

Synthesis and Characterization of Novel One-dimensional Chalcogenide Compound of $K_5NaTi_6Se_{27}$

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Low-dimensional chalcogenide compounds are quite interesting due to their unique structures and properties.¹ Their anionic frameworks often exhibit structural diversity depending on relative counter cation sizes as found in Na^+ and K^+ salts of $[AuSe_2]^{-1,2}$. K^+ salt exhibit one-dimensional chain structure while Na^+ salt shows two-dimensional layer structure. As an effort to search for novel structural compounds in chalcogenide system, we have designed the system that contains mixed alkali metals. Depending on the relative size of alkali metal ions in the reaction system, each may have preferential packing site to stabilize $[M_xQ_y]^{n-}$ anionic frameworks that the reaction system could provide. Both types of alkali metal cations can incorporate into the anionic framework simultaneously or only one type may do exclusively. If both alkali metal cations incorporate into the anionic framework at the same time, one can expect novel structural compounds, otherwise impossible in ternary system. This is because two cations with different sizes may require their own packing volumes in the structure, therefore stabilizing various chain length of polychalcogenide ligands. Structures of $Na_3AuSe_8^3$ and $K_3AuSe_{13}^4$ exhibit profound cation size effect on stabilizing Se_3^{2-} and Se_5^{2-} polychalcogenide ligands respectively depending on relative size of Na^+ and K^+ ions. Therefore, incorporating two types of alkali metal cations into the chalcogenide anionic framework, if possible, could provide an interesting structural features in (poly)chalcogenide chemistry.

Using this synthetic strategy, we have encountered new quaternary compound, $K_5NaTi_6Se_{27}$. The structure of $K_5NaTi_6Se_{27}$ is composed of charge compensating K^+/Na^+ cations and infinite one-dimensional $[Ti_6Se_{27}]_n^{6n-}$ chains running parallel to c -axis as shown in Figure 1. In the $[Ti_6Se_{27}]_n^{6n-}$ chain as shown in Figure 2, there are two crystallographically unique Ti atoms. Each Ti atom is seven-coordinated by two chelating Se_2^{2-} , two bridging Se_2^{2-} , and one bridging Se^{2-} ligands. There are only four crystallographically unique Se_2^{2-} units in the structure. Therefore, all the Se_2^{2-} units are bonded to Ti atoms through not only chelating but also bridging ligation mode. The chelating Se_2^{2-} units bridges the neighboring Ti atoms via one of terminal Se atoms. One interesting feature of this bridging mode is that two chelating Se_2^{2-} units on Ti(2) atom bridge only one neighboring Ti(1) atom in one direction via terminal

Se(4) and Se(9) respectively to form a dimeric $[Ti_2(Se_2)_4]$ unit, while two chelating Se_2^{2-} units on Ti(1) atom bridge two neighboring Ti(2) atoms via terminal Se(6) and Se(2) respectively to form an infinite chain. Therefore, one can easily imagine that $[Ti_2(Se_2)_4]$ units are linked together along the crystallographic c -axis via terminal Se(2) atom of the Se_2^{2-} unit on Ti(1) atom and additional monoselenide Se(1) atom to form an infinite one-dimensional chain in the formula of $[Ti_2(Se_2)_4Se]_n^{2n-}$.

In the literature, one-dimensional chain compounds, $K_4Ti_3S_{14}^5$ and $Na_2Ti_2Se_8^6$, are known. They are very similar in structure to $K_5NaTi_6Se_{27}$. However, $K_4Ti_3S_{14}$ contains eight- and seven-coordinated Ti atoms, which is not relevant to $K_5NaTi_6Se_{27}$, while the structure of $Na_2Ti_2Se_8$ can be easily compared with $K_5NaTi_6Se_{27}$ even though their ligation

