研究简报

# 系列新铌酸盐 $A_6^{n+}[B_x^{m+}Nb_{12-x}]Nb_4O_{42}$ 的合成及粉晶 X 射线衍射分析

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## Syntheses and X-ray Powder Diffraction Analyses of a New Family of Niobate with Formula $A_6^{n+}[B_x^{m+}Nb_{12-x}]Nb_4O_{42}$

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A new series of niobates $A_6^{n+}[B_x^{m+}Nb_{12-x}]Nb_4O_{42}$ (A = K, Ba; B = Ni, Cr, Fe, Ti and Zr) has been synthesized by solid state reaction and the flux method. The morphology, optical properties and chemical stability of the new compounds were studied. The composition of the compounds were determined by chemical analyses and electron probe X-ray microanalysis (EPMA). The results of X-ray powder diffraction (XRPD) analyses confirmed that the compounds crystallized in the hexagonal system with space group $P6_3/mcm$ (193), and which are isostructure with $K_6CrNb_{15}O_{42}$. X-ray powder diffraction lines for these compounds were well indexed.

**Keywords:** niobate chemical synthesis X-ray powder diffraction hexagonal compound

## 0 Introduction

Niobates have many kinds of structures. These are perovskite type $ABO_3$ ($KNbO_3$), tungsten bronze type $ANb_2O_6$ ($Ba_2NaNb_5O_{15}$), chain and lamellar types[1-11]. Since the new compound $K_6CrNb_{15}O_{42}$ with a kind of tunnel structure in the potassium niobate system was found in our laboratory for the first time[12], we have synthesized a series of compounds with the same structure, for example, $K_6FeNb_{15}O_{42}$, $K_6Ni_{0.67}Nb_{15.33}O_{42}$, $Ba_6Cr_4Nb_{12}O_{42}$ and $Ba_6Ni_{2.67}Nb_{13.33}O_{42}$ etc. These compounds may be described by the general chemical formula $A_6^{n+}[B_x^{m+}Nb_{12-x}]Nb_4O_{42}$ [$A = K^+$, $Ba^{2+}$; $B = Ni^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Ti^{4+}$, $Zr^{4+}$; $x = (6n-4)/(5-m)$, $0.67 \leqslant x \leqslant 7$; $n+$ and $m+$ are the valence state of A and B]. A is alkali or alkaline earth metal; B is a transition metal. In this paper, we report the synthesis and data of XRPD of the series compounds.

## 1 Experimental

### 1.1 Synthesis

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The samples that was used for XRPD analysis of the series of $A^{n+}[B_x^{m+}Nb_{12-x}]Nb_4O_{42}$ compounds were prepared by solid state-reaction. The starting materials using analytical grade $Nb_2O_5$ $K_2CO_3$, $BaCO_3$, $ZrO_2$, $TiO_2$, NiO, $Fe_2O_3$ and $Cr_2O_3$, were weighed in stoichiometric proportions and thoroughly mixed in alcohol. The mixture was dried and then pressed into pellets under 200kg · $cm^{-2}$ pressure. The polycrystalline samples of the compounds $K_6[B_x^{m+}Nb_{12-x}]Nb_{24}O_{42}$ (B = Ni, Cr, Fe, Ti, Zr) were prepared by firing the pellets of mixtures in a platinum crucible at 1100 ~ 1185℃ for 24h in air for B = Ni, Ti, Zr, Fe and in protective atmosphere of Ar for B = Cr, and then cooled to room temperature. The samples of $Ba_6[B_x^{m+}Nb_{12-x}]Nb_4O_{12}$ were synthesized by firing the pellets of mixture in platinum crucible at 1350 ~ 1420℃ for 48h in air for B = Ni and in protective atmospere of Ar for B = Cr, Ti and then cooled to room temperature.

The single crystal of the compounds were prepared by the flux method at higher temperature. The single crystal of the well crystallized compound were selected for EPMA or X-ray analysis with a four-circle diffractonmeter.

The morphology and optical properties were studied by *stereomicroscope and polarization microscope*.

## 1.2 Chemical Analyses

Barium, zirconium and niobium of the compounds were analyzed by gravimetric method. Potassium, iron, nickel and chromium were determined by atomic absorption spectrophotometry (AAS) on varian-spectra-30A atomic absorption spectrophotometer. Titanium was analyzed by $H_2O_2$ spectrophotometric method. The contents of the elements in the single crystal were determined by EPMA on JCXA-733 electron probe X-ray microanalyzer.

The solubilities of the compounds in some solvents (HCl, $H_2SO_4$, $HNO_3$ and water etc) were studied.

