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Distribution, structures and nonlinear properties of noncentrosymmetric niobates and tantalates

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Abstract

The distribution of 117 noncentrosymmetric niobates and tantalates over different crystal systems and types of space formation of Nb, Ta–O polyhedrons have been revealed. The dependence of polyhedron space formation in the crystal lattice of the compound on stoichiometric concentration (SC) of niobium and tantalum is established. Individual Nb, Ta–O octahedrons are found for $SC = 19–7.5$, and chains and layers of the octahedrons appear in the range $SC = 11.0–5.2$. Only frame formations of Nb, Ta–O octahedrons are possible under $SC < 5.2$.

Keywords: Noncentrosymmetric compounds; Nonlinear optics; Polyhedron space formation; Chemical replacement

1. Introduction

Many of the niobate and tantalate crystals are related to basic materials of present electronics and optics because of high piezoelectrical and electrooptical coefficients and optical nonlinearity [1–6]. Nevertheless, searching for new Nb and Ta oxides with outstanding physical properties is evidently occuring, because the metals are forming the covalent oxide bonds with great polarizability. High electronic polarizability is a key factor for the creation of new effective nonlinear optical crystals. However, to reveal the combinations of cations promising for high properties, the empirical relations yielding common regularities applicable for wide diversity of the compounds are of great importance. From a symmetry point of view, only the compounds with crystal structure without center of inversion can have "noncentrosymmetric" properties, optical nonlinearity in particular [7]. So, to predict new nonlinear niobates and tantalates, it is reasonable to define the rules for selection of cation combinations promising for generation of crystal structure without center of inversion on the one hand, and strong optical nonlinearity on the other hand. As it seems, specific features of space arrangement of Nb, Ta–O polyhedrons are among the factors essential for optical nonlinearity of the compounds.

Structurally, for any particular metal ion *Me* in oxide compound such as *Me*–O polyhedron arrangements can be considered as isolated (simple) zero-dimensional (0D), one-dimensional (chain) (1D), two-dimensional (layer) (2D) and three-dimensional (frame) (3D). In the case of 0D formation, the bonds *Me*–O–*Me* are absent in the crystal lattice and *Me*–O polyhedrons are individual. While the 1D formation appears, however, the *Me*–O polyhedrons are linked into –O–*Me*–O–*Me*–O– infinite chains along a dominant direction. Furthermore, in 2D and 3D formations the –O–*Me*–O–*Me*–O– constructions can be found, respectively, in two and three dimensions providing the generation of layers and frame. Even this simple classification of the crystals reveals the presence of particular directions in the crystal framework, for example, the direction along the chains in 1D formation or the direction perpendicular to the layer plane in 2D formation. So, if relatively high optical nonlinearity observed frequently for niobate and tantalate oxides is governed by high polarizability of distorted (Nb, Ta–O) octahedrons, then the existence of these particular directions in metal polyhedron arrangement and volume concentration of the octahedrons would influence the optical nonlinearity of the crystal. This

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hypothesis may be tested by direct correlation of the nonlinear optical coefficients reported in literature with (Nb, Ta–O) octahedron packaging specified for known niobates and tantalates from crystal structure analysis.

Space formation of (Nb, Ta–O) octahedrons in the crystal lattice seems to be a significant factor controlling the presence of center of inversion when chemical substitution of other cations in the compound takes place. Owing to this reason, it would be valuable to define the relations between the (Nb, Ta–O) octahedron arrangement and stability of initial noncentrosymmetric crystal structure in reference to type of cation substituted for the constituent metal. Presumably, frame formation of (Nb, Ta–O) octahedrons seems to be the most symmetry-sensitive to the introduction of substituting cation into crystal, with stringent limitations imposed by cation size. So, this study is aimed to define the quantitative criterion for frame formation in niobate and tantalate oxides. Besides this, we are intended to look for the relationship between the level of second-order nonlinear optical susceptibility $\chi^{(2)}$ of the compound and type of (Nb, Ta–O) octahedron arrangement in the crystal lattice.

