In Search of Inorganic Nonlinear Optical Materials for Second Harmonic Generation[1]

J. Gopalakrishnan,[2] K. Ramesha, K. Kasthuri Rangan, and Sonal Pandey

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

In a search for inorganic oxide materials showing second-order nonlinear optical (NLO) susceptibility, we investigated several borates, silicates, and a phosphate containing *trans*-connected MO_6 octahedral chains or MO_5 square pyramids, where $M = d^0$: Ti(IV), Nb(V), or Ta(V). Our investigations identified two new NLO structures: batisite, $Na_2Ba(TiO)_2Si_4O_{12}$, containing *trans*-connected TiO_6 octahedral chains, and fresnoite, $Ba_2TiOSi_2O_7$, containing square-pyramidal TiO_5. Investigation of two other materials containing square-pyramidal TiO_5, viz., $Cs_2TiOP_2O_7$ and $Na_4Ti_2Si_8O_{22} \cdot 4H_2O$, revealed that isolated TiO_5 square pyramids alone do not cause a second harmonic generation (SHG) response; rather, the orientation of TiO_5 units to produce −Ti−O−Ti−O− chains with alternating long and short Ti−O distances in the fresnoite structure is most likely the origin of a strong SHG response in fresnoite. © 1999 Academic Press

INTRODUCTION

There is great interest at present in the design and development of new nonlinear optical (NLO) materials (1, 2) that exhibit efficient second harmonic generation (SHG) especially in the blue region (3). Well-known inorganics that show NLO-SHG effects are KH_2PO_4 (KDP), $LiNbO_3$, $KTiOPO_4$ (KTP), and borates such as β-BaB_2O_4, LiB_3O_5, and $Sr_2Be_2B_2O_7$ (4). Design of new NLO materials entails a fundamental understanding of the structure and bonding features that promote efficient SHG response. The necessary but not always sufficient crystallographic requirement for NLO-SHG effects is a noncentrosymmetric (NCS) structure. Structure–property relationships among NCS oxide materials have recently been reviewed in the literature (5).

From a crystal-chemistry viewpoint, two structural features seem to give rise to inorganic NLO materials. One is the presence of borate anions, $B_2O_5^{4-}$, $B_3O_6^{3-}$, and $B_3O_7^{5-}$,

containing polarizable conjugated π electrons and the other is the presence of d^0-transition metal–oxygen octahedra (MO_6) [$M =$ Ti(IV), Nb(V), Mo(VI), and W(VI)] which are continuously connected. It is known (6–8) that MO_6 octahedra of d^0 cations undergo a characteristic out-of-center distortion creating unequal M–O bond lengths. The origin of this distortion is a second-order Jahn–Teller (SOJT) effect (6), which mixes the cationic LUMO and anionic HOMO states, stabilizing a distorted MO_6 octahedron. The effect of this distortion is to give rise to a net charge polarization and a dipole moment to the MO_6 octahedron. When the distorted MO_6 octahedra are continuously connected in an unsymmetric manner so as to add up the polarization of the individual MO_6 octahedra, an NCS structure showing a large NLO response would result. In the NCS structures, the MO_6 could be directly linked among themselves without other anions as in $BaTiO_3$ and $LiNbO_3$ or linked through intervening rigid tetrahedral anionic groups as in $KTiOPO_4$ and $K_2(NbO)_2Si_4O_{12}$.

$K_2(NbO)_2Si_4O_{12}$ is a recent example of a NLO material that contains d^0-Nb(V) (9). The acentric (space group $P4bm$) structure[3] (Fig. 1) consists of *trans*-connected chains of NbO_6 octahedra running parallel to the tetragonal fourfold axis which are linked together by tetrahedral Si_4O_{12} quartet rings. The NbO_6 octahedra are distorted to produce alternating short (1.76, 1.78 Å) and long (2.32, 2.28 Å) Nb–O bonds in the chain. The orientation of the chains in the structure is such as to sum up the polarization of the individual NbO_6 octahedra giving rise to a strong SHG response to 1.06-μm Nd:YAG laser light.

