A Single-Crystal X-Ray Diffraction Study of $Sr_2Nb_5O_9$

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Single crystals of $Sr_2Nb_5O_9$ have been prepared by heating pellets containing $Sr_5Nb_4O_{15}$, NbO_2 and NbO (1:0.25:17) together with 10 % SrF_2 as a flux for 24 h in a sealed niobium ampoule at 1600 °C. The crystal structure has been refined using single-crystal data (CAD4: 226 unique, $R = 2.5$ %, $R_w = 2.2$ %). $Sr_2Nb_5O_9$ crystallizes in $P4/mmm$ (No. 123), $Z = 1$, with $a = 4.1409(5)$ and $c = 12.044(2)$ Å. The structure of $Sr_2Nb_5O_9$ contains Nb_6O_{12} clusters linked to two-dimensional sheets and can be described in terms of an intergrowth between slabs of perovskite and NbO-type structures. $Sr_2Nb_5O_9$ is metallic and exhibits a weak temperature-independent paramagnetism. The Madelung part of the lattice energy has been calculated and is discussed.

Among the reduced oxoniobates the compound groups ANb_4O_6 (A = $K^{1,2}$ and $Ba^{3,4}$) and $A_2Nb_5O_9$ (A = K,[2] Sr,[2,5,7] $Ba^{4,6,8,9}$ and $Eu^{6,10}$) have been found. They exhibit structures of the one-dimensional intergrowth type, which can be described as consisting of alternating slabs of ($ANbO_3$) perovskite and the NbO^{11} type (ordered deficient NaCl-type structure). The NbO-type slabs can alternatively be described as layers of two-dimensionally condensed Nb_6O_{12} clusters wherein the central Nb_6 octahedra are corner-sharing. In ANb_4O_6 both slabs are a single unit wide, while in $A_2Nb_5O_9$ the perovskite-type slabs are two units wide. For A = K or Ba both ANb_4O_6 and $A_2Nb_5O_9$ have been synthesised. They can be considered as being members of the homologous series $A_nNb_{n+3m}O_{3n+m}$ (n = width of the perovskite-type slab, m = width of the NbO-type slab).

The structure of $Sr_2Nb_5O_9$ has been studied by means of X-ray powder diffraction techniques and high-resolution electron microscopy,[6] but the atomic coordinates were not refined. In this paper we report on the growth of single crystals of $Sr_2Nb_5O_9$ and X-ray single-crystal studies of its structure.

Experimental

The starting materials used were NbO (99.9 %, Alfa), NbO_2 (99.9 %, Alfa), Nb_2O_5 (p.a., Merck), and $Sr_5Nb_4O_{15}$ and SrF_2 (p.a., Merck). The latter was used as a flux. $Sr_5Nb_4O_{15}$ was synthesised as the starting material by heating appropriate amounts of $SrCO_3$ (p.a., Merck) and Nb_2O_5 at 1000 °C for 10 h. The sample was reground and reheated for another 10 h at 1100 °C. Appropriate amounts of the starting materials $Sr_5Nb_4O_{15}$, NbO_2 and NbO (1:0.25:17), with addition of 10 % SrF_2 as flux, was ground together, pressed into a pellet and heated in an open Nb

ampoule under vacuum (2×10^{-4} Torr) at 350 °C to remove any moisture. The Nb ampoule was then sealed under an argon atmosphere, heated for 24 h at 1600 °C in an argon atmosphere, slowly cooled to 1200 °C (400 °C/5 h), whereafter the ampoule was taken out from the furnace.

Fine whiskers had grown on the surface of the pellet. On the surface and inside the pellet rather irregular plate-like crystals with a grey metallic lustre had formed. The X-ray powder diffraction patterns of the bulk material showed reflections corresponding to only $Sr_2Nb_5O_9$ and a phasoid[12] called α,[5,9,13] which indicated a drift in composition. This can be explained by the fact that SrF_2 acts not only as a flux but also as an Sr source, and that niobium oxoflourides are known to be volatile at high temperatures.[14]

Table 1. Summary of single-crystal data and X-ray intensity collection for $Sr_2Nb_5O_9$.