2. Classification and parameters

Searching for published results on the crystal structure of simple and binary noncentrosymmetric niobate and tantalate compounds yields a collection of 117 crystals. Only the crystals not having chalcogens, halogens, hydrogen, nitrogen and carbon and whose structure has been defined with $R<15\%$ were accounted. Niobates and tantalates were considered together because crystal chemistry of the Nb and Ta ions in oxides is very similar. The distribution of centrosymmetrical and noncentrosymmetric niobates and tantalates over the crystal systems is shown in Fig. 1. Evidently, noncentrosymmetric compounds are most widely presented in hexagonal, including rhombohedral, ~35%, and orthorhombic, ~44%, and other systems show the contributions lower than ~8%. In contrast, the niobates and tantalates with the presence of center of inversion are distributed nearly uniformly over the crystal systems with averaged level ~17–24%, except anorthic compounds whose contribution is only 2%.

Table 1 shows the distribution of the compounds over symmetry systems and space arrangements of (Nb, Ta–O)

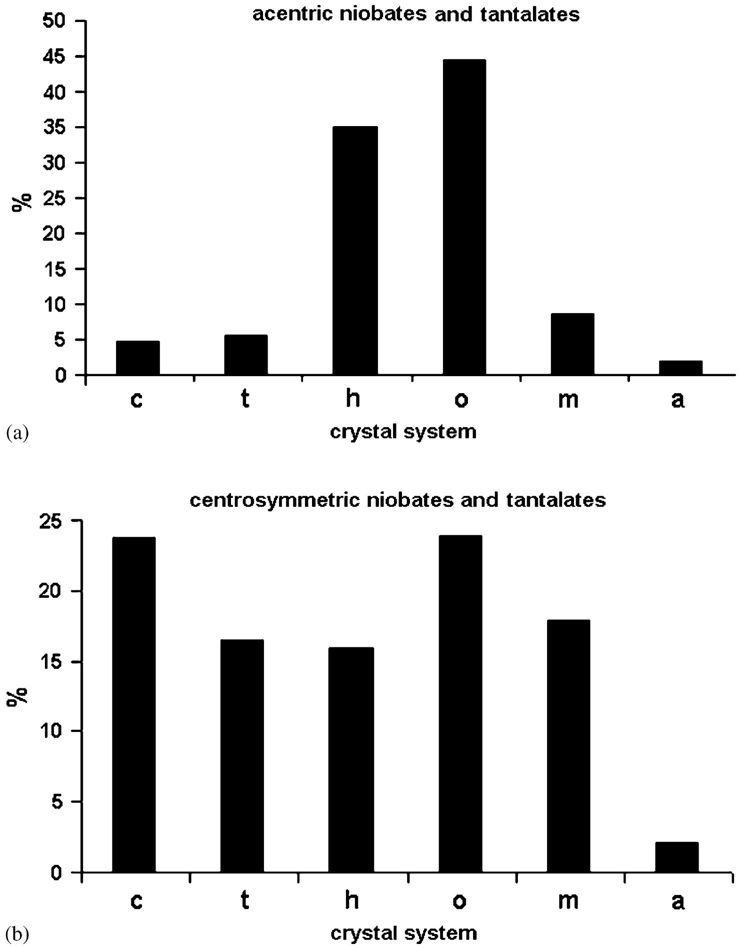

Fig. 1. Distributions of acentric (a) and centrosymmetric (b) niobates and tantalates over crystal systems: c—cubic, t—tetragonal, h—hexagonal (rhombohedral is included), o—orthorhombic, m—monoclinic, a—anorthic.

Table 1
Symmetry system and space formation of Nb(Ta)–O octahedrons for acentric niobates and tantalates

