JOURNAL OF SOLID STATE CHEMISTRY **108**, 87–93 (1994)

Synthesis, Characterization, and Crystal Structure of $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$

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Received February 8, 1993; in revised form April 29, 1993; accepted May 13, 1993

Single crystals of rare-earth hydrated hydrogenselenite $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$ have been obtained by pseudohydrothermal synthesis, using a glass of composition $10SeO_2 : Nd_2O_3$ as precursor. Material characterization was supported by chemical analysis, infrared absorption spectroscopy, and thermal analysis. The latter technique shows the presence of a new rare-earth selenite, $Nd_2Se_4O_{11}$, as a subproduct of the thermal decomposition. The $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$ compound crystallizes in the orthorhombic system, space group $P2_12_12_1$, with unit cell parameters a = 6.699(4) Å, b = 7.101(1) Å and c = 16.39(2) Å. The structure has been determined by X-ray single crystal techniques and refined down to R = 0.043. It can be described as infinite chains of bicapped trigonal prisms $(NdO_7(H_2O))$ sharing edges interconnected by (SeO_3E) tetrahedra (E lone pair) via corner and edge sharing making a layer $(NdSeO_6)$ upon which (SeO_2OHE) groups are grafted, assuming the stability of the network via hydrogen bonding. Free water molecules occupy channels developed along [100]. Particular similarities between the layers $(NdSeO_6)$ of this structure and the slabs along [010] of the $ZrSiO_4$ structure are emphasized. The coordination number (CN = 8) of Zr and Nd, bisdisphenoid and bicapped trigonal prisms respectively, can be related by a simple topological distorsion. The (SeO_3E) tetrahedra play a connecting role analogous to that of SiO_4 tetrahedra in the formation of $(NdSeO_6)$ layers.

INTRODUCTION

Although rare-earth selenites were discovered by Berzelius in 1818 (1), more than a century and a half elapsed before investigations were resumed (2, 3). Thus considerable efforts have been made to obtain and characterize in an aqueous solution new rare-earth (Ln) hydrated selenites and hydrogenselenites (4). However, owing to the size of the isolated crystals, X-ray diffraction studies have seldom been done. Of particular interest is the family of hydrogenselenites $LnH(SeO_3)_2 \cdot nH_2O$ that has been known for some time (5–7). Polycrystalline samples were first studied using X-ray diffraction (particularly for n = 2.5) and showed a monoclinic symmetry with cell parameters in the ranges $7.09 \leq a \leq 7.13$ Å, $6.66 \leq b \leq 6.75$ Å, $16.66 \leq c \leq 16.80$ Å, $100.8 \leq \beta \leq 101.3°$, but the structural determination was not reported. On the other hand, a large number of compounds with elements possessing a lone pair, such as Te(IV), Sb(III), or As(III), (8–12) and specially Se(IV) (13–15), have been systematically investigated in an attempt to understand their particular structural chemistry. Certain rare-earth compounds were also examined (11, 16–18). To extend the study to materials involving Se(IV), selenite $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$ was prepared using an original method reported here along with its physicochemical characterization and thermal behavior. The crystal structure, determined by X-ray single crystal methods, is described and some remarkable structural features are compared with those of $ZrSiO_4$.

EXPERIMENTAL

Synthesis

Glass was prepared as precursor for the crystal growth of $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$ for pseudohydrothermal synthesis. Glass was obtained by heating a mixture of SeO_2 and Nd_2O_3 oxides (molar ratio 10 : 1) 24 hr at 450°C in a sealed outgassed Pyrex ampoule and followed by quenching in liquid nitrogen; 0.5 g of glass, together with 12 ml of water, were introduced in a Teflon tube (25 ml of total volume) placed in a tightly closed steel container and maintained at 110°C for a week; slow cooling was applied ($10°C \cdot hr^{-1}$). The light pink crystals obtained were washed with water and dried air.