## 1.3 X-ray Diffraction Analysis

The new compounds samples were prepared for XRPD analyses by manually grinding the bulk material to pestle with an agate mortar, followed by sieving to −325mesh( < 45μm) particle size. The powder diffraction measurements were performed with a Rigaku D/MAX-RB diffractometer. The experimental conditions were: Cu target, 40kV, 120mA, 0.15mm receiving slit, and curved graphite diffracted monochromatic beam(Cu $K\alpha_1$ = 1.5405981Å).

The powder diffraction data were collected by step scan between 5°and 70° in 2 with a step size of 0.01° and a count time of 5s step. The diffractometer was calibrated using a Si powder standard(SRM 640a $a$ = 5.430825Å). The ambient temperature was maintained at 20 ± 1℃. The Rigaku software was used for $K\alpha_2$ peak stripping and the "full width at half maximum middle point" method for determining peak intensities and position.

The resulting peak position was corrected by means of an internal standand(SRM 640a). The patterns were indexed using a PC-version of TREOR-4 program.

**Table 1 Results of Quantitative Analysis of Compounds**

| compounds | $K_6FeNb_{15}O_{42}$ | $K_6Ni_{0.67}Nb_{13.33}O_{42}$ | $K_6Ti_2Nb_{14}O_{42}$ | $K_6Zr_2Nb_{14}O_{42}$ | $Ba_6Cr_4Nb_{12}O_{42}$ | $Ba_6Ni_{2.67}Nb_{13.33}O_{42}$ | $Ba_6Ti_7Nb_9O_{42}$ |
|---|---|---|---|---|---|---|---|
| mole ratio | K: Fe: Nb | K: Ni: Nb | K: Ti: Nb | K: Zr: Nb | Ba: Cr: Nb | Ba: Ni: Nb | Ba: Ti: Nb |
| chemical analyses | 5.98: 1.00: 15.03 | 5.92: 0.65: 15.40 | 5.96: 1.99: 14.02 | 5.98: 2.00: 14.06 | 6.02: 3.98: 12.01 | 6.08: 2.68: 13.35 | 5.98: 7.00: 9.03 |
| EPMA | 6.02: 1.00: 15.01 | 6.04: 0.70: 15.35 | 5.91: 1.99: 14.05 | 6.04: 2.00: 13.98 | 5.99: 3.93: 12.09 | 6.06: 2.68: 13.36 | 6.04: 7.00: 8.98 |
| theoretical composition | 6.00: 1.00: 15.00 | 6.00: 0.67: 15.33 | 6.00: 2.00: 14.00 | 6.00: 2.00: 14.00 | 6.00: 4.00: 12.00 | 6.00: 2.67: 13.33 | 6.00: 7.00: 9.00 |

**Table 2 Cell Parameters of some Compounds**

| compound | $a$/Å | $c$/Å | compound | $a$/Å | $c$/Å |
|---|---|---|---|---|---|
| $K_6CrNb_{15}O_{42}$ | 9.126(3) | 12.068(3) | $K_6Zr_2Nb_{14}O_{42}$ | 9.1607(9) | 12.1336(8) |
| $K_6FeNb_{15}O_{42}$ | 9.1320(3) | 12.0689(3) | $Ba_6Cr_4Nb_{12}O_{42}$ | 9.030(1) | 12.001(5) |
| $K_6Ni_{0.67}Nb_{13.33}O_{42}$ | 9.1341(4) | 12.090(6) | $Ba_6Ni_{2.67}Nb_{13.33}O_{42}$ | 9.040(3) | 12.003(5) |
| $K_6Ti_2Nb_{14}O_{42}$ | 9.1106(5) | 12.013(6) | $Ba_6Ti_7Nb_9O_{42}$ | 9.0527(3) | 11.701(5) |

