$ sample obtained from flux syntheses. The peak positions of the impurity phase $NaTiO[AsO_4]$ are also indicated.

Table 1. Crystallographic data and structure refinement for $NaTi_2[AsO_4]_3$.

Formula	$NaTi_2[AsO_4]_3$
Crystal color / shape	colorless / cube
M_r, g mol^{-1}	535.5
Crystal system	trigonal
Space group	$R\bar{3}c$
Lattice parameters, Å	
a, Å	8.8057(5)
c, Å	22.2406(15)
Cell volume V, Å^3	1493.5(2)
Z	6
$F(000)$, e	1500
Density calcd., g cm^{-3}	3.57
Temperature, K	293(1)
Diffractometer	Stoe IPDS-II
Radiation; λ, Å	MoK_α; 0.71073
Monochromator	oriented graphite
Scan mode	multi-scan
hkl range	±13, ±13, ±32
θ_{min} / θ_{max}, deg	3.24 / 31.94
Linear absorption coeff., mm^{-1}	11.6
Absorption correction	Gaussian
T_{min} / T_{max}	0.592 / 0.657
No. of reflections	5121
No. of independent refl. / R_{int}	576 / 0.0296
Reflections used [$I \geq 0\ \sigma(I)$]	576
Refinement technique	F^2
No. of refined parameters	30
R factors $R(F)$ / $wR(F^2)$	0.0315 / 0.0617
GOF	1.15
Weighting scheme	$w = 1/(\sigma^2(I) + 0.0016I^2)$
Diff. Fourier residues, e Å^{-3}	−0.57 / +0.58

Table 2. Atom positions and equivalent isotropic displacement parameters (Å^2) for $NaTi_2[AsO_4]_3$.

Atom	Site	x	y	z	U_{eq}
Na	6*b*	0	0	0	0.0283(9)
Ti	12*c*	0	0	0.14354(3)	0.00755(18)
As	18*e*	0.28614(4)	0	1/4	0.00772(13)
O1	36*f*	0.1664(4)	−0.0269(4)	0.18842(10)	0.0246(10)
O2	36*f*	0.1827(3)	0.1548(3)	0.08635(9)	0.0177(7)

$NaTiO[AsO_4]$ (needles or octahedra) and $KTiO[AsO_4]$ (plates). $NaTi_2[AsO_4]_3$ was then synthesized from a stoichiometric mixture of Na_2CO_3, $NH_4H_2AsO_4$ and TiO_2. The mixture was fired at 400 °C for 6 h and at 750 °C for 48 h with intermediate grindings. The analysis of the obtained powder showed the presence of $NaTiO[AsO_4]$ beside the major phase $NaTi_2[AsO_4]_3$. When one fires the mixture at higher temperature (950 °C) the amount of $NaTi_2[AsO_4]_3$ decreases in favor of $NaTiO[AsO_4]$.

EDX data

Semiquantitative EDX analyses of many crystals including the one investigated on the diffractometer (Fig. 1) were carried out with a Leica 420i scanning electron microscope with Ti, InAs, MAD-10 feldspar (for K), and albite (for Na) as standards. The experimentally observed compositions were close to the ideal ones ($NaTi_2[AsO_4]_3$, $NaTiO[AsO_4]$ and $KTiO[AsO_4]$).

X-Ray diffraction

The polycrystalline sample obtained after dissolving the salt flux in demineralized water was characterized by a Guinier pattern (imaging plate detector, Fujifilm BAS-1800) with Cu$K_{\alpha1}$ radiation and α-quartz (a = 4.9130, c = 5.4046 Å) as an internal standard. Taking the presence of two phases ($NaTi_2[AsO_4]_3$ and $NaTiO[AsO_4]$) into account, a full pattern matching refinement was performed with the JANA2006 program package [19]. The background was estimated by a Legendre function, and the peak shapes were described by a pseudo-Voigt function. This allowed us to con-

Table 3. Anisotropic displacement parameters (Å^2) for $NaTi_2[AsO_4]_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11}+\ldots+2hka^*b^*U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	0.0381(13)	U_{11}	0.0086(11)	0.0191(6)	0	0
Ti	0.0074(2)	U_{11}	0.0079(3)	0.00369(12)	0	0
As	0.00652(16)	0.00745(19)	0.00949(18)	0.00373(10)	0.00099(6)	0.00198(11)
O1	0.0240(12)	0.0331(13)	0.0226(9)	0.0187(10)	−0.0131(9)	−0.0012(10)
O2	0.0107(9)	0.0143(9)	0.0158(8)	−0.0032(8)	0.0041(7)	0.0006(7)

Table 4. Interatomic distances (Å) and bond valence sums (BVS) for $NaTi_2[AsO_4]_3$. Average distance values are given in brackets.