Characterization

The exact formula of the single crystals, $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$ was derived from the crystal structure determination and was found to be in good agreement (% calculated for Nd, Se, and H: 33.14, 36.29, and 0.93) with the chemical analysis (% observed: 33.16, 36.00, and 0.96 respectively). Elemental analysis of Nd and Se was done by emission spectroscopy ICP using a

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Perkin–Elmer Plasma 40, while the H analysis was carried out with a Perkin–Elmer 2400 CHN analyzer. Thermogravimetric and differential thermal curves (TG and DTA) were obtained in static air atmosphere pressure in the temperature range 25 to 1200°C on a Stanton Redcroft STA-781 thermal analyzer, at a heating rate of 5°C · $\min^{-1}$, and an initial weight of about 10 mg. Standard platinum crucibles were used, alumina being the reference material. The IR spectrum (KBr pellets) was performed on a FTIR 1725X Perkin–Elmer spectrometer.

Crystal Structure Determination

A single crystal was studied using a CAD4-Enraf-Nonius diffractometer. Orientation matrix and cell parameters were obtained from least-squares refinements of setting angles of 25 reflections in the 5.8–21.6(°) θ range. Crystal data and conditions of intensity measurements are listed in Table 1. Corrections of Lorentz-polarization and absorption (19) were applied to *hkl* data. Atomic scattering factors were corrected for anomalous dispersion (20). Weighting scheme and reliability factors are listed in Table 1. The calculations and drawings relied on SHELX (21) and ORTEP (22) programs run on a superminicomputer VFX/80 Alliant. The structure was determined using Patterson's method and subsequent refinements were made using full matrix least-squares calculations. Difference Fourier synthesis first revealed a hydrogen atom associated with the oxygen atom (O6) bonded to selenium Se2 and then two hydrogen atoms of isolated an water molecule (O8) and finally two hydrogen atoms of a water molecule bonded to neodymium atom (O7). Hydrogen atoms were introduced in the calculations with fixed O–H distances (0.98 Å) and isotropic factors (4.8 Å^2). The enantiomorph configuration does not yield different results of particular significance. On a final difference Fourier synthesis the maximum residual peak corresponding to 2.5 $e^-/\text{Å}^3$ is observed at 1.5 Å of Se1 atom. The final parameters are given in Tables 2 and 3. Selected bonds and angles are gathered in Table 4.

TABLE 1
Physical and Crystallographic Data for $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$

Crystal data	
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.699(4)
b	7.101(1)
c	16.39(2)
V (Å^3)	779.6(9)
Z	4
Molecular weight	435.2
ρ_{calc} (g/cm^3)	3.71
μ (Mo$K\alpha$ cm^{-1})	163.4
Morphology	platelet
Color	light pink
Dimension (mm)	0.100 × 0.025 × 0.0063
Transmission coeff. range	0.61–1.00
Data collection	
Temperature (°C)	20
Wavelength (Mo$K\alpha$) (Å)	0.71073
Monochromator	graphite
Scan mode	ω–2θ
Scan width (°)	$0.90 + 0.35 \tan\theta$
Take-off angle (°)	5.0
Max Bragg angle (°)	35
T_{max} (sec)	120
Intensity control reflections	0 −4 0/0 0 −4/4 0 0 (every 3600 sec)
Orientation control reflections	0 −2 1/0 −6 −5 (every 200 refl.)
Indices range	$h \rightarrow 0$–$10/k \rightarrow 0$–$11/l \rightarrow 0$–26
Structure refinement	
Reflections collected	2135
Reflections unique measured	1038
Reflections unique used	987 ($I > 2\sigma(I)$)
Parameters refined	113
Weighting w^{-1}	$\sigma^2(F_o) + 0.00023\, F^2$
Goodness of fit	1.12
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.043
$R_w = [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma w F_o^2]^{1/2}$	0.036

TABLE 2
Final Least-Squares Atomic Parameters for $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$

Atom	x	y	z	B_{eq} (Å^2)
Nd	0.1265(1)	0.3899(1)	0.28630(5)	0.65(3)
Se1	0.6562(2)	0.3858(3)	0.22623(9)	0.84(6)
Se2	−0.1511(3)	0.6908(3)	0.4204(1)	1.26(6)
O1	0.809(2)	0.211(2)	0.2617(7)	1.1(5)
O2	0.477(1)	0.392(2)	0.2977(7)	1.3(4)
O3	0.808(2)	0.563(2)	0.2562(7)	1.1(4)
O4	0.074(2)	0.594(2)	0.4036(7)	1.4(5)
O5	−0.149(2)	0.884(2)	0.3634(6)	2.0(5)
O6	−0.089(2)	0.795(2)	0.5134(6)	2.0(6)
O7	0.113(2)	0.192(2)	0.4081(8)	2.7(6)
O8	0.386(3)	0.698(3)	0.0628(8)	5.3(9)

Note. $B_{eq} = 8\,\pi^2/3$ trace u (u diagonalized U matrix).