Formulae	Sys	Structure	SC	$n_O/n_{Nb,Ta}$
$TaKP_4O_{13}$	o	Simple	19.0	13.0
$TaAgP_4O_{13}$	o	Simple	19.0	13.0
$TaRbGe_3O_9$	h	Simple	14.0	9.0
$TaTlGe_3O_9$	h	Simple	14.0	9.0
$TaKGe_3O_9$	h	Simple	14.0	9.0
$TaLi_7O_6$	tr	Simple	14.0	6.0
$Nb_2K_2Si_4O_{14}$	tet	Chain	11.0	7.0
TaY_3O_7	o	Chain	11.0	7.0
$Ta_2Li_5La_3O_{12}$	c	Simple	11.0	6.0
$Nb_2Li_5La_3O_{12}$	c	Simple	11.0	6.0
$Nb_2P_4O_{15}$	a	Simple	10.5	7.5
$NbCsB_2O_6$	o	Chain	10.0	6.0
$TaCsB_2O_6$	o	Chain	10.0	6.0
$NbSr_2TmO_6$	o	Simple	10.0	6.0
$NbKB_2O_6$	m	Chain	10.0	6.0
$NbRbB_2O_6$	m	Chain	10.0	6.0
$TaRbB_2O_6$	m	Chain	10.0	6.0
$TaTlB_2O_6$	o	Chain	10.0	6.0
$TaCa_2LaO_6$	o	Simple	10.0	6.0
$Ta_3Bi_7O_{18}$	a	Chain	9.3	6.0
$NbRbSiO_5$	o	c. chain	8.0	5.0
$TaKGeO_5$	o	Chain	8.0	5.0
$Ta_2Na_2Ca_3O_9$	tr	Simple	8.0	4.5
$TaLi_3O_4$	m	Chain	8.0	4.0
$NbLi_3O_4$	c	c. simple	8.0	4.0
$Nb_2ZnMn_3O_9$	tr	Simple	7.5	4.5
$Nb_2Zn_2Mn_2O_9$	tr	Simple	7.5	4.5
$Nb_2Ni_4O_9$	o	Simple	7.5	4.5
$Nb_2BaBi_2O_9$	o	Layer	7.0	4.5
$Ta_6K_6Ge_4O_{26}$	h	Chain	7.0	4.3
$NbPO_5$	o	Chain	7.0	5.0
$Nb_2PbBi_2O_9$	o	Layer	7.0	4.5
$Nb_2SrBi_2O_9$	o	Layer	7.0	4.5
$Ta_2SrBi_2O_9$	o	Layer	7.0	4.5
$Ta_6K_6Si_4O_{26}$	h	Chain	7.0	4.3
$Nb_3K_3Si_2O_{13}$	h	c. chain	7.0	4.3
$Ta_6Na_{2.67}P_4O_{26}$	o	Chain	7.0	4.3
$NbLiZnO_4$	tet	Chain	7.0	4.0
$Ta_3Ba_4LiO_{12}$	h	c. layer	6.7	4.0
$Nb_3Ba_4LiO_{12}$	h	c. layer	6.7	4.0
$Nb_3K_3B_2O_{12}$	o	c. layer	6.7	4.0
$Ta_3K_3B_2O_{12}$	h	c. chain	6.7	4.0
$Nb_3K_3B_2O_{12}$	tr	c. chain	6.7	4.0
$Nb_5K_{3.8}Ge_4O_{20.4}$	o	c. chain	6.6	4.1
$Nb_8Na_6P_5O_{35}$	tr	c. layer	6.6	4.4
$Nb_6Ba_3Si_4O_{26}$	h	c. chain	6.5	4.3
$Ta_6Ba_3Si_4O_{26}$	h	c. chain	6.5	4.3
$Ta_6Sr_3Si_4O_{26}$	h	c. chain	6.5	4.3
$Ta_2Th_2O_9$	o	c. chain	6.5	4.5
$Nb_2Pb_{2.8}O_{7.8}$	o	c. layer	6.3	3.9
$Ta_6Ce_6O_{25}$	m	Chain	6.2	4.2
$Nb_2Pb_{2.44}O_{7.44}$	tr	c. layer	6.0	3.7
$TaLaO_4$	o	c. chain	6.0	4.0
$NbSbO_4$	o	Chain	6.0	4.0
$TaSbO_4$	o	Chain	6.0	4.0
$Nb_8Na_4P_4O_{32}$	m	c. layer	6.0	4.0
$TaNdO_4$	m	Chain	6.0	4.0
$NbFeO_4$	m	c. chain	6.0	4.0
$NbGaO_4$	m	Chain	6.0	4.0
$Nb_8Sr_6Ti_2O_{30}$	o	Framework	5.7	3.7
$Ta_8Sr_6Ti_2O_{30}$	o	Framework	5.7	3.7