Formula	$Sr_2Nb_5O_9$
Molar weight/amu	783.76
Lattice constants[a]/Å	$a = 4.1409(5)$, $c = 12.044(2)$
Space group	$P4/mmm$, $Z = 1$
d_{calc}/g cm⁻³	6.30
$\mu(MoK\alpha)$/cm⁻¹, λ/Å	187.71, 0.71069
Dimensions of the single crystal/mm	0.1, 0.1, 0.2
Data collection	Four-circle diffractometer CAD4 graphite monochromator, scintillation counter
Range of data/°, method	$4 \leq 2\theta \leq 60$, ω-scan
Scan speed	variable depending on I
Number of reflections	1338
Independent	226 of 1304 with $F \geq 3\sigma(F)$
Absorption correction	Ψ-scan with five reflections
Refinement	SHELX program, full matrix, least-squares
Number of parameters	25
R(aniso) (%)	2.5
R_w(aniso) (%)	2.2

[a] Modified Guiner technique.

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Table 2. Positional parameters and U_{ij} values[a] (1×10^4) of the anisotropic temperature factors (in Å^2) (standard deviations) for $Sr_2Nb_5O_9$.

Atom	Site	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}
Sr	2g	0	0	0.1690(1)	150(4)	150(4)	128(6)
Nb(1)	2e	0	1/2	1/2	79(4)	79(4)	50(6)
Nb(2)	2h	1/2	1/2	0.3346(1)	68(3)	68(3)	44(4)
Nb(3)	1c	1/2	1/2	0	66(5)	66(5)	54(4)
O(1)	1b	0	0	1/2	126(23)	126(23)	135(29)
O(2)	4i	0	1/2	0.3218(5)	138(21)	98(20)	119(21)
O(3)	2h	1/2	1/2	0.1591(7)	217(22)	217(22)	48(25)
O(4)	2f	0	1/2	0	112(26)	186(27)	269(27)

[a] The U_{ij} are defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}k/b^*c^*)]$. $U_{12} = U_{23} = U_{13} = 0$ for all atoms.

The unit-cell parameters for $Sr_2Nb_5O_9$ (Table 1) were obtained from X-ray powder photographs ($CuK\alpha_1$ = 1.540598 Å, Guinier–Simon technique) which were analysed using a film scanner system[15] with silicon[16] as internal standard.[+]

Details of the structure investigation and the atomic parameters for $Sr_2Nb_5O_9$ are given in Tables 1 and 2, respectively. The positional parameters for $Ba_2Nb_5O_9$ were used as starting values. From the refinement there is no evidence that any position is not fully occupied.

When using fluorides as a flux for the synthesis of oxoniobates, fluorine is sometimes incorporated to some extent into the structures.[17,18] However, since a refinement of a data set collected from a single crystal obtained by using $SrCl_2$ as a flux resulted in the same atomic coordinates and similar anisotropic displacement factors,[19] we do not think that any fluorine is present in the crystal.

Electrical conductivity measurements between 300 and 4 K (on a ceramic material) show $Sr_2Nb_5O_9$ to be metallic.[2,7]

Measurements of the magnetic susceptibility of $Sr_2Nb_5O_9$ (ceramic material, with some $Sr_{0.83}NbO_3$ as a second phase) have been performed between 5 and 350 K in a Squid magnetometer employing a field of 10 kG.[7] $Sr_2Nb_5O_9$ exhibits a weak temperature-independent paramagnetism of 4.45×10^{-5} emu mol^{-1} at 300 K (corrected for diamagnetism and the presence of a second phase $Sr_{0.83}NbO_3$).

Description of the structure

The structure of $Sr_2Nb_5O_9$ is shown in Fig. 1. Interatomic distances are given in Table 3. Motifs of mutual adjunctions[20] together with bond-order sums[21] are summarised in Table 4. As mentioned above, $Sr_2Nb_5O_9$ is isostructural with $Ba_2Nb_5O_9$. The structure can be described as an intergrowth between two perovskite and one NbO-type slabs, respectively, with boundary atoms in common.

In the perovskite slab the Sr atoms are surrounded by 12 oxygen atoms forming a cube octahedron, and the Nb(3) atom is octahedrally coordinated by six oxygen atoms.