**Table 3　Indexation of the X-ray Diffraction Patterns of the Series Compounds**

| $K_6CrNb_{13}O_{42}$ | | $K_6FeNb_{13}O_{42}$ | | $K_6Ni_{0.67}Nb_{15.33}O_{42}$ | | $K_6Ti_2Nb_{14}O_{42}$ | | $K_6Zr_2Nb_{14}O_{42}$ | | $Ba_6Cr_4Nb_{12}O_{42}$ | | $Ba_6Ni_{2.67}Nb_{13.33}O_{42}$ | | $Ba_6Ti_6Nb_6O_{42}$ | | *hkl* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *d* | $I/I_0$ | *d* | $I/I_0$ | *d* | $I/I_0$ | *d* | $I/I_0$ | *d* | $I/I_0$ | *d* | $I/I_0$ | *d* | $I/I_0$ | *d* | $I/I_0$ | |
| 7.92 | 6 | 7.9288 | 17 | 7.9217 | 19 | 7.907 | 18 | 7.9434 | 12 | 7.893 | 3 | 7.897 | 1 | | | 100 |
| 6.05 | 100 | 6.0332 | 60 | 6.0455 | 98 | 6.021 | 60 | 6.0748 | 76 | 6.005 | 3 | 5.956 | 2 | 5.8895 | 2 | 002 |
| | | | | | | | | | | 4.756 | 2 | 4.761 | 2 | 4.7112 | 1 | 102 |
| | | | | | | | | | | 4.543 | 4 | 4.576 | 8 | 4.5277 | 8 | 110 |
| 4.271 | 12 | 4.2730 | 29 | 4.2780 | 34 | 4.261 | 33 | 4.2897 | 32 | 4.250 | 1 | 4.261 | 1 | 4.2288 | 8 | 111 |
| 3.955 | 16 | 3.9552 | 26 | 3.9552 | 47 | 3.948 | 37 | 3.9694 | 42 | 3.934 | 4 | | | 3.9242 | 5 | 200 |
| 3.645 | 13 | 3.6420 | 26 | 3.6464 | 32 | 3.632 | 29 | 3.6585 | 32 | 3.615 | 50 | 3.627 | 43 | 3.5913 | 53 | 112 |
| 3.311 | 19 | 3.3080 | 42 | 3.3104 | 38 | 3.300 | 41 | 3.3215 | 35 | 3.287 | 85 | 3.297 | 54 | 3.2640 | 74 | 202 |
| 3.020 | 68 | 3.0184 | 100 | 3.0234 | 100 | 3.008 | 100 | 3.0336 | 100 | 2.993 | 100 | 2.995 | 100 | 2.9674 | 100 | 113 |
| 2.991 | 18 | 2.9897 | 49 | 2.9897 | 44 | 2.983 | 61 | 3.0007 | 41 | | | | | | | 210 |
| 2.901 | 19 | 2.9024 | 50 | 2.9033 | 52 | 2.895 | 70 | 2.9118 | 47 | 2.886 | 87 | 2.902 | 58 | 2.8712 | 62 | 211 |
| 2.820 | 20 | 2.8168 | 21 | | | 2.808 | 19 | 2.8352 | 28 | 2.789 | 25 | 2.782 | 19 | 2.7584 | 17 | 104 |
| 2.679 | 15 | 2.6782 | 15 | 2.6805 | 14 | 2.671 | 13 | 2.6893 | 15 | 2.662 | 6 | 2.674 | 8 | 2.6474 | 8 | 212 |
| 2.636 | 8 | 2.6310 | 19 | | | 2.629 | 34 | 2.6453 | 22 | 2.622 | 20 | 2.639 | 30 | 2.6137 | 24 | 300 |
| 2.518 | 15 | 2.5156 | 19 | 2.5211 | 23 | 2.509 | 15 | 2.5309 | 21 | 2.491 | 3 | 2.494 | 1 | | | 114 |
| 2.416 | 4 | 2.4156 | 8 | 2.4174 | 22 | 2.410 | 17 | 2.4239 | 10 | | | | | | | 302 |
| 2.398 | 9 | 2.3994 | 15 | 2.4014 | 11 | 2.391 | 13 | 2.4107 | 15 | 2.375 | 20 | 2.379 | 10 | 2.3552 | 7 | 204 |
| 2.283 | 2 | 2.2828 | 4 | 2.2839 | 17 | 2.278 | 4 | 2.2913 | 7 | | | | | | | 220 |
| 2.241 | 3 | 2.2446 | 5 | 2.2419 | 5 | 2.238 | 9 | 2.2517 | 7 | 2.231 | 10 | 2.247 | 8 | 2.2218 | 12 | 221 |
| | | | | | | | | | | | | | | 2.1746 | 5 | 310 |
| 2.157 | 3 | 2.1587 | 5 | 2.1587 | 11 | 2.153 | 8 | 2.1658 | 7 | 2.147 | 40 | 2.161 | 20 | 2.1382 | 33 | 311 |