In a search for new inorganic NLO materials, we have focused on the *trans*-connected d^0:MO_6 octahedral chains as the crucial structural feature and tried to identify other structures/materials that contain this feature as possible candidates for NLO-SHG response. The mineral batisite, $Na_2BaTi_2Si_4O_{14}$, has a structure (Fig. 2) (10) that is closely

---

[3]The structures are drawn from the crystallographic data given in the literature using DIAMOND software.
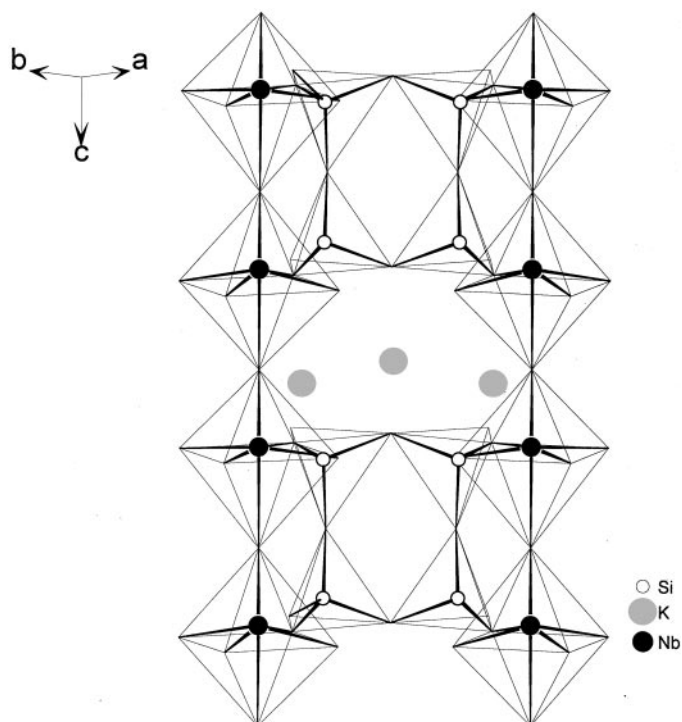
FIG. 1. Structure of $K_2(NbO)_2Si_4O_{12}$ showing octahedral NbO_6 chains.

FIG. 3. Structure of $CsNbOB_2O_5$ showing two adjacent NbO_6 octahedral chains where the direction of short and long Nb–O bonds are reversed.

related to that of $K_2(NbO)_2Si_4O_{12}$, containing d^0:TiO_6 octahedral chains; the bridging Si_4O_{12} groups, however, have a configuration different from that in $K_2(NbO)_2$ Si_4O_{12}. Similarly, borates of the formula $AMOB_2O_5$ ($M = Nb, Ta$) (11–14) also possess structures (Fig. 3) topologically related to the structure of $K_2(NbO)_2Si_4O_{12}$ where two B_2O_5 groups replace one Si_4O_{12} unit.
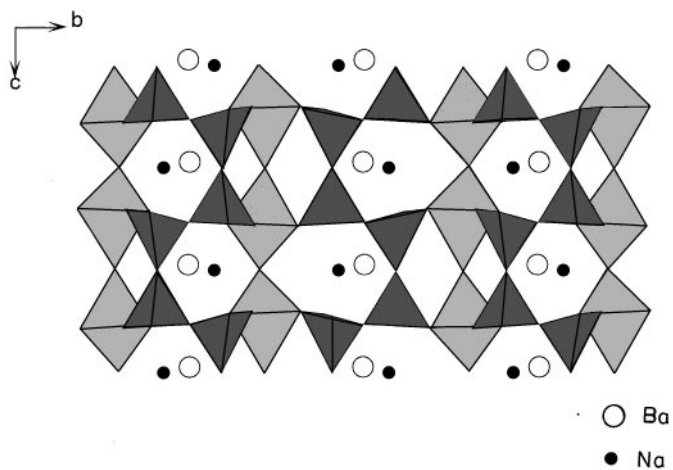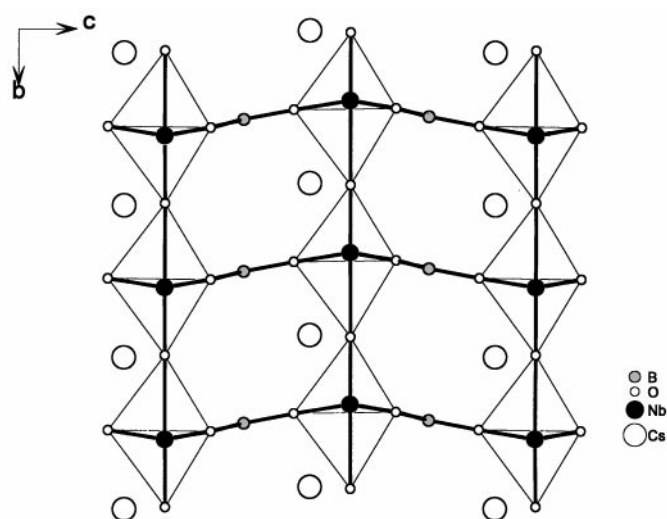
The mineral fresnoite, $Ba_2TiOSi_2O_7$, is another NCS structure (15) where TiO_5 square pyramids are connected by Si_2O_7 units (Fig. 4). Interestingly, the connectivity of NbO_6 octahedra/TiO_5 square pyramids and silicate tetrahedra in the (001) planes is identical in both structures (Fig. 5). We