$Ta_8Ba_6Ti_2O_{30}$	tet	Framework	5.7	3.7
$Nb_8Ba_6Zr_2O_{30}$	tet	Framework	5.7	3.7
$Ta_8Ba_6Zr_2O_{30}$	tet	Framework	5.7	3.7
$Nb_8Ba_6Hf_2O_{30}$	tet	Framework	5.7	3.7
$Ta_8Ba_6Hf_2O_{30}$	tet	Framework	5.7	3.7
$Nb_8Pb_6Ti_2O_{30}$	o	Framework	5.7	3.7
$Nb_8Ba_6Ti_2O_{30}$	tet	Framework	5.7	3.7
$Nb_{17}Pb_{17}O_{60}$	tr	c. layer	5.5	3.5
$Ta_2Sr_2O_7$	o	c. layer	5.5	3.5
$Nb_2Sr_2O_7$	o	c. layer	5.5	3.5
$Nb_2Ca_2O_7$	m	c. layer	5.5	3.5
$Nb_2Ca_2O_7$	o	c. layer	5.5	3.5
$Nb_5Sr_5O_{17}$	o	c. layer	5.4	3.4
$Ta_3KCa_2O_{10}$	o	c. layer	5.3	3.3
$Nb_2PbTlO_{6.5}$	c	Framework	5.3	3.2
$Nb_4Na_2Ca_2O_{13}$	o	c. layer	5.3	3.2
$Nb_5Sr_5O_{16}$	o	c. layer	5.2	3.2
$Ta_6Zn_3Mn_2O_{20}$	m	Framework	5.2	3.3
$Nb_{14}Ba_6Si_4O_{47}$	h	Framework	5.1	3.4
$NbKO_3$	tet	Framework	5.0	3.0
$TaAgO_3$	tr	Framework	5.0	3.0
$NbNaO_3$	o	Framework	5.0	3.0
$TaNaO_3$	o	Framework	5.0	3.0
$NbLiO_3$	tr	Framework	5.0	3.0
$Ta_2Li_{1.2}Cu_{0.8}O_6$	tr	Framework	5.0	3.0
$TaLiO_3$	tr	Framework	5.0	3.0
$Ta_6Li_5O_{18}$	tr	Framework	4.8	3.0
$Nb_{22}K_{10}Ge_4O_{68}$	h	Framework	4.7	3.1
Ta_3KCuO_9	o	Framework	4.7	3.0
$Nb_4Li_{1.3}Cu_{1.3}O_{12}$	c	Framework	4.7	3.0
$Ta_5TlCa_2O_{15}$	o	Framework	4.6	3.0
$Ta_5NaBa_2O_{15}$	o	Framework	4.6	3.0
$Nb_5NaBa_2O_{15}$	o	Framework	4.6	3.0
$Nb_6K_4O_{17}$	o	Layer	4.5	2.8
Nb_2BaO_6	o	Framework	4.5	3.0
Nb_2PbO_6	o	Framework	4.5	3.0
$Ta_{10}Ba_4FeO_{30}$	o	Framework	4.5	3.0
$Ta_{10}Ba_4MgO_{30}$	o	Framework	4.5	3.0
$Ta_{10}Ba_4NiO_{30}$	o	Framework	4.5	3.0
$Ta_{10}Ba_4CoO_{30}$	o	Framework	4.5	3.0
$TaNd_{0.33}O_3$	tet	c. chain	4.3	3.0
$Nb_4Rb_2O_{11}$	o	Framework	4.3	2.7
$Nb_4Cs_2O_{11}$	o	Framework	4.3	2.7
$Ta_{11}Cu_5O_{30}$	h	Framework	4.2	2.7
$Nb_{35}Na_{13}O_{94}$	o	Framework	4.1	2.7
Ta_4SrO_{11}	h	Framework	4.0	2.7
$Ta_{2.82}Nb_{1.18}CaO_{11}$	h	Framework	4.0	2.7
Ta_4CaO_{11}	h	Framework	4.0	2.7
$Nb_{17}Bi_3O_{47}$	o	Framework	3.9	2.8
$Ta_{11}Pr_2O_{30}$	h	Framework	3.9	2.7
Nb_9PO_{25}	tet	Framework	3.9	2.8
Ta_7NdO_{19}	h	Framework	3.9	2.7
Ta_7LaO_{19}	h	Framework	3.9	2.7
Nb_6SrO_{16}	o	Framework	3.8	2.7
$Nb_6K_3VO_{19}$	h	Framework	3.3	1.9
$Nb_{10}BaSiO_{19}$	h	Framework	3.1	1.9