| 2.133 | 2 | | | | | | | | | 2.111 | 4 | 2.111 | 7 | 2.0896 | 3 | 222 |
| | | | | | | | | | | 2.091 | 1 | 2.085 | 5 | | | 214 |
| | | | | | | | | | | 2.049 | 3 | 2.062 | 5 | 2.0408 | 15 | 312 |
| 2.012 | 36 | 2.0107 | 14 | 2.0132 | 25 | 2.004 | 15 | 2.0214 | 21 | 1.998 | 20 | 1.981 | 20 | 1.9665 | 12 | 006 |
| | | 1.9848 | 6 | | | | | 1.9924 | 15 | | | | | | | 223 |
| 1.977 | 8 | 1.9779 | 28 | 1.9783 | 24 | 1.973 | 23 | 1.9841 | 20 | 1.968 | 25 | | | 1.9569 | 14 | 400 |
| 1.949 | 12 | 1.9497 | 9 | 1.9537 | 15 | 1.941 | 9 | 1.9590 | 12 | | | | | | | 106 |
| | | | | | | | | | | 1.911 | 10 | 1.923 | 8 | 1.9031 | 8 | 313 |
| 1.878 | 3 | 1.8780 | 4 | 1.8798 | 5 | 1.872 | 5 | 1.8861 | 6 | 1.861 | 10 | | | 1.8461 | 9 | 215 |
| 1.840 | 16 | 1.8390 | 16 | 1.8440 | 18 | 1.833 | 21 | 1.8494 | 16 | 1.821 | 20 | 1.829 | 17 | 1.824 | 12 | 116 |
| 1.820 | 9 | 1.8206 | 13 | 1.8223 | 15 | 1.815 | 12 | 1.8279 | 16 | 1.808 | 10 | 1.797 | 1 | | | 224 |
| | | | | | | 1.810 | 12 | | | | | | | | | 320 |
| 1.793 | 5 | 1.7945 | 8 | 1.7961 | 10 | 1.790 | 9 | 1.7992 | 9 | 1.783 | 5 | | | 1.7781 | 5 | 321 |
| 1.774 | 7 | 1.7743 | 12 | 1.7756 | 32 | 1.768 | 7 | 1.7815 | 25 | 1.761 | 20 | 1.767 | 17 | 1.7493 | 17 | 314 |
| 1.736 | 3 | 1.7392 | 9 | 1.7385 | 8 | 1.734 | 6 | 1.7438 | 8 | 1.728 | 20 | 1.737 | 11 | 1.7197 | 15 | 322 |
| 1.725 | 8 | 1.7257 | 21 | 1.7263 | 22 | 1.722 | 16 | 1.7312 | 20 | 1.715 | 18 | 1.728 | 10 | 1.7110 | 11 | 410 |
| 1.668 | 2 | | | | | | | | | 1.651 | 20 | 1.666 | 11 | 1.6421 | 13 | 216 |
| 1.658 | 6 | 1.6593 | 16 | | | 1.655 | 14 | 1.6652 | 19 | 1.644 | 32 | 1.649 | 17 | 1.6375 | 8 | 412 |
| 1.653 | 20 | 1.6538 | 43 | 1.6551 | 37 | 1.649 | 42 | 1.6602 | 40 | 1.644 | 32 | | | 1.6321 | 19 | 404 |
| 1.623 | 2 | | | | | | | | | 1.611 | 7 | 1.614 | 7 | | | 315 |
| 1.613 | 7 | 1.6120 | 17 | 1.6156 | 8 | 1.606 | 12 | 1.6217 | 14 | | | | | | | 117 |
| | | | | | | | | | | 1.573 | 5 | | | | | 413 |
| 1.581 | 2 | | | 1.5823 | 4 | | | | | | | 1.584 | 5 | 1.5679 | 9 | 500 |
| | | | | | | | | | | 1.544 | 4 | 1.551 | 4 | 1.5354 | 3 | 324 |
| | | | | | | | | | | 1.520 | 10 | 1.531 | 5 | 1.5154 | 14 | 502 |
| 1.509 | 8 | 1.5094 | 13 | 1.5105 | 16 | 1.503 | 10 | 1.5157 | 19 | 1.502 | 11 | 1.498 | 12 | | | 226 |
| | | | | | | | | | | 1.493 | 12 | 1.493 | 12 | 1.4964 | 8 | 331 |
| 1.493 | 11 | | | 1.4953 | 16 | 1.491 | 10 | 1.4993 | 15 | | | | | 1.4818 | 5 | 420 |
| | | | | | | | | | | | | | | 1.4702 | 6 | 421 |
| 1.493 | 11 | 1.4932 | 14 | 1.4953 | 16 | | | | | | | 1.485 | 3 | 1.4642 | 10 | 217 |
| | | | | | | | | 1.4900 | 5 | 1.478 | 15 | 1.479 | 11 | | | 108 |