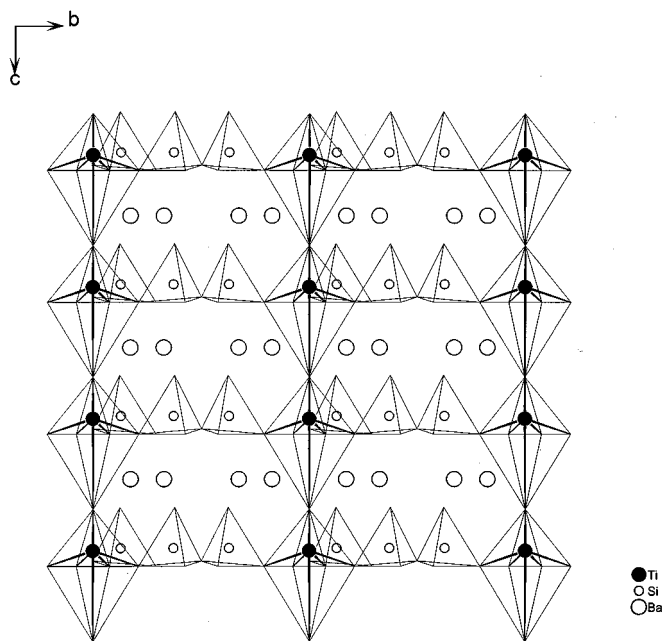**FIG. 2.** Structure of batisite, $Na_2Ba(TiO)_2Si_4O_{12}$, showing TiO_6 chains.

FIG. 4. Structure of fresnoite, $Ba_2TiOSi_2O_7$, showing the highly distorted TiO_6 octahedra forming short and unusually long Ti–O interactions along the c direction. Oxygens at the corners of the polyhedra are not shown.
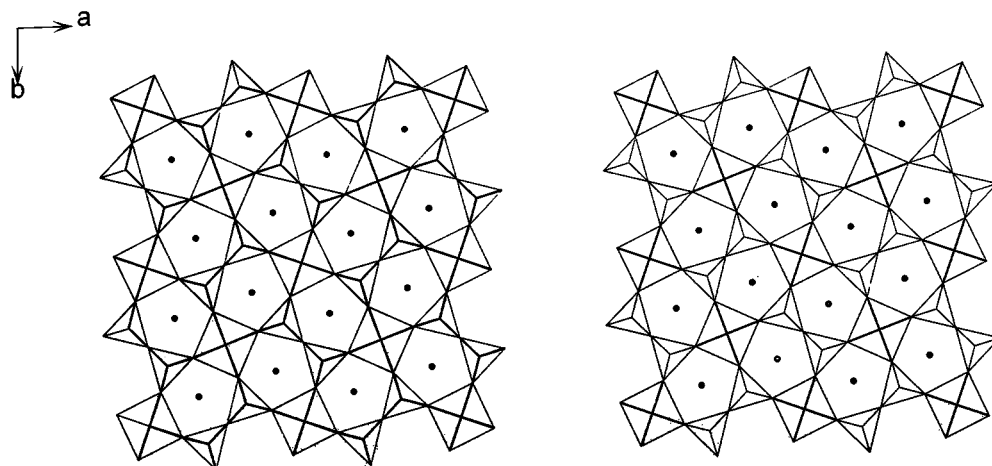
FIG. 5. (001) planes of $K_2(NbO)_2Si_4O_{12}$ (left) and $Ba_2TiOSi_2O_7$ (right).

could perceive the presence of *trans*-connected TiO_6 octahedral chains in the fresnoite structure, if we include the sixth oxygen at a longer distance (~ 3.5 Å) from the TiO_5 units in the adjacent (001) plane. There are two other NCS Ti(IV) oxides containing square-pyramidal TiO_5 units: $Cs_2TiOP_2O_5$ (16) (Fig. 6) and $Na_4Ti_2Si_8O_{22} \cdot 4H_2O$ (17) (Fig. 7). Considering that fresnoite is a potential NLO structure (18, 19), we believed that it is important to establish the role of square-pyramidal TiO_5 toward SHG properties.