	Distance	BV
Na–O2(2×)	2.4376(19)	0.180
Na–O2(4×)	2.438(3)	0.180
	⟨2.438⟩	BVS = 1.08
Ti–O1(3×)	1.883(3)	0.832
Ti–O2(3×)	1.967(3)	0.663
	⟨1.925⟩	BVS = 4.485
As–O2(2×)	1.665(3)	1.317
As–O1(2×)	1.672(3)	1.293
	⟨1.668⟩	BVS = 5.22

$BV = e^{(r_0-r)/b}$ with the following parameters: $b = 0.37$, $r_0(Na^I–O) = 1.803$, $r_0(As^V–O) = 1.767$ and $r_0(Ti^{IV}–O) = 1.815$ [25, 26].

firm the biphasic mixture of the sample (Fig. 2). The refined lattice parameters ($R\bar{3}c$, $a = 8.8191(3)$, $c = 22.2749(7)$ Å and $P2_1/c$, $a = 6.7288(5)$, $b = 8.7820(4)$, $c = 7.2583(5)$ Å, $\beta = 114.961(4)^\circ$) are in agreement with those obtained by single-crystal diffraction for $NaTi_2[AsO_4]_3$ and $NaTiO[AsO_4]$ [18], respectively.

A suitable crystal for X-ray diffraction was selected on the basis of Laue photographs on a Buerger camera (using white Mo radiation). The data collection was carried out on a Stoe IPDS-II diffractometer using MoK_α radiation. Data processing and all refinements were performed with the JANA2006 program package [19]. A Gaussian-type absorption correction was applied, and the shape was determined with the video microscope of the Stoe CCD camera. Details about the data collection and crystallographic parameters are summarized in Table 1.

Structure refinement

The extinction conditions observed for the $NaTi_2[AsO_4]_3$ crystal agreed with space group $R\bar{3}c$. The atomic positions of isotypic $NaTi_2[PO_4]_3$ [20] were used as starting parameters. With anisotropic displacement parameters for all positions, the residuals converged to the values listed in Table 1. The refined atomic positions and anisotropic displacement parameters (ADPs) are given in Tables 2 and 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-421531.

Discussion

As emphasized in Fig. 3, the $NaTi_2[AsO_4]_3$ structure consists of a three-dimensional network of corner-sharing AsO_4 tetrahedra and TiO_6 octahedra. The

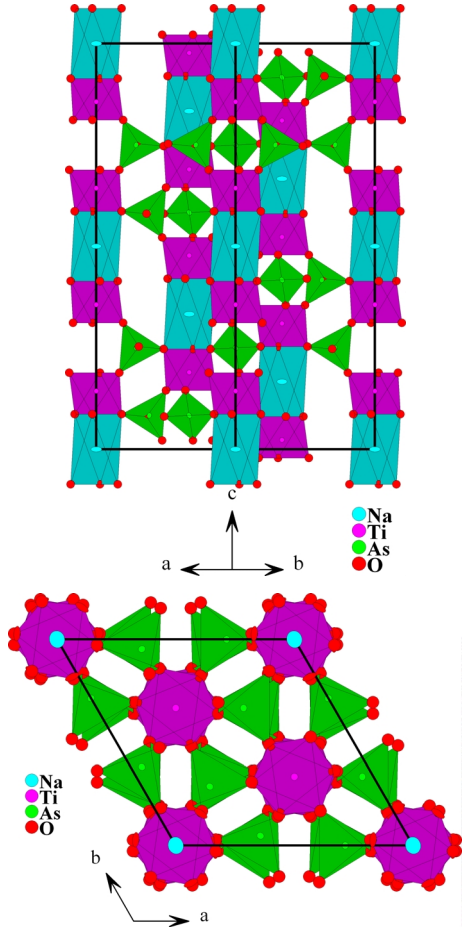

Fig. 3. (color online) View of the $NaTi_2[AsO_4]_3$ structure along [110] (top) and [001] (bottom). Relevant polyhedra are emphasized. For details see text.

$[Ti_2As_3O_{12}]^{1-}$ framework contains two interstices. The Na atom is found in a six-coordinated trigonal antiprismatic site formed by two faces of two TiO_6 octahedra along the *c* axis with Na–O distances of 2.489 Å. This corresponds to the alkali ion position in $NaTi_2[PO_4]_3$ [20], $KTi_2[PO_4]_3$ [21] and $RbTi_2[PO_4]_3$ [22]. The enhanced anisotropic displacement parameters ($U_{11} = U_{22} = 0.0381(13)$ Å^2) are indicative of sodium mobility as frequently observed in NASICON materials [8, and refs. therein]. The bond valence sum (BVS) of 1.08 is in good agreement with the value expected for Na^+ (Table 4).

A distortion is observed in the TiO_6 octahedra, *i. e.* 3×1.883 and 3×1.967 Å. The average Ti–O distance of 1.925 Å is smaller than the value of 2.005 Å estimated from the effective ionic radii of six-coordinated Ti^{4+} and O^{2-} [23]. Such short distances occur often in titanates with NASICON structure such as in $LiTi_2[PO_4]_3$ (d_{min} = 1.880 and d_{max} = 1.976 Å) [21], $CuTi_2[PO_4]_3$ (d_{min} = 1.896 Å and d_{max} = 1.958 Å) [24] or $KTi_2[PO_4]_3$ (d_{min} = 1.886 Å and d_{max}= 1.933 Å) [21]. This explains the slight overbonding of the titanium with a BVS = 4.485. Due to this steric strain the anisotropic displacement parameters of the O1 oxygen atoms are enhanced (Table 3). The arsenic atoms are four-coordinated to oxygen atoms. The $[AsO_4]$ tetrahedra are quite regular with an average As–O distance of 1.668 Å which is lower than the value of 1.735 Å estimated from the effective ionic radii of four-coordinated As^{5+} and O^{2-} [23]. The calculated BVS value 5.22 shows that the As^{5+} cation is also slightly overbonded.

Acknowledgements

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