Prefix “c.” means “complex”.

polyhedrons. Here, simple noncentrosymmetric oxides NbO_2 (tetragonal), Nb_2O_5 (monoclinic) and Ta_2O_5 (monoclinic and orthorhombic structures) are not included. To describe the space formation of (Nb, Ta–O) polyhedrons in the crystal, a stoichiometric concentration (SC) is introduced as a quantitative criterion. Mathematically, the parameter SC is the ratio between total number of elements in nominal chemical formula of the compound and the number of niobium or tantalum atoms. So, for noncentrosymmetric compounds in Table 1, the SC is a minimum for $Nb_{10}BaSiO_{19}$ ($SC = 31/10 = 3.1$) and maximum for $TaKP_4O_{13}$ ($SC = 19/1 = 19.0$). For the compounds in our total collection, the minimal value of $SC = 3.0$ occurs for NbO_2. The distribution of polyhedron space types as a function of SC level is presented below:

1. Simple space structures (0D), $SC = 19–7.5$; examples: $TaKP_4O_{13}$, $Nb_2P_4O_{15}$, $Nb_2Ni_4O_9$.
2. Chain (1D) and layer (2D) formations, $SC = 11.0–5.2$; examples: TaY_3O_7, $Nb_2BaBi_2O_9$, $Nb_4Na_2Ca_2O_{13}$.
3. Frame (3D) type, $SC = 5.2–3.1$; examples: $NbKO_3$, $Nb_{10}BaSiO_{19}$, $Ta_6Zn_3Mn_2O_{20}$.

There is a distinct boundary value $SC = 5.2$, with few exceptions, above which only frame formation is possible in niobates and tantalates. The SC intervals of chain and layer arrangements superpose on one another and cannot be selected definitely by using SC. The boundary between (0D) structures and (1D) and (2D) structures is broad and lies in the range $SC = 11.0–7.5$. Several records in Table 1 are presented with prefix "complex". This is done to show gradual behavior of the transition between the dimensions of space structures of (Nb, Ta–O) polyhedrons. The cases of "complex chain" and "complex layer" are intermediate between pure layers and frames. The complex chain and layer formations are generated by two or more conjugated chains or layers of (Nb, Ta–O) octahedrons in the crystal lattice. Complex layer may also be conceived as a frame disrupted along one plane. To illustrate the cases, some representative "complex" formations are displayed in Fig. 2. As to simple formations, there is a case of isolated cluster of five Nb–O octahedrons in $NbLi_3O_4$ and this crystal is noted as "complex simple".

Another quantitative criterion $n_O/n_{Nb,Ta}$ is presented in Table 1 for comparison for every compound. Earlier, this parameter has been proposed for using as a variable for characterization of anion complexes in borates ($Me = B$) and borophosphates ($Me = B$, P) [8,9]. Now, taking $Me = Nb$, Ta, we try to use the ratio of the number of Nb or Ta to the number of oxygens in nominal chemical formula for the specification of (Nb, Ta–O) octahedron arrangement. The analysis shows that, except some details