In view of the foregoing, we prepared and examined several members of borates, silicates, and phosphates of the above-mentioned structure types containing NbO_6/TiO_6 octahedral chains as well as isolated TiO_5 square pyramids and examined their SHG response toward 1064-nm laser radiation. Our results, which are presented in this paper, reveal certain unique structure–property correlations, which we believe would be of value in the search and design of new inorganic NLO materials.
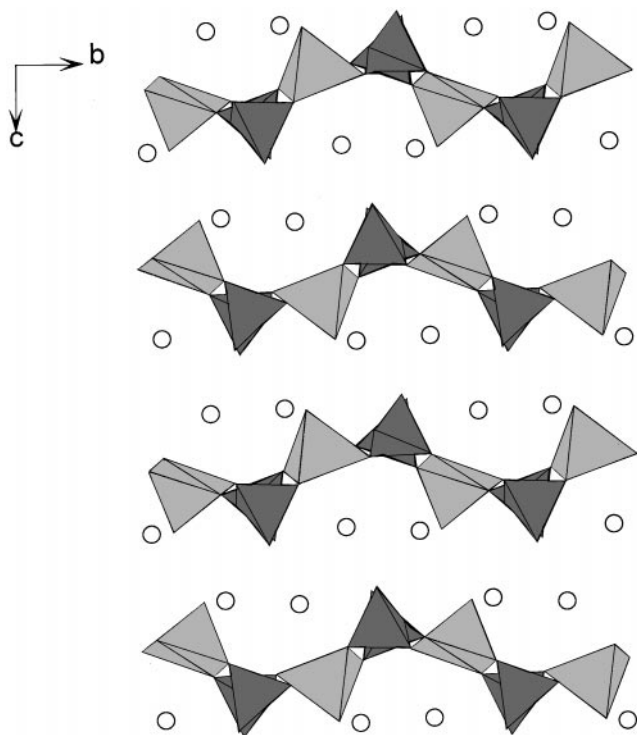

FIG. 6. Structure of $Cs_2TiOP_2O_7$. Hatched pyramids are TiO_5 units.
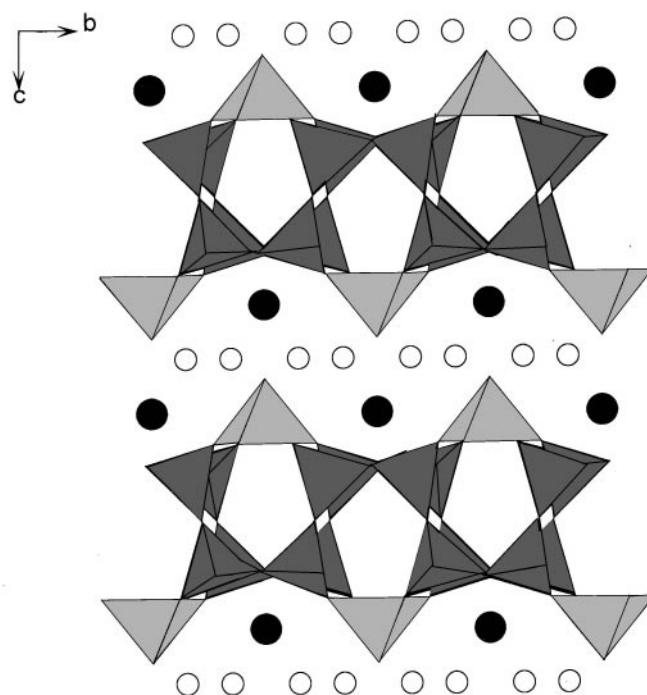

FIG. 7. Structure of $Na_4Ti_2Si_8O_{22} \cdot 4H_2O$. Hatched pyramids are TiO_5 units; filled circles, sodium atoms; and open circles, water molecules.

GOPALAKRISHNAN ET AL.