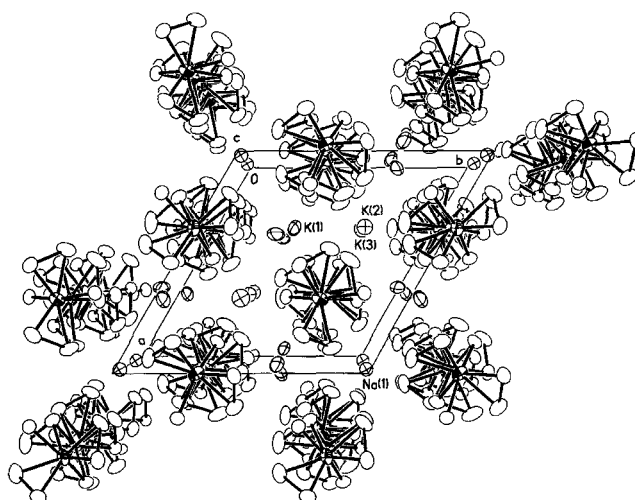


Figure 1. A view of packing diagram of one-dimensional compound of $K_5NaTi_6Se_{27}$ looking down the crystallographic c direction. Shaded ellipsoids are Ti and open ellipsoids are Se.

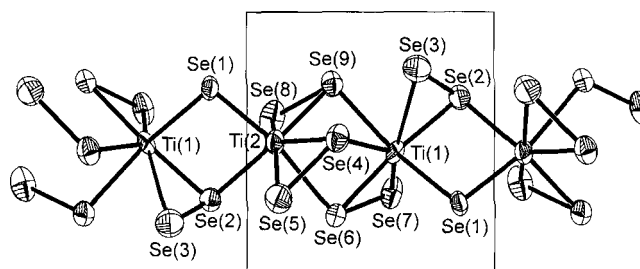


Figure 2. A view of one-dimensional $[Ti_2(Se_2)_4Se]_n^{2n-}$ chain highlighting dimeric unit linked by monoselenide. Se(1) and terminal Se(2) of Se_2^{2-} to form an infinite one-dimensional chain.

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modes are somewhat different. $[\text{Ti}_2\text{Se}_8]_n^{2n-}$ chain is composed of seven-coordinated Ti atoms bridged and chelated by three Se_2^{2-} units as well as two Se^{2-} in the structural formula of $[\text{Ti}_2(\text{Se}_2)_3\text{Se}_2]_n^{2n-}$. Simple comparison of the structural formulae between $\text{Na}_2\text{Ti}_2\text{Se}_8$ and $\text{K}_5\text{NaTi}_6\text{Se}_{27}$ reveals that one of the Se^{2-} units in the former has been replaced with one Se_2^{2-} unit to form $[\text{Ti}_2(\text{Se}_2)_4\text{Se}]_n^{2n-}$ which can be rewritten as $[\text{Ti}_6(\text{Se}_2)_{12}\text{Se}_3]_n^{6n-}$. This is probably because the mixed K^+ and Na^+ ions require more roomy space due to the larger cation size of K^+ compared to the Na^+ only system. Therefore, K^+ containing system pushes Ti/Se anionic chains further apart and then provide Ti/Se anionic frameworks with enough space to be able to accommodate another Se_2^{2-} unit instead of Se^{2-} . In this mixed alkali metal compound, K-Se bond distances are found at min. 3.256(9) Å much longer than Na-Se distance (d_{ave} 2.93(1) Å). These are compared well with the K-Se and Na-Se distances found in the known

alkali metal ternary chalcogenide compounds.⁷ Ti-Se bond distances are observed quite irregular ranging from 2.534(6) to 2.797(6) Å for Ti(1) and from 2.533(7) to 2.747(7) Å for Ti(2). This is probably due to the steric demands of the Se_2^{2-} units in the structure. Similar or even more irregular Ti-Se distances (2.383(4)-2.822(4) Å) are also found in $\text{Na}_2\text{Ti}_2\text{Se}_8$. Average Ti-Se distances are 2.59(10) Å for Ti(1) and 2.59(8) Å for Ti(2). For a simple comparison, the Ti-Se bond distance found in the known TiSe_2 ⁸, where Ti atom is six-coordinated, is 2.554(1) Å. On the other hand, the Se-Se distances are normal at 2.349(5) to 2.370(5) Å compared well with those of the known polyselenide compounds.^{3,4,7} In the chain, Ti(1)-Ti(2) contact at 3.365(8) Å is found but are not short enough to be considered as any significant bonding. This is due to the structural demands induced by bridging selenide ligands. Selected bond distances and angles are given in Table 1.