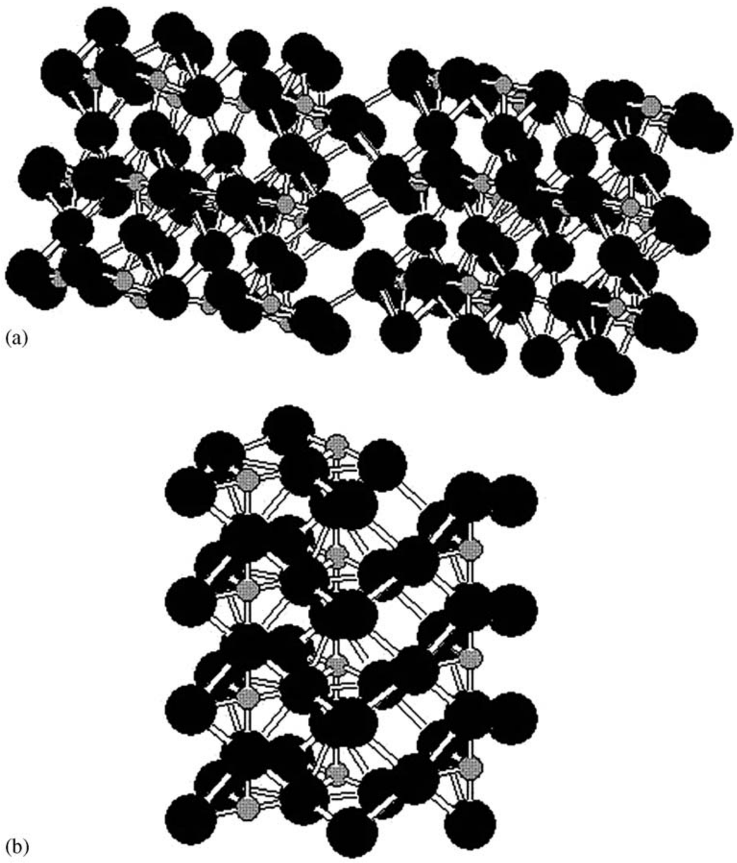

Fig. 2. Examples of "complex" space formations of (a) complex layers of (Nb–O) octahedrons in $Sr_2Nb_2O_7$ and (b) complex chains of (Ta–O) octahedrons in $LaTaO_4$. Here, gray balls display niobium or tantalum ions and dark balls show oxygens.

of secondary importance, the sensitivity of both the criteria SC and $n_O/n_{Nb,Ta}$ to the octahedron arrangement variations is nearly the same. Whilst the criteria are practically equivalent for the set of noncentrosymmetric niobates and tantalates considered in this study, the sensitivity of the parameter SC seems to be potentially higher for many more numerous set of compounds due to smoother variation because of higher number of cations accounted.

3. Comparison with borates

The distributions of centrosymmetric and noncentrosymmetric borates over symmetry systems have been discussed previously [10]. Respectively, it is very interesting to compare the results with those for niobates and tantalates displayed in Fig. 1. Contrary to roughly uniform distribution of centrosymmetric niobate and tantalate crystals, the distribution of borates with center of inversion has pronounced maximum for orthorhombic (36%) and monoclinic (37%) systems. As to noncentrosymmetric crystals, evident preference is obtained for borates related to hexagonal (39% including trigonal) and orthorhombic (26%) systems. Similar dominance of these two systems is also observed for noncentrosymmetric niobates and tantalates.

There are several noncentrosymmetric boroniobates and borotantalates related to families $AMeB_2O_6$, A = Rb, Cs, Tl and Me = Nb, Ta and $K_3Me_3B_2O_{12}$, Me = Nb, Ta, for which the test would be reasonable for simultaneous ability of SC criteria calculated for (Nb, Ta–O) and (B–O) polyhedrons. It has been found earlier that individual B–O polyhedrons appear when SC(B) = 50.0–5.0, chain and layer formations of the polyhedrons are typical for SC(B) = 5.0–3.5 and frame arrangements exist in the range SC(B) = 4.0–2.5 [10]. For the compounds with common formula $AMeB_2O_6$, we have SC(Me) = 10.0 and SC(B) = 5.0. From the crystal structure analysis, it is known that the (Nb, Ta–O) polyhedrons in $AMeB_2O_6$ phases are arranged by chains, and B–O polyhedrons are presented by simple structures (isolated doubled triangles). The calculation for $A_3Me_3B_2O_{12}$ gives SC(Me) = 6.7 and (Nb, Ta–O) polyhedrons are linked into complex chains, SC(B) = 10.0 and B–O polyhedrons are presented by simple structures (isolated triangles). Both the cases well relate with regularities evaluated for SC limitations specified for borates [10] and niobates and tantalates that confirm our model.