RESULTS AND DISCUSSION

Thermal Decomposition

The thermal decomposition of this material was performed in six steps between 69 and 1162°C corresponding to the successive losses of H_2O and SeO_2 (Fig. 1). The first and second processes, from 69 to 136°C and 147 to

TABLE 3
Hydrogen Atomic Positions for $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$

Atom	x	y	z
H1	−0.160	0.850	0.560
H2	0.020	0.090	0.416
H3	0.210	0.200	0.453
H4	0.370	0.590	0.025
H5	0.390	0.650	0.120

TABLE 4
Selected Distances (Å) and Angles [°] for $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$

Nd environment			
Nd–O1*a*	2.510(5)	Nd–O1*b*	2.448(5)
Nd–O2	2.358(5)	Nd–O3*a*	2.510(5)
Nd–O3*c*	2.461(5)	Nd–O4	2.432(5)
Nd–O5*d*	2.458(5)	Nd–O7	2.444(6)
⟨Nd–O⟩ = 2.453			
Se environment			
Se1–O1	1.676(5)	O1–O2	2.634(7)
Se1–O2	1.694(5)	O1–O3	2.505(8)
Se1–O3	1.713(5)	O2–O3	2.621(7)
⟨Se1–O⟩ = 1.694		⟨O–O⟩ = 2.587	
O1–Se1–O2	102.0(3)		
O1–Se1–O3	94.7(2)		
O2–Se1–O3	102.1(3)		
⟨O–Se1–O⟩ = 99.6			
Se2–O4	1.679(6)	O4–O5	2.628(9)
Se2–O5	1.659(6)	O4–O6	2.543(8)
Se2–O6	1.745(5)	O5–O6	2.570(7)
⟨Se2–O⟩ = 1.694		⟨O–O⟩ = 2.580	
O4–Se2–O5	103.8(3)		
O4–Se2–O6	95.9(2)		
O5–Se2–O7	98.0(3)		
⟨O–Se2–O⟩ = 99.2			

H environment					
Se2–H1	2.553(3)				
O4–H1e	1.924(4)	O4–O6*e*	2.751(7)	O4–H1*e*–O6*e*	140.8(3)
O5–H2f	2.022(5)	O5–O7*f*	2.898(7)	O5–H2*f*–O7*f*	146.9(5)

Note. Symmetry codes. *a*: $x - 1, y, z$; *b*: $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$; *c*: $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; *d*: $-x, y - \frac{1}{2}, \frac{1}{2} - z$; *e*: $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; *f*: $x, 1 + y, z$.

272°C, are attributed to the loss of one and four H_2O molecules respectively, leading to an anhydrous rare-earth selenite, $Nd_2Se_4O_{11}$, which has not been reported yet (*16*). The third process, from 287 to 397°C, corresponds to the degradation of this phase with the elimination of SeO_2, leading to the formation of $Nd_4Se_7O_{20}$ whose scheme of decomposition has been described elsewhere (17). Chemical analysis were made in order to confirm the formula of $Nd_2Se_4O_{11}$, $Nd_4Se_7O_{20}$, $Nd_2Se_3O_9$, and Nd_2SeO_5, and Nd_2O_3 was characterized by X-ray powder diffraction. The DTA curve shows five endothermic peaks, in accordance with each mass loss observed in the thermogravimetric analysis curve, except for the decomposition of $Nd_2Se_4O_{11}$ which shows an exothermic peak. This could be regarded as the elimination of SeO_2 and the simultaneous crystallographic transformation. On the basis of the results obtained, the general decomposition scheme of the $Nd(HSeO_3)(SeO_3)$. $2H_2O$ can be formulated as follows: $2[Nd(HSeO_3)(SeO_3) \cdot 2H_2O] - 1H_2O \rightarrow Nd_2Se_4O_{11} \cdot 4H_2O - 4H_2O \rightarrow Nd_2Se_4O_{11} - \frac{1}{2}SeO_2 \rightarrow \frac{1}{2}[Nd_4Se_7O_{20}] - \frac{1}{2}SeO_2 \rightarrow Nd_2Se_3O_9 - 2SeO_2 \rightarrow Nd_2SeO_5 - 1SeO_2 \rightarrow Nd_2O_3$.