Table 4 Cell Volume and the Sum of the Ionic Radii of the $A^{n+}$ Cations and the Cations in the Hexagonal Ring Unit

| compound | $Ba_6Ti_7Nb_9O_{42}$ | $Ba_6Cr_4Nb_{12}O_{42}$ | $Ba_6Ni_{2.67}Nb_{13.33}O_{42}$ | $K_6Ti_{12}Nb_{14}O_{42}$ | $K_6CrNb_{15}O_{42}$ | $K_6FeNb_{15}O_{42}$ | $K_6Ni_{0.67}Nb_{15.33}O_{42}$ | $K_6Zr_2Nb_{14}O_{42}$ |
|---|---|---|---|---|---|---|---|---|
| $V/Å^3$ | 836.8 | 847.5 | 849 5 | 863.5 | 870.4 | 871.5 | 873 6 | 881.8 |
| $\Sigma r/Å$ | 18 51 | 18.64 | 18.64 | 18.66 | 18.70 | 18.73 | 18.76 | 18.88 |

## 2 Result and Discussion

### 2.1 Composition and Chemical Stability

Stereomicroscope analysis and polarization microscope analysis showed that the single crystal of the compounds is transparent with hexagon-thin schistose shape. They are uniaxial crystal with negative sign.

The compounds can be dissolved in the hot mixture of $(NH_4)_2SO_4$ and concentrated $H_2SO_4$ or in melt NaOH or KOH. Results of quantitative analyses of the compounds are showed in Table 1. The results of chemical analysis are in good agreement with the theoretical elemental compositions of compounds, and were confirmed by EPMA.

### 2.2 XRD Analysis

The crystal structures of the compounds were determined using single crystal X-ray diffraction data. The results have been reported[11], The compounds crystallized in the hexagonal system with space group $P6_3/mcm$(193) and $z = 1$.

The values of the cell parameter in the $P6_3/mcm$ (193) as obtained after a least-square refinements are given in Table 2. The XRPD data of the compounds $A_6^{n+}[B_x^{m+}Nb_{12-x}]Nb_4O_{42}$(A = K, Ba, B = Ni, Cr, Fe, Ti and Zr[13]) are shown in Table 3. It is found, by comparing the XRPD data of these compounds, that these patterns are very similar. For the compounds of A = K, the peak heights and positions of the patterns show very slightly difference. For the compounds of A = Ba. The $d$-values of the patterns are slightly smaller than that of the compounds of A = K. The (002) peak height of the compounds of A = Ba is obviously lower than that of the compounds of A = K. It is clear that the composition of the compounds has important impact on these changes. All of the peaks of XRPD patterns of these compounds were well indexed according to the systematic absences of the $P6_3/mcm$ space group obtained by the result of X-ray single crystal diffraction[12]. Those facts suggest that these compounds are isostructural with $K_6CrNb_{15}O_{42}$.

These compounds formula may be described by $A_n^{+}[B_x^{m+}Nb_{12-x}]Nb_4O_{42}$, where $A^{n+} = K^+$, $Ba^{2+}$ and $B^{m+} = Ni^{2+}$, $Fe^{3+}$, $Cr^{3+}$, $Ti^{4+}$, $Zr^{4+}$ etc. Generally, according to the following formula: $x = (6n-4)/(5-n)$, $x = 2/3$, 1 and 2 for $n = 1$, $m = 2$, 3 and 4; $n = 2$, $m = 2$ and 3, so $x = 8/3$ and 4. However, the mole ratio of the $B_x^{m+}$ ions in the structure is with $x = 7$ ($< 8$ calculated) if $A_n^{+} = Ba^{2+}$, $B^{m+} = Ti^{4+}$, $Zr^{4+}$ and $Sn^{4+}$ here, The mixed valence of niobium Nb (V)/Nb (IV) exists in the structure of $Ba_6[Ti_7Nb_5]Nb_4O_{42}$. $A^{n+}$ ions are located at tunnels with 12 O-neighbors, the atoms of Nb and B are 6 coordinated.

The unit cell volume of these compounds depends on the sum of the ionic radii of the $A^{n+}$ cations and the cations in the hexagonal ring unit (given in Table 4).

## 3 Conclusion

The series compounds $A_6^{n+}[B_x^{m+}Nb_{12-x}]Nb_4O_{42}$ were synthesized. Their lattice parameters were gained and X-ray patterns have been well indexed. The series compounds are with the $K_6CrNb_{15}O_{42}$ type structure.

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