As assigning -2 charges on Se_2 and Se units and +1 charge on K and Na ions, charges on Ti atoms are expected to be +4 suggesting valence-precise semiconductor nature. Optical diffuse reflectance measurement reveals the presence of optical band gap at 1.05 eV confirming the semiconductor nature and suggesting a most likely direct band gap semiconductor as shown in Figure 3.

The result presented here further illustrates the structural diversity induced by the alkali metal cation size effect in chalcogenide chemistry. At present, the controlling and designing of mixed alkali metal cation size effects on the structure diversity are not well understood. However, using this synthetic strategy, we are expecting novel structural compounds and their structure related properties, otherwise impossible in the ternary system. Novel one-dimensional mixed alkali-metal compound of $\text{K}_5\text{NaTi}_6\text{Se}_{27}$ shows that the structural modification could be possible by introducing two types of alkali metal cations with different sizes.

Table 1. Selected Bond lengths [Å] and angles [°] for $\text{K}_5\text{NaTi}_6\text{Se}_{27}$

Ti(1)-Se(1)	2.526(6)	Ti(2)-Se(1)	2.533(7)
Se(2)	2.551(6)	Se(2)	2.607(6)
Se(3)	2.583(7)	Se(4)	2.642(6)
Se(4)	2.635(6)	Se(5)	2.546(7)
Se(6)	2.534(6)	Se(6)	2.747(7)
Se(7)	2.523(6)	Se(8)	2.535(7)
Se(9)	2.797(6)	Se(9)	2.509(7)
Ti(1)-Se(mean)	2.59(10)	Ti(2)-Se(mean)	2.59(8)
Ti(1)-Ti(2)	3.365(8)	Na(1)-Se(mean)	2.93(1)
Se(2)-Se(3)	2.370(5)	K(1)-Se(mean)	3.36(11)
Se(4)-Se(5)	2.358(5)	K(2)-Se(mean)	3.75(13)
Se(6)-Se(7)	2.349(5)	K(3)-Se(mean)	3.49(6)
Se(8)-Se(9)	2.353(5)		
Se(1)-Ti(1)-Se(2)	90.73(19)	Se(1)-Ti(2)-Se(2)	89.3(2)
Se(1)-Ti(1)-Se(3)	101.4(2)	Se(1)-Ti(2)-Se(4)	101.3(2)
Se(1)-Ti(1)-Se(4)	100.8(2)	Se(1)-Ti(2)-Se(5)	97.3(2)
Se(1)-Ti(1)-Se(6)	99.9(2)	Se(1)-Ti(2)-Se(6)	167.7(3)
Se(1)-Ti(1)-Se(9)	172.0(3)	Se(1)-Ti(2)-Se(8)	98.5(2)
Se(2)-Ti(1)-Se(3)	54.98(17)	Se(2)-Ti(2)-Se(4)	138.8(3)
Se(2)-Ti(1)-Se(4)	130.0(2)	Se(2)-Ti(2)-Se(6)	82.25(18)
Se(2)-Ti(1)-Se(9)	84.02(18)	Se(4)-Ti(2)-Se(6)	79.71(18)
Se(3)-Ti(1)-Se(4)	74.99(18)	Se(5)-Ti(2)-Se(2)	85.3(2)
Se(3)-Ti(1)-Se(9)	70.62(17)	Se(5)-Ti(2)-Se(4)	54.04(16)
Se(4)-Ti(1)-Se(9)	78.27(17)	Se(5)-Ti(2)-Se(6)	73.11(18)
Se(6)-Ti(1)-Se(2)	142.1(3)	Se(8)-Ti(2)-Se(2)	78.08(19)
Se(6)-Ti(1)-Se(3)	152.3(3)	Se(8)-Ti(2)-Se(4)	137.6(3)
Se(6)-Ti(1)-Se(4)	83.85(19)	Se(8)-Ti(2)-Se(5)	156.9(3)
Se(6)-Ti(1)-Se(9)	87.95(19)	Se(8)-Ti(2)-Se(6)	88.6(2)
Se(7)-Ti(1)-Se(1)	98.2(2)	Se(9)-Ti(2)-Se(1)	102.8(2)
Se(7)-Ti(1)-Se(2)	87.3(2)	Se(9)-Ti(2)-Se(2)	133.2(3)
Se(7)-Ti(1)-Se(3)	137.1(3)	Se(9)-Ti(2)-Se(4)	83.47(19)
Se(7)-Ti(1)-Se(4)	137.4(3)	Se(9)-Ti(2)-Se(5)	135.9(3)
Se(7)-Ti(1)-Se(6)	55.35(17)	Se(9)-Ti(2)-Se(6)	89.5(2)
Se(7)-Ti(1)-Se(9)	87.57(19)	Se(9)-Ti(2)-Se(8)	55.60(17)