Infrared Spectrum

In addition to the SeO_3^{2-} vibrations between 843 and 442 cm^{-1}, this spectrum exhibits water molecule bands at 3456 and 3520 cm^{-1}, a very significative band at 1227 cm^{-1} ascribed to a hydrogenselenite ($HSeO_3^-$) anion (4, 23–24).

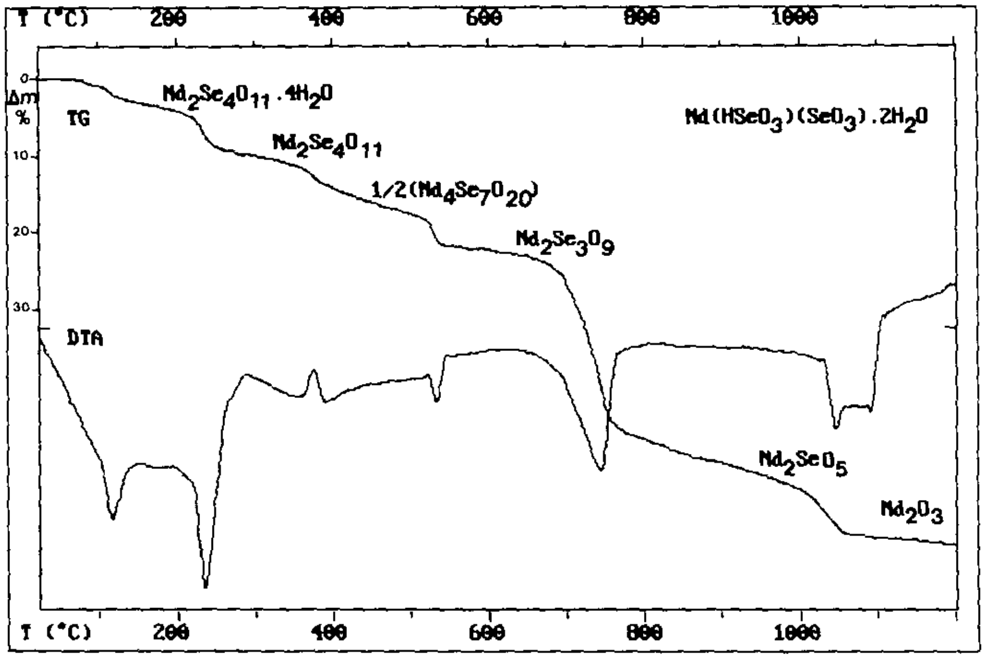

FIG. 1. TG and DTA curves for $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$.

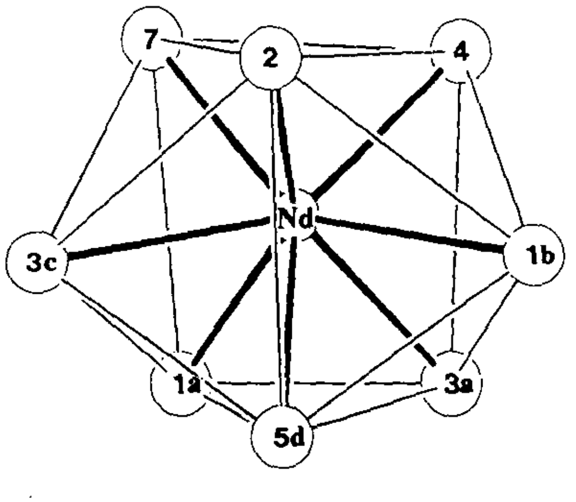

FIG. 2. Neodymium coordination polyhedron.

Description of the Structure

The structure consists of:

—A neodymium atom surrounded by eight oxygen atoms located at the vertices of a bicapped trigonal prism (Nd: O5*d* O1*a* O3*a* O1*b* O2 O3*c* O4 O7). The trigonal prism is formed by O1*a* O5*d* O3*a* O2 O4 O7. It is worth pointing out that O7 is the oxygen of a water molecule, the capping oxygen atoms being O1*b* and O3*c*. This coordination polyhedron ($CN = 8$) is clearly depicted in Fig. 2.