EXPERIMENTAL

Polycrystalline samples of $AMOB_2O_5$ (A = K, Rb, Cs; M = Nb, Ta, Sb), $K_2(NbO)_2Si_4O_{12}$, $Na_2BaTi_2Si_4O_{14}$, $Ba_2TiOSi_2O_7$, and $Cs_2TiOP_2O_7$ were prepared by ceramic methods by reacting the component oxides/carbonates at elevated temperatures in air. H_3BO_3, SiO_2, and $NH_4H_2PO_4$ were used as sources for boron, silicon, and phosphorus. For the preparation of antimony oxides, Sb_2O_3 was used as the starting material which oxidized *in situ* to Sb(V) in the product. $Na_4Ti_2Si_8O_{22} \cdot 4H_2O$ was prepared by the hydrothermal method as described by Roberts *et al.* (17). In all cases, formation of the desired products was ascertained by powder X-ray diffraction (JEOL JDX-8P powder diffractometer, CuKα radiation). Powder SHG intensity data were obtained using 1064-nm laser radiation with equipment similar to that described by Kurtz and Perry (20). Polycrystalline samples were sieved to uniform grain size (150–200 μm). A pulsed Q-switched Nd:YAG laser (Quanta Ray DCR-2A) with pulse duration of 8 ns was used to generate the second harmonic signal from the samples. The backscattered SHG light from the sample was collected and passed through a filter that transmits only 532-nm radiation. Measured SHG intensity of the samples was normalized with respect to that of α-quartz, which was taken as unity.

RESULTS AND DISCUSSION

In Table 1, we list the chemical compositions, structural details, and powder SHG intensity data for the various borates, silicates, and a phosphate containing d^0 cations.

Among the borates listed, several have already been reported in the literature (12–14) except for the antimony(V) borates. The structures of the niobium(V) and tantalum(V) borates (Fig. 3) contain *trans*-connected MO_6 octahedral chains extending along the b axis (13, 14). The individual chains are similar to the NbO_6 chains in the $K_2(NbO)_2Si_4O_{12}$ structure. However, adjacent chains in the borate structure are related by a 2_1 screw axis along the c direction, effectively canceling the dipole moment. Accordingly, the $-M-O-M-O-$ chains in the borate structure would not make a significant contribution to the second-order NLO susceptibility. The weak SHG intensity of $AMOB_2O_5$ borates most likely arises from the B_2O_5 groups (14). This inference is further supported by the weak SHG response of the Sb(V) derivative, $RbSbOB_2O_5$, which is isostructural with the corresponding niobium(V) borate (Table 1). Since Sb(V) is not a d^0 cation, we do not expect a polarization of Sb-O bonds in the SbO_6 octahedra and hence $-Sb-O-Sb-O-$ chains would not contribute to the NLO susceptibility. Since all the M(V) = Nb, Ta, Sb borates show approximately similar SHG responses, clearly it is the B_2O_5 groups and not the $-M-O-M-O-$ chains that cause the observed SHG response in these materials. We expected that if niobium(V) and antimony(V) could be ordered in adjacent chains in the borate structure, cancellation of the dipole moments of $-Nb-O-Nb-O-$ chains could be avoided, resulting in a more efficient SHG response. To test this possibility, we prepared $RbNb_{0.5}Sb_{0.5}OB_2O_5$. Its SHG intensity, however, is nearly the same as that of other borates (Table 1), indicating that niobium(V) and antimony(V) are most likely not ordered in this material.

TABLE 1
Chemical Composition, Crystal Structure, and SHG Data for Borates, Silicates, and Phosphates Containing d^0 Cations

Composition	Space group	Lattice parameters (Å)			SHG intensity[a]
		a	b	c	
$KNbOB_2O_5$[b]	—	7.234(6)	3.866(1)	9.197(6)	54
$RbNbOB_2O_5$[b]	$Pmn2_1$	7.401(3)	3.930(1)	9.481(3)	49
$CsNbOB_2O_5$	$Pmn2_1$	7.521(1)	3.978(6)	9.658(3)	48
$KTaOB_2O_5$[b]	—	7.269(6)	3.870(1)	9.304(6)	41
$RbTaOB_2O_5$[b]	—	7.409(4)	3.875(1)	9.490(1)	45
$CsTaOB_2O_5$	$Pmn2_1$	7.530(2)	3.886(5)	9.758(6)	47
$RbSbOB_2O_5$	—	7.242(9)	3.719(3)	9.483(5)	41
$RbNb_{0.5}Sb_{0.5}OB_2O_5$	—	7.387(4)	3.769(2)	9.624(6)	42
$K_2(NbO)_2Si_4O_{12}$	$P4bm$	8.740(4)	8.740(4)	8.136(5)	200
$Na_2Ba(TiO)_2Si_4O_{12}$	$Ima2$	10.405(5)	13.848(5)	8.087(6)	110
$Ba_2TiOSi_2O_7$	$P4bm$	8.521(3)	8.521(3)	5.215(5)	1250
$Cs_2TiOP_2O_7$	$P2_12_12_1$	7.278(2)	9.458(1)	13.600(3)	<5
$Na_4Ti_2Si_8O_{22} \cdot 4H_2O$	$P42_12$	7.368(2)	7.368(2)	10.705(2)	<5