4. Relationship between polyhedron formation and optical nonlinearity

A set of niobates and tantalates with measured nonlinear properties is presented in Table 2. There is no evident relation between the level of optical nonlinearity and (Nb, Ta–O) polyhedron formations. As expected, increased nonlinearity should be in the crystals with layer and chain space structure due to the presence of expressed direction for these polyhedron formations. The frame and simple formations, however, are supposed as those having low nonlinearity due to the absence of expressed direction because adjacent polyhedrons are rotated with each other forming the space structures with zigzag geometry. Besides this, the simple structures (0D) are characterized by low volume density of (Nb, Ta–O) polyhedrons, and this would be the main cause of low integrated nonlinearity of the crystal. For example, both $SbNbO_4$ and $KNbB_2O_6$ possess chain formation of (Nb–O) polyhedrons but the compounds show very different nonlinear optical properties:

Table 2
Correlation between space formation of d-elements-octahedrons and level of optical nonlinearity

Formulae	Sys	Space formation of d-elements-octahedrons	Reference data	d_p[a]
$RbNbB_2O_6$	m	Nb-chain	$d_p = 5d$(KDP), $d_{24} = 2.40$, $d_{32} = 2.30$, $d_{33} = 0.94$ [1]	2.18
$KNbB_2O_6$	m	Nb-chain	$d_p = 7d$(KDP), $d_{24} = 6.10$, $d_{32} = 3.00$, $d_{33} = 1.44$ [1]	3.05
$SbNbO_4$	o	Nb-chain	$d_p = 11.0$, $d_{333} = 18$ [2]	11.00
$SbTaO_4$	o	Ta-chain	$d_p = 10.1$, $d_{311} = 5.10$, $d_{223} = 5.00$, $d_{333} = 17$ [2]	10.10
$Rb_2Nb_4O_{11}$	m	Nb-frame	$d_p = 1.8I(SiO_2)$ [6]	0.62
$Cs_2Nb_4O_{11}$	o	Nb-frame	$d_p = 1.1I(SiO_2)$ [6]	0.46
$LiNbO_3$	Tr	Nb-frame	$d_{33} = 6.9$ [11], $d_p = 3.79$ [4]	3.79
$Ba_2NaNb_5O_{15}$	o	Nb-frame	$d_{31} = 14.6$ [3]	14.60
$Ca_2Nb_2O_7$	m	Nb-complex layer	$d_p = 5.2d$(KDP) [12]	2.00
$KNbO_3$	tet	Nb-frame	$d_p = 4.42$ [4]	4.42
$Sr_6Ti_2Nb_8O_{30}$	o	Nb-frame, Ti-simple	$d_p = 2.5$ [5]	2.50
$Sr_6Ti_2Ta_8O_{30}$	o	Ta-frame, Ti-simple	$d_p = 1.7$ [5]	1.70
$Ba_6Ti_2Nb_8O_{30}$	tet	Nb-frame, Ti-simple	$d_p = 12.3$ [5]	12.30
$Ba_6Ti_2Ta_8O_{30}$	tet	Ta-frame, Ti-simple	$d_p = 1.7$ [5]	1.70
$Ba_6Zr_2Nb_8O_{30}$	tet	Nb-frame, Zr-simple	$d_p = 9.6$ [5]	9.60
$Ba_6Zr_2Ta_8O_{30}$	tet	Ta-frame, Zr-simple	$d_p = 1.7$ [5]	1.70
$Ba_6Hf_2Nb_8O_{30}$	tet	Nb-frame, Hf-simple	$d_p = 3.9$ [5]	3.90
$Ba_6Hf_2Ta_8O_{30}$	tet	Ta-frame, Hf-simple	$d_p = 1.7$ [5]	1.70
$Pb_6Ti_2Nb_8O_{30}$	o	Nb-frame, Ti-simple	$d_p = 28.2$ [5]	28.20

[a] Here d_p is related to powder measurement. This column is introduced for unification of SHG data.