—Two independent selenium atoms with their lone pair E, threefold coordinated to oxygen atoms (Se1: O1 O2 O3) and (Se2: O4 O5 O6); note that O6 represents the oxygen atom of a hydroxyl group OH. The selenium atoms can be considered as occupying tetrahedra formed by the three oxygen atoms and the lone pair (SeO_3E).

—A free water molecule, the corresponding oxygen atom being O8.

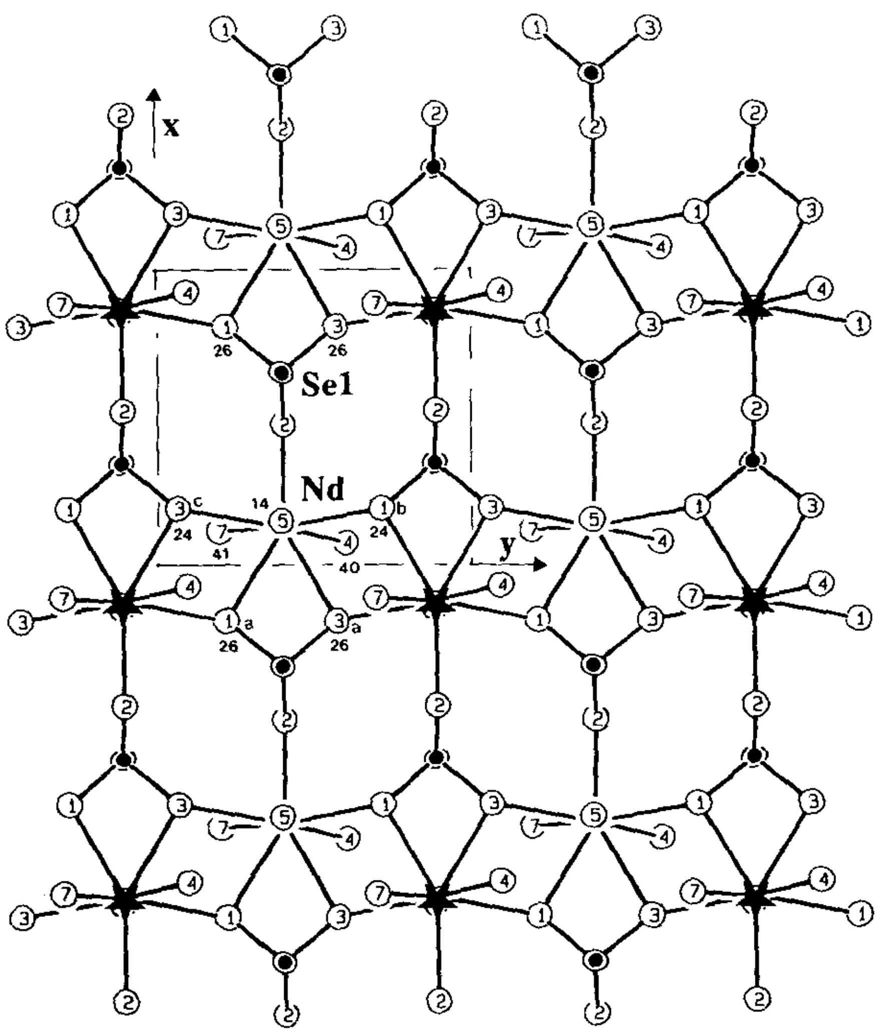

FIG. 3. Nd and Se1 network; projection onto the (001) plane. (z values are mentioned outside of oxygen atoms; stars represent the Nd atoms when they are not masked by O5 oxygen atoms.)

The (NdO_8) polyhedra share edges O1*a* O3*c* and O3*a* O1*b* along the [010] direction making up infinite chains $(NdO_6)_n$. These chains are held together by bridging $(Se1O_3E)$ groups, with a common edge O1 O3 (chelation) and a corner O2 with two adjacent chains (Fig. 3). This organization builds up a two-dimensional network, layers $(NdSeO_6)_n$ being parallel to the (001) plane. The hydrogenselenite Se2 is bismonodentate via O4 and O5 towards neodymium atoms of the $(NdO_6)_n$ chains; the hydroxyl group forms a bridge between the layers, via a hydrogen bonding O6–H1 . . . O4, along the [001] direction (Fig. 4). This ensures the stability of the three-dimensional network. Free water molecules between the layers are inserted in the channels running along the [100] and defined along the [010] by the H bonding Se2–O6–H1 . . . O4.