[a] Normalized with respect to that of α-quartz which is taken as unity.
[b] The real unit cell is a supercell of approximately $8 \times b$ and $5 \times b$ for the K and Rb compounds.

We expected that the mineral batisite, $Na_2Ba(TiO)_2Si_4O_{12}$, containing $-Ti-O-Ti-O-$ chains (Fig. 2) that are similar to $-Nb-O-Nb-O-$ chains in $K_2(NbO)_2Si_4O_{12}$ (Fig. 1), would show a significant SHG response. Indeed, the SHG response of batisite is comparable to that of $K_2(NbO)_2Si_4O_{12}$ (Table 1), revealing that *trans*-connected chains of TiO_6 octahedra oriented appropriately in a NCS structure constitute a crucial structural feature for the realization of second-order NLO material. Significantly, the isotypic tantalum(V) analog of $K_2(NbO)_2Si_4O_{12}$ adopts a centrosymmetric structure (space group $P4/mbm$) where the distortion of TaO_6 octahedra is much less (21). As a rule, out-of-center distortion of MO_6 octahedra decreases as we move from $3d^0$ to $4d^0$ to $5d^0$ cations in a group (8). Accordingly, Ti(IV) and Nb(V) oxides are expected to show better NLO-SHG response than the corresponding Zr(IV) and Ta(V) analogs.

Our results on the three titanium(IV) oxides containing square-pyramidal TiO_5 units are most interesting (Table 1). Among the three titanium(IV) oxides, fresnoite, $Ba_2TiOSi_2O_7$, shows the highest SHG intensity (~ 1250 times that of α-quartz), the other two oxides, $Cs_2TiOP_2O_7$ (22) and $Na_4Ti_2Si_8O_{22} \cdot 4H_2O$, showing only a very weak SHG response. The result immediately reveals that square-pyramidal TiO_5 by itself does not produce an efficient SHG response because all three oxides contain TiO_5 units with more or less identical Ti–O bond lengths (four Ti–O $\simeq 2$ and one Ti–O $\simeq 1.65$–1.70 Å). The occurrence of a strong SHG response in $Ba_2TiOSi_2O_7$ [and the near absence of such a response in the other two titanium(IV) oxides] is most likely related to the orientation of the TiO_5 square pyramids in the structures. In $Ba_2TiOSi_2O_7$ (Fig. 4), the square pyramids are arranged one over the other in the c direction so that the apical oxygen of each square pyramid is directed toward the base of the adjacent square pyramid in the next layer. Accordingly, it is possible to visualize the existence of $-Ti-O-Ti-O-$ chains with alternating short and long Ti–O bonds, although the long Ti–O bond would be usually long (~ 3.5 Å) in this structure. That such a bonding possibiliy transforming the TiO_5 square pyramids into highly distorted TiO_6 octahedra that are *trans*-connected in this structure is not unlikely is suggested by the "undersaturation of the bond valence in the apical oxygen" (15). Bond valence calculations (23) using the more recent structural data on fresnoite (19) give a value of 1.368 for the apical oxygen, indeed showing considerable valence undersaturation for this oxygen. The geometric orientation of the TiO_5 square pyramids in the structures of $Cs_2TiOP_2O_7$ (Fig. 6) and $Na_4Ti_2Si_8O_{22} \cdot 4H_2O$ (Fig. 7) does not permit the formation of $-Ti-O-Ti-O-$ chains. Accordingly, we believe that it is *not* the presence of square-pyramidal TiO_5 units but their orientation in the structure to produce extended $-Ti-O-Ti-O-$ interactions, with alternating long and short Ti–O distances as occurs in the $Ba_2TiOSi_2O_7$ structure, that causes a significant SHG response.