$d_p = 11.0$ [2] and $d_p = 7d(\mathrm{KDP}) = 3.1\,\mathrm{pm/V}$ [1], respectively. Also, the levels of $d_p(\mathrm{Cs_2Nb_4O_{11}}) = 0.46\,\mathrm{pm/V}$ [6] and $d_{31}(\mathrm{NaBa_2Nb_5O_{15}}) = 14.6\,\mathrm{pm/V}$ [3] are principally different, although both the compounds have frame formation of (Nb–O) octahedrons. So, any preference of high level of optical nonlinearity to certain space polyhedron structure is not observed for this set of the crystals, and more detailed factors such as polyhedron distortion and space orientation of chemical bonds should be considered.

5. Chemical replacement

Space structure of (Nb, Ta–O) polyhedrons is useful for better insight into effects of chemical replacement of other cations in a compound on isovalent ions. If effective ionic radii of initial cation and ghost cation are very different, the persistence of noncentrosymmetric crystal structure occurs on the substitution only for 0D–2D space formations of (Nb, Ta–O) polyhedrons. Contrary to this, the frame of (Nb, Ta–O) polyhedrons will be destroyed by the substitution with appearance of center of inversion. For example, both $\mathrm{BaNb_2O_6}$ and $\mathrm{PbNb_2O_6}$ have Nb–O frame formations and noncentrosymmetric structure, but the replacement of Ba or Pb with large ionic radii (1.50 and 1.32 Å respectively [13]) by relatively small cations Ca or Mn (1.14 and 0.97 Å, respectively) changes crystal structure with appearance of center of inversion. Contrary to this, there exist many noncentrosymmetric compounds with common composition $\mathrm{Nb}A^{\mathrm{III}}\mathrm{O_4}$, $A^{\mathrm{III}} = \mathrm{Fe}$, Ga, Sb, Ln with ionic radii 0.55, 0.62, 0.76, 0.86–1.03 Å, respectively, so the radius of A^{III} cation varies by two times over the $\mathrm{Nb}A^{\mathrm{III}}\mathrm{O_4}$ family. This can be explained by the fact that in the compounds, the Nb–O polyhedrons form chain (1D) structure without stringent cage for A^{III} ions and the size of A^{III} cation is not a limiting factor. Another interesting example of influence of ion size factor is a case of $A\mathrm{NbO_3}$ compounds (A—alkali metal) because $\mathrm{LiNbO_3}$, $\mathrm{KNbO_3}$ and $\mathrm{LiTaO_3}$ are widely used industrial materials. In these compounds, the (Nb, Ta–O) polyhedrons are linked into frame structure, so the radius of A cation is principal. Indeed, for $A = \mathrm{Li}$, Na and K, the frame structure of (Nb, Ta–O) octahedrons and absence of inversion center are observed. For large cations $A = \mathrm{Rb}$, Cs, however, the frame formation is disrupted with generation of layer formation in $\mathrm{CsNbO_3}$, space group $P2_1/c$ [14] and $\mathrm{RbTaO_3}$, space group $C2/m$ [15] and complex chain formation of Nb–O octahedrons in $\mathrm{RbNbO_3}$, space group P-1 [16]. These structure modifications on the cation substitution are accompanied by appearance of center of inversion. So, a priori information about space formation of (Nb, Ta–O) polyhedrons is useful for prediction of effects of chemical substitution.

6. Conclusions

The distributions of 117 acentric niobates and tantalates over different crystal systems and space formations of (Nb, Ta–O) polyhedrons have been revealed. Distributions of centrosymmetrical and noncentrosymmetric niobates and tantalates over crystal systems are very different. The noncentrosymmetric compounds are most frequently presented in hexagonal (35%, including rhombohedral system) and orthorhombic (44%) systems, while other systems show only <8% contributions. From another side, centrosymmetric niobates and tantalates are distributed very uniformly with contribution of each system ~17–24%, except anorthic compounds with only 2% contribution. The dependence of (Nb, Ta–O) polyhedron space formation on SC of niobium and tantalum in nominal chemical formula of the compound is established. Individual polyhedrons are found for SC = 19–7.5, chains and layers of the octahedrons are observed for the range SC = 11.0–5.2 and frame formation appears for SC = 5.2–3.0. There is no clear relationship between SC value and the level of optical nonlinearity. However, the account of SC value is reasonable for understanding of the effects of chemical replacement of cations in stoichiometric composition of compound by isovalent ions.

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