The Nb(1) and Nb(2) atoms in the NbO-type slab form an octahedron coordinated by oxygen atoms above the edges to form clusters of the M_6X_{12} type. The Nb(1) atoms within the NbO slabs have a planar coordination of oxygen atoms as in NbO. The Nb(2) atoms are shared between the perovskite and the NbO-type slabs and have a five-fold coordination of oxygen atoms similar to that found in compounds with discrete Nb_6O_{12} clusters, e.g. $SrNb_8O_{14}$.[22]

O(1) has a square-planar coordination of Nb(1) atoms as in NbO, while O(2) is coordinated by two Sr atoms and three Nb atoms [Nb(1) and two Nb(2)]. O(3) and O(4) in the perovskite slab are both surrounded by four Sr atoms and two Nb atoms, [O(3) to Nb(2) and Nb(3), O(4) to two Nb(3)].
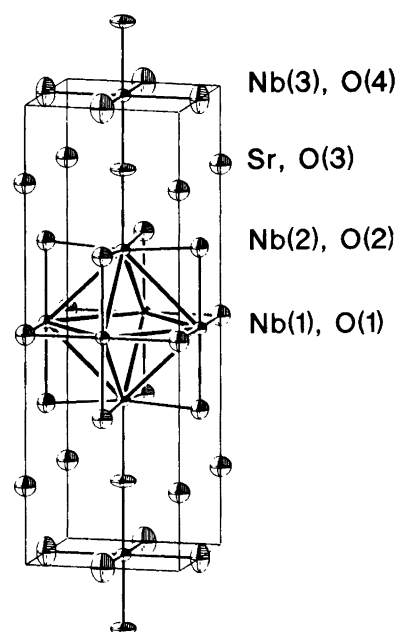
Nb(3), O(4)

Sr, O(3)

Nb(2), O(2)

Nb(1), O(1)

Fig. 1. ORTEP drawing of the structure of $Sr_2Nb_5O_9$. The displacement ellipsoids have been drawn with a probability of 90 %. The same setting of the atoms as in Table 2 has been used in the figure.

Table 3. Important interatomic distances in $Sr_2Nb_5O_9$ (in Å).

Sr–4O(2)	2.770(4)
Sr–4O(4)	2.903(1)
Sr–4O(3)	2.930(1)
Nb(1)–2O(1)	2.070(1)
Nb(1)–2O(2)	2.146(6)
Nb(1)–4Nb(2)	2.873(1)
Nb(1)–4Nb(1)	2.928(1)
Nb(2)–4O(2)	2.076(1)
Nb(2)–O(3)	2.114(9)
Nb(2)–4Nb(1)	2.873(1)
Nb(3)–2O(3)	1.917(9)
Nb(3)–4O(4)	2.070(1)

Discussion

The difference in the lattice constants between bulk $Sr_{0.95}NbO_3$ ($a = 4.02$ Å)[23,24] and NbO ($a = 4.21$ Å)[11] is 4.5%, which is larger than the 3.1% difference between $Ba_{0.95}NbO_3$[24–26] and NbO. This means that the considerable strain relief by mutual adjustment of the different kinds of slabs, when forming the structure, has to be much larger than in the case of barium. As a consequence of this larger misfit, the a axis of $Sr_2Nb_5O_9$ is shorter compared with the Ba analogue, giving a larger distortion of the perovskite-type slab. The perovskite slab is enlarged by 3% in the ab plane and contracted 4% along the c axis [using O(2) as a reference point], compared with bulk $Sr_{0.95}NbO_3$, while the comparable differences are ca. 2% for $BaNb_4O_6$ and $Ba_2Nb_5O_9$. This distortion is also reflected in the cube octahedron of oxygen atoms around the strontium atom. The Sr–O distances are between 2.770(4) and 2.930(1) Å, but the average value of 2.868(5) Å is close to the value of 2.842(1) Å found for $Sr_{0.95}NbO_3$.[23,24] The coordination octahedron around Nb(3) is tetragonally compressed [$4d_{Nb(3)-O(4)} = 2.070(1)$ Å and $2d_{Nb(3)-O(3)} = 1.917(7)$ Å].