Experimental Section

Synthesis. All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab

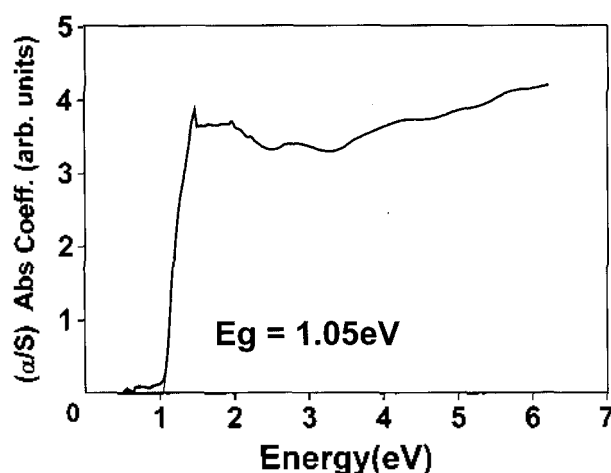


Figure 3. The optical absorption spectrum of $\text{K}_5\text{NaTi}_6\text{Se}_{27}$.

Table 2. Crystal data and structure refinement for $K_5NaTi_6Se_{27}$

Empirical formula	$K_5NaTi_6Se_{27}$	
Formula weight	2637.81	
Temperature	293(2) K	
Wavelength	0.71073	
Crystal system	Trigonal	
Space group	P31c	
Unit cell dimensions	a = 13.2000(19) Å	$\alpha = 90^\circ$
	b = 13.2000(19) Å	$\beta = 90^\circ$
	c = 13.925(3) Å	$\gamma = 120^\circ$
Volume	2101.2(6) Å ³	
Z	2	
Density (calculated)	4.169 Mg/m ³	
Absorption coefficient	24.985 mm ⁻¹	
F(000)	2312	
Crystal size	0.15×0.07×0.07 mm ³	
Theta range for data collection	1.78 to 24.98 °	
Index ranges	-15 ≤ h ≤ 1, -14 ≤ k ≤ 14, -16 ≤ l ≤ 13	
Reflections collected	4950	
Independent reflections	1963 [R(int) = 0.0972]	
Observed reflections	1603 with I > 2σ(I)	
Absorption correction	empirical	
Transmission range	0.248-1.0	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1963 / 1 / 120	
Goodness-of-fit on F ²	1.117	
Final R indices [I > 2σ(I)]	R1 = 0.0666, wR2 = 0.1456	
R indices (all data)	R1 = 0.0848, wR2 = 0.1518	
Absolute structure parameter	0.18(6)	
Extinction coefficient	0.00032(7)	
Largest diff. peak and hole	2.067 and -1.262 eÅ ⁻³	

glovebox. Chemicals in this work were used as obtained: (i) Ti powder, 99.5 % purity, -325 mesh, Cerac Inc. Milwaukee, WI, (ii) Se powder, 99.5% purity, -100 mesh; K metal, 98% purity; Na metal, 99% purity, Aldrich Chemical Co., Inc., Milwaukee, WI, (iii) DMF, analytical reagent, Dong Yang Chemicals Co., Seoul. For the preparation of Na_2Se and K_2Se we used a modified literature procedure.⁹