The detailed bonding in the structure shows that:

–in the bicapped trigonal prism (NdO_8) the shortest bond Nd–O arises with the oxygen atom shared with Se1, i.e., Nd–O2 = 2.358 Å, indicating a strong association between the chains along [100] (Fig. 3, Table 4). The bond between Nd and the oxygen of the water molecule O7 is of the same order of magnitude as the shortest Nd–O, i.e., Nd–O7 = 2.444 Å and establishes an intrachain hydrogen bond with O5 strengthening its cohesiveness (Fig. 4).

—selenium (IV) exhibits a classical stereochemistry, being at the center of a pseudotetrahedron, with the lone pair E occupying one apex; it is 0.8 Å above the oxygen triangle. With the mean O–O distances (2.584 Å) and mean Se–O bonds (1.694 Å) (Table 4) the calculated distance Se–E = 1.12 Å is in good agreement with those proposed in many structures with the scheme put forward by Galy *et al.* (9).

Comparison with the ZrSiO4 Structure

The layers built up by the bicapped trigonal prisms (NdO_8) and tetrahedra (SeO_3E) exhibit remarkable similarities with those of the zircon structure $ZrSiO_4$ (Fig. 6) (tetragonal, $I4_1/amd$, a = 6.6164(5) Å, c = 6.0150(5) Å (25)). In $ZrSiO_4$, the bisdisphenoids (ZrO_8) and the tetrahedra (SiO_4) associated by edges form a network whose parameters a and c are of the same order as those of the a and b parameters of the orthorhombic cell of $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$ (Fig. 5b). The bisdisphenoid (ZrO_8) described by Hyde and Andersson (25) as two interpenetrating tetrahedra can also be viewed as deriving from a pentagonal bipyramid (Fig. 6a) in which a couple of oxygens parallel to the fivefold axis is substituted for one vertex of the equatorial pentagon (Fig. 6b). The bisdis-