The Nb–O' [Nb(1)–O(1,2) and Nb(2)–O(2)] distances in the NbO slab are 2.070(1)–2.146(6) Å, which is similar to that found for the Ba analogues.

Also, the Nb_6 octahedron in the NbO slab is tetragonally compressed (4.14 Å along the a axis and 3.98 Å along the c axis). This relative compression (4%) is of the same size as found for the Ba analogues.[3] The Nb(1)–Nb(2) distances

[2.873(1) Å] are shorter than those between the Nb(1) atoms [2.928(1) Å]. Both distances, Nb(1)–Nb(1) and Nb(1)–Nb(2), are significantly shorter than in $BaNb_4O_6$ [$d_{Nb(1)-Nb(1)} = 2.958(1)$, $d_{Nb(1)-Nb(2)} = 2.913(1)$ Å] and $Ba_2Nb_5O_9$ [$d_{Nb(1)-Nb(1)} = 2.950(1)$, $d_{Nb(1)-Nb(2)} = 2.890(1)$ Å].[3]

The average Nb–Nb distances decrease from $BaNb_4O_6$ [2.928(2) Å] via $Ba_2Nb_5O_9$ [2.910(2) Å] to $Sr_2Nb_5O_9$ [2.891 (2) Å]. As a result of this change the repulsion between the O(2) and the Nb(1) and Nb(2) atoms in the Nb_6O_{12} cluster increases, which is also reflected in a decreasing O(2)–Nb(2)–O(2) angle [$BaNb_4O_6$ 175.5(4)°, $Ba_2Nb_5O_9$ 173.8(4)° and $Sr_2Nb_5O_9$ 171.5(4)°]. One reason for this trend in average Nb–Nb bond length could be an increase in the number of electrons involved in Nb–Nb bonding. In $BaNb_4O_6$ the number of available valence electrons for metal–metal bonding is 10. This is also the case for the comparable cluster sheet in $Ba_2Nb_5O_9$ and $Sr_2Nb_5O_9$, assuming that Nb(3) is +4. However, there is a possibility for a charge transfer δ, from Nb(3) to the NbO slab, resulting in $10+\delta$ valence electrons available, which anyway is the case to some extent. In KNb_4O_6, which contains only nine available valence electrons per unit cell, the longer Nb–Nb bonds [average 2.96(1) Å, obtained from powder data][1] fit well into this picture.

The bond-order sums[21] for $Sr_2Nb_5O_9$ show values far from normal (Table 4) and should be interpreted with some care. It is interesting to note the high value $\Sigma s_i = 2.60$ for O(1), which is already high in $Ba_2Nb_5O_9$ ($\Sigma s_i = 2.49$), and the somewhat low value $\Sigma s_i = 1.76$ for O(4). The bond-order sums for Sr ($\Sigma s_i = 1.61$) and Nb(3) ($\Sigma s_i = 4.57$) are close to those found for Sr and Nb in $Sr_{0.95}NbO_3$ [$\Sigma s_i = 1.68$, Nb(3) $= 4.57$] and $SrNb_8O_{14}$ [$\Sigma s_i = 1.55$, Nb(3) $= 4.55$].[22] The value for Nb(3) is higher than for $Ba_2Nb_5O_9$, but it is not possible to make any conclusions from that finding. The remaining bond-order sums are similar to those found in $BaNb_4O_6$ and $Ba_2Nb_5O_9$.

From our analysis within the bond-length/bond-strength concept, the local strain built up due to the mutual size adjustment of the perovskite and the NbO-type slabs seems to focus mainly on the Sr atom, besides the O(1) atom which is 'squeezed' in the rigid cluster framework. Considerations based on Biltz's volume increments[27] also reflect such strain. Comparing the molar volume of $Sr_{0.95}NbO_3$ and

Table 4. Motifs of mutual adjunction[20] and bond-order sums[21] Σs_i in $Sr_2Nb_5O_9$.