$K_5NaTi_6Se_{27}$. Ti (0.125 g, 1.5 mmol), Na_2Se (0.125 g, 1.0 mmol), K_2Se (0.157 g, 1.0 mmol), and Se (0.632 g, 8.0 mmol) were measured and roughly mixed with a spatula in a glass vial. The mixture was transferred to Pyrex tube and then the reaction tube was flame-sealed under vacuum ($\sim 10^{-3}$ Torr). The tube was placed in a temperature programmable furnace and heated to 400 °C with a rate of 10 °C/hr. It was isothermed at 400 °C for 72 hours, followed by cooling to 150 °C at a rate of 2 °C/hr, then to 50 °C in 2 hr. Black needle crystals were obtained by removing excess K_2Se_x/Na_2Se_x with degassed DMF under a N_2 atmosphere. It was washed with DMF repeatedly until the washings were colorless and then with ethanol and ether. EDS analysis on a black needle single crystals, using scanning electron microscope, confirms the existence of K, Na, Ti, Se elements. The homogeneity of $K_5NaTi_6Se_{27}$ was confirmed by comparing the observed and calculated X-ray powder diffraction patterns.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $K_5NaTi_6Se_{27}$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Ti(1)	3327(5)	9882(5)	3970(4)	13(1)
Ti(2)	3376(5)	9869(5)	6563(4)	18(1)
Se(1)	3439(3)	8580(3)	5244(2)	16(1)
Se(2)	3311(3)	1250(3)	5256(2)	20(1)
Se(3)	5093(3)	1890(3)	4420(3)	32(1)
Se(4)	4978(3)	5127(3)	7812(2)	20(1)
Se(5)	5763(3)	4438(3)	6629(2)	26(1)
Se(6)	2021(3)	8349(3)	2760(2)	17(1)
Se(7)	1132(3)	8963(3)	3902(2)	22(1)
Se(8)	1211(3)	9196(3)	6495(2)	25(1)
Se(9)	1876(3)	8417(3)	7697(2)	21(1)
K(1)	3332(7)	3752(7)	5282(8)	49(3)
K(2)	3333	6667	7057(11)	36(4)
K(3)	3333	6667	3462(10)	33(3)
Na(1)	10000	10000	7789(18)	25(5)

The d_{hkl} spacings observed for the bulk materials were compared, and found to be in good agreement with the d_{hkl} spacings calculated from the single crystal data using POWD10¹⁰.

Crystallographic Study. The X-ray single crystal data were collected at room temperature on a Siemens P4 four circle diffractometer with graphite monochromated Mo-K α radiation using the ω -2 θ scan mode. The stability of the crystal was monitored by measuring three standard reflections periodically (every 97 reflections) during the course of data collection. No crystal decay was observed. An empirical absorption correction based on 6 ψ scans was applied to the data. The structure was solved by direct methods using SHELXTL¹¹ and refined by full-matrix least square techniques provided in the SHELXTL package of programs. All calculations were performed on a Pentium PC. The crystallographic data and detailed information of structure solution and refinement are listed in Table 2. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 3.

UV/Vis/Near-IR Spectroscopy. Optical band gap measurement were made at room temperature with a Shimadzu UV-3101PC UV-Vis-NIR Scanning Spectrophotometer equipped with ISR-3100 intergrating sphere and controlled by a personal computer. BaSO₄ powder was used as reference at all energies (100% reflectance). Reflectance data were collected from 2600 nm to 200 nm at room temperature and then the digitized spectra were processed using the Origin5.0 software program. Absorption data were calculated from the reflectance data using the Kubelka-Munk function¹².

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crystal data collection.

Supplementary Material Available. Tables of anisotropic thermal parameters of all non-hydrogen atoms, calculated and observed X-ray powder diffraction patterns, and a listing of calculated and observed ($10F_o/F_c$) structure factors. The supporting materials will be given upon your request to the correspondence author.

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