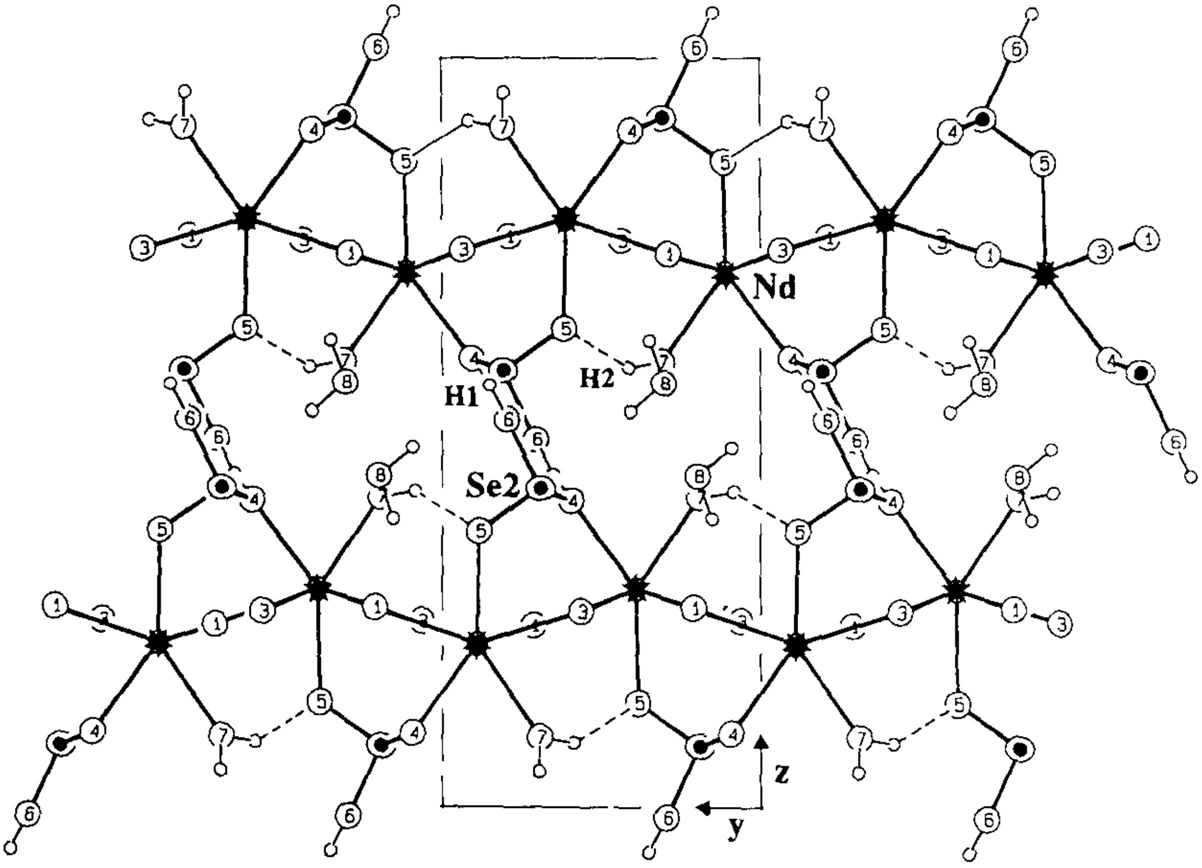

FIG. 4. Nd and Se2 network; projection onto the (100) plane.

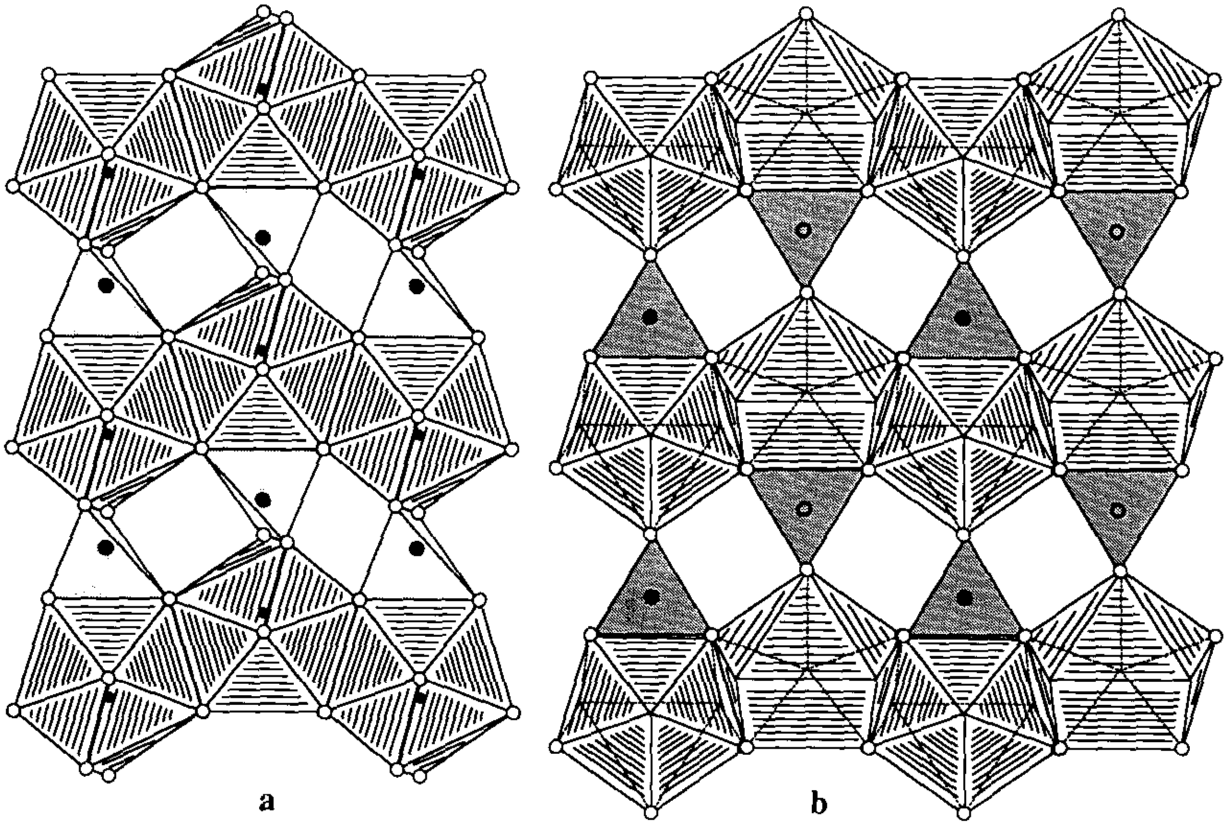

FIG. 5. Comparison of the structures $ZrSiO_4$ (a) (following (25)) and $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$ (b).