Atom	$O(1)^{i-i}$	$4O(2)^{i-i}$	$2O(3)^a$	$2O(4)$	Coordination number	Σs_i
2Sr	–	4/2	4/4	4/4	12	1.61
2Nb(1)	2/4	2/1	–	–	4	2.36
2Nb(2)	–	4/2	1/1	–	5	3.14
Nb(3)	–	–	2/1	4/2	6	4.57
Coordination number	4	5	6	6		
Σs_i	2.60	2.15	2.04	1.76		

$Ba_{0.95}NbO_3$,[23-26] the experimentally determined change ΔV ≈ 2 cm^3 is much less than expected from the increments for Sr^{2+} and Ba^{2+} (ca. 5 cm^3). Obviously, the rigid covalent Nb–O framework cannot fully adjust for different cation sizes. The rigidity of the framework is even more obvious in the case of $Sr_2Nb_5O_9$ and $Ba_2Nb_5O_9$. Instead of a volume change of 10 cm^3 one finds 3 cm^3. In agreement with what has been argued earlier,[28] the cluster layer is more rigid than the perovskite slab.

In spite of the rigidity of the cluster layer the Nb–Nb distances in $Sr_2Nb_5O_9$ are significantly shorter compared to the Ba compound. The question remains to what extent strain relief is possible due to charge transfer, δ, between the Nb atoms in the different kinds of slabs, which would lead to stronger M–M bonding in the case of the Sr compound.

Preliminary extended Hückel calculations[29] resulted in a Fermi level below the t_{2g} orbitals of Nb(3), indicating an oxidation state of +5 for the niobium in the perovskite-type slab and thus a charge transfer into the cluster layer. However, it should be mentioned that there is no significant difference to the band filling in $Ba_2Nb_5O_9$, in contrast to what one would expect owing to the longer Nb–Nb distances there.

Calculations of the Madelung part of the lattice energy (MAPLE)[30,31] show an obvious difference between the cluster layers (see below) in the compounds of Sr and Ba. The calculation for $Sr_2Nb_5O_9$ is summarised in Table 5. The MAPLE value of a sheet of condensed Nb_6O_{12} clusters with the composition 'Nb_4O_5' is calculated according to eqn. (1),

$$MAPLE(Sr_2Nb_5O_9) - MAPLE(NbO_2) - 2\ MAPLE(SrO)$$

$$= MAPLE('Nb_4O_5') \tag{1}$$

| 9928.8 | – 3071.7 | – 2 × 899.9 |

$$= 5059.1\ kcal\ mol^{-1}$$

where the value of the segment 'Nb_4O_5' is found as the difference between that of the entire structure and the contributions from the residual binary oxides. According to experience, the MAPLE values of a particular structure segment found in different structures should not deviate by more than 1 %, at least for highly ionic compounds. The corresponding value for $Ba_2Nb_5O_9$ is 5169.7 kcal mol^{-1}, thus more than 2 % different. This deviation indicates some difference of bonding in the cluster layers of both compounds, yet one should be careful with any definite conclusion, as the value for $BaNb_4O_6$ (5122.7 kcal mol^{-1}, Ref. 3) lies nearly midway between the two.

There might be some indirect experimental evidence for a charge transfer, δ, drom the Nb(3) atom to the atoms Nb(1) and Nb(2), which helps to contract the cluster layer in $Sr_2Nb_5O_9$ and thus stabilizes the compound: in a phase '$SrNb_4O_6$' such a stabilizing effect would be missing, and in fact the isotypic compound to $BaNb_4O_6$ can not be prepared so far.

Table 5. Contribution of atoms to the Madelung part of the lattice energy (MAPLE in kcal mol^{-1})[30,31] in $Sr_2Nb_5O_9$.[a]

Atom		MAPLE	Σ MAPLE
Sr	2×	598.2	1196.4
Nb(1)	2×	290.1	580.2
Nb(2)	2×	660.3	1320.6
Nb(3)	1×	2451.6	2451.6
O(1)	1×	850.9	850.9
O(2)	4×	560.5	2242.0
O(3)	2×	334.3	668.6
O(4)	2×	309.3	618.6
		Σ =	9928.8

[a]The following charge distributions have been used: Sr, +2; Nb(1), +2.5; Nb(2), +2.5; Nb(3), +4; O(1)···O(4), –2.

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