In conclusion, the present work has shown that oxide materials containing *trans*-connected MO_6 octahedral chains [where $M = d^0$ cations such as Ti(IV) and Nb(V)] which are oriented appropriately in a NCS structure produce a significant NLO-SHG response. Among the several structures, the fresnoite structure appears to be most promising in terms of a large SHG response, although fresnoite ($Ba_2TiOSi_2O_7$) itself suffers from a small double refraction that does not allow phase-matched SHG (18). Investigation of isostructural derivatives of the fresnoite structure containing d^0 cations together with a different combination of other constituents is likely to yield new NLO materials with phase-matched SHG response. In view of the topological identity and dimensional compatibility of (001) layers of both $BaTiOSi_2O_7$ and $K_2(NbO)_2Si_4O_{12}$ structures, it is possible to visualize intergrowths between the two structures, for example, $Ba_2K_2(TiO)(NbO)_2(Si_2O_7)(Si_4O_{12})$ and $Ba_3K(TiO)_2(NbO)(Si_2O_7)(Si_4O_{12})$, which would also be potential NLO candidates.

ACKNOWLEDGMENTS

REFERENCES

1. D. F. Eaton, *Science* **253,** 281 (1991).
2. C. S. Liang, H. Eckert, T. E. Gier, and G. D. Stucky, *Chem. Mater.* **5,** 597 (1993).
3. L. T. Cheng, L. K. Cheng, R. L. Harlow, and J. D. Bierlein, *Appl. Phys. Lett.* **64,** 155 (1994).
4. C. Chen, Y. Wang, B. Wu, K. Wu, W. Zeng, and L. Yu, *Nature* **373,** 322 (1995).
5. P. S. Halasyamani and K. R. Poeppelmeier, *Chem. Mater.* **10,** 2753 (1998).
6. R. A. Wheeler, M.H. Whangbo, T. Hughbanks, R. Hoffmann, J. K. Burdett, and T. A. Albright, *J. Am. Chem. Soc.* **108,** 2222 (1986); S. K. Kang, H. Tang, and T. A. Albright, *J. Am. Chem. Soc.* **115,** 1971 (1993).
7. M. Kunz and I. D. Brown, *J. Solid State Chem.* **115,** 395 (1995).
8. N. S. P. Bhuvanesh and J. Gopalakrishnan, *J. Mater. Chem.* **7,** 2297 (1997).
9. M. P. Crosnier, D. Guyomard, A. Verbaere, Y. Piffard, and M. Tournoux, *J. Solid State Chem.* **98,** 128 (1992); *Ferroelectrics* **124,** 51 (1991).
10. A. V. Nikitin and N. V. Belov, *Dokl. Akad. Nauk SSSR* **146,** 1401 (1962).
11. M. Gasperin, *Acta Crystallogr., Sect. B* **30,** 1182 (1974).
12. A. Baucher and M. Gasperin, *Mater. Res. Bull.* **10,** 469 (1974).
13. A. Baucher, M. Gasperin, and B. Cervelle, *Acta Crystallogr., Sect. B* **32,** 2211 (1976).

14. A. Akella and D. A. Keszler, *J. Solid State Chem.* **120,** 74 (1995).
15. P. B. Moore and S. John Louisnathan, *Z. Kristallogr.* **130,** 438 (1969).
16. J. Protas, B. Menaert, G. Marnier, and B. Boulanger, *Acta Crystallogr., Sect. C* **47,** 698 (1991).
17. M. A. Roberts, G. Sankar, J. M. Thomas, R. H. Jones, H. Du, J. Chen, W. Pang, and R. Xu, *Nature* **381,** 401 (1996).
18. P. S. Bechthold, S. Haussühl, E. Michael, J. Eckstein, K. Recker, and F. Wallrafen, *Phys. Lett.* **65A,** 453 (1978).
19. S. A. Markgraf, A. Halliyal, A. S. Bhalla, R. E. Newnham, and C. T. Prewitt, *Ferroelectrics* **62,** 17 (1985).
20. S. K. Kurtz and T. T. Perry, *J. Appl. Phys.* **39,** 3798 (1968).
21. J-G. Lee, P. Höhn, and M. Greenblatt, *J. Solid State Chem.* **123,** 123 (1996).
22. M. Wiegel and G. Blasse, *Eur. J. Solid State Inorg. Chem.* **30,** 837 (1993).
23. I. D. Brown, *J. Appl. Crystallogr.* **29,** 479 (1996).