phenoids (ZrO_8) can be linked, via two opposite edges at 90°, by (SiO_4) tetrahedra (Fig. 7a) along [001] and edge sharing along [100] and [010]. From these types of slabs the general organization of the $(NdSeO_6)_n$ layers can be obtained. The (SeO_3E) tetrahedron cannot share its lone pair; therefore it is shifted to share an edge and the opposite corner with two consecutive (NdO_8) polyhedra along [100] (Fig. 7b). This comparison shows that a topotactic operation can transform a bisdisphenoid (MO_8) into a bipyramidal trigonal prism (MO_8) (Fig. 6c).

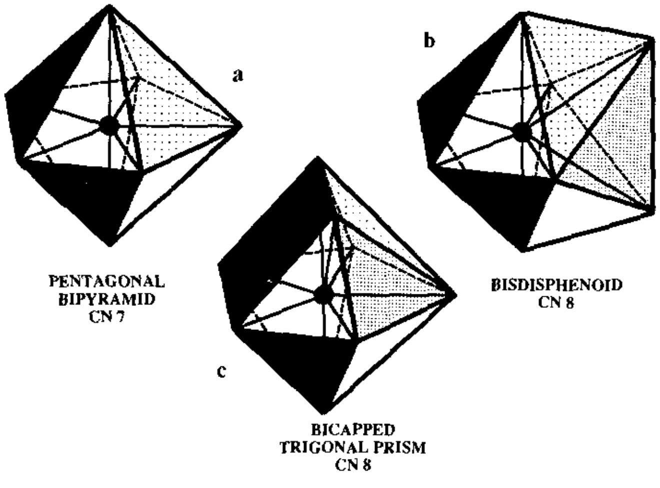

FIG. 6. Polyhedra evolution from $CN = 7$ (a) to $CN = 8$ bisdisphenoid (b) or $CN = 8$ bicapped trigonal prism (c).

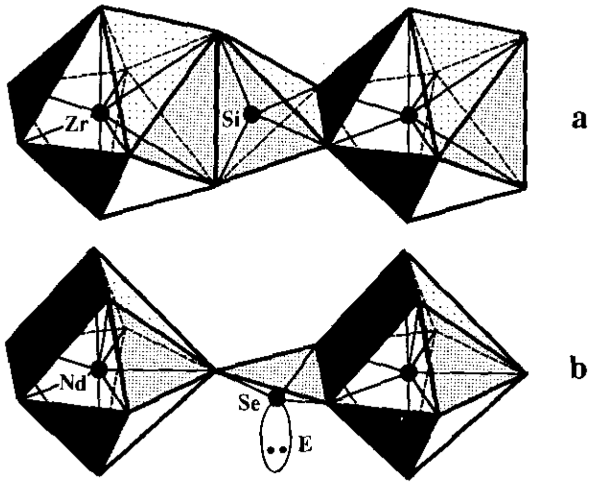

FIG. 7. Comparison between: (a) $[ZrO_8][SiO_4]$ slabs; (b) $[NdO_8][SeO_3E]$ layers.

In this paper it has been shown that the crystal structure of $Nd(NSeO_3)(SeO_3) \cdot 2H_2O$ allows establishment of a structural relationship between "solid state chemistry" compounds and those phases containing water molecules and weaker bonds. Also, the $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$ phase may serve as a starting point for a new anhydrous rare-earth selenite chemistry, as several compounds cannot be obtained by direct solid state methods.

ACKNOWLEDGMENTS

The authors thank the Centre National de la Recherche Scientifique of France and the Consejo Superior de Investigationes Cientificas of Spain for the financial support under its reciprocal International Program of Scientific Cooperation (PICS).

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