ELSEVIER

Journal of Alloys and Compounds 218 (1995) 13–16

Journal of ALLOYS AND COMPOUNDS

Crystalline structure of the strontium niobates $Sr_4Nb_2O_9$ and $Sr_5Nb_4O_{15}$

M. Weiden [a], A. Grauel [a], J. Norwig [b], S. Horn [c], F. Steglich [a]

[a] *Institut für Festkörperphysik, Technische Hochschule Darmstadt, Hochschulstrasse 8, D-64289 Darmstadt, Germany*
[b] *Strukturforschung Materialwissenschaft, Technische Hochschule Darmstadt, Petersenstrasse 20, D-64287 Darmstadt, Germany*
[c] *Institut für Physik, Universität Augsburg, Memminger Strasse 6, D-86159 Augsburg, Germany*

Received 3 June 1993

Abstract

The strontium niobate compounds $Sr_4Nb_2O_9$ and $Sr_5Nb_4O_{15}$ were prepared by solid state reactions and studied by high-resolution X-ray powder diffraction measurements. The structures of the two systems $Sr_4Nb_2O_9$ and $Sr_5Nb_4O_{15}$ were obtained by Rietveld analysis, indicating triclinic and monoclinic unit cell parameters, respectively. Both structures reveal a layering of Sr–O planes. The Nb ions are located in octahedral holes between the Sr–O layers.

Keywords: Strontium niobates; Solid state reactions; X-ray powder diffraction

1. Introduction

Since the discovery of high-T_C superconductivity in the copper–oxide system $La_{2-x}Ba_xCuO_4$ by Bednorz and Müller [1], the physics of copper–oxide compounds are a major topic in solid state sciences. The question whether there are copper-free materials with similar or even better superconducting properties still has not been answered; all known non-copper–oxide superconductors show comparable low superconducting critical temperatures $T_C \leqslant 35$ K. The electronically important ions of the known oxide superconductors are concentrated in three regions of the periodic table. Apart from the Cu–O systems, there are compounds like NbO [2], $Li_{0.5}NbO_2$ [3], $Li_{1+x}Ti_{2-x}O_4$ [4], $BaPb_{0.75}Bi_{0.25}O_3$ [5] and $Ba_{0.6}I_{0.4}K_{0.4}BiO_3$ [6] with strongly anisotropic two-dimensional or isotropic three-dimensional electronic properties. For some of these compounds, the superconducting properties are well described by a phonon mediated BCS-like Cooper pairing [7,8], while the nature of the pairing mechanism of the Cu–O superconductors has to be unravelled.

The large variety of oxide superconductors without copper encouraged us to study the system $Sr_xNb_yO_{x+2.5y}$. As there already exists some information concerning the compounds within the ratio $x/y \leqslant 1$ [9,10], we concentrated on the as yet unknown systems with $x>y$. Here we report the synthesis and structural characterization of the two compounds $Sr_4Nb_2O_9$ and $Sr_5Nb_4O_{15}$.

2. Experimental

The samples were prepared by mixing stoichiometric amounts of dried strontium carbonate $SrCO_3$ and niobium dioxide NbO_2. The compounds were formed by the solid state reactions

$$5SrCO_3+4NbO_2 \longrightarrow Sr_5Nb_4O_{15}+2CO+3CO_2$$

$$4SrCO_3+2NbO_2 \longrightarrow Sr_4Nb_2O_9+CO+3CO_2$$

The mixed powders were heated in Al_2O_3 crucibles for 60 h at $T=1100$ °C in order to calcine the $SrCO_3$. Furthermore, we used a flowing argon atmosphere to prevent reaction of the niobium with carbon monoxide. After regrinding, the reacted powders were pressed into pellets of 1 cm in diameter. For the final sintering process, the pellets were heated for 70 h at $T=1100$ °C in a flowing argon atmosphere to prevent contamination with carbon. Using Nb_2O_5 instead of NbO_2 leads to inhomogeneous samples with small amounts of secondary phases, clearly resolved in the X-ray pattern.

The two compounds $Sr_5Nb_4O_{15}$ and $Sr_4Nb_2O_9$ were white and yellow coloured insulators with resistivities $\rho > 1 M\Omega$ at room temperature. Measurements of the

SSDI 0925-8388(94)01461-2

Table 1
The fractional atomic coordinates of $Sr_4Nb_2O_9$

Atom	*x*	*y*	*z*
Sr1	0.000	0.000	0.000
Sr2	0.644	0.082	0.325
Sr3	0.998	0.249	0.999
Sr4	0.000	0.500	0.000
Sr5	0.329	0.661	0.642
Nb1	0.714	0.835	0.357
Nb2	0.325	0.414	0.663
O1	0.645	0.098	0.766
O2	0.234	0.098	0.879
O3	0.122	0.098	0.355
O4	0.042	0.250	0.565
O5	0.436	0.250	0.478
O6	0.522	0.250	0.958
O7	0.355	0.598	0.234
O8	0.766	0.598	0.122
O9	0.879	0.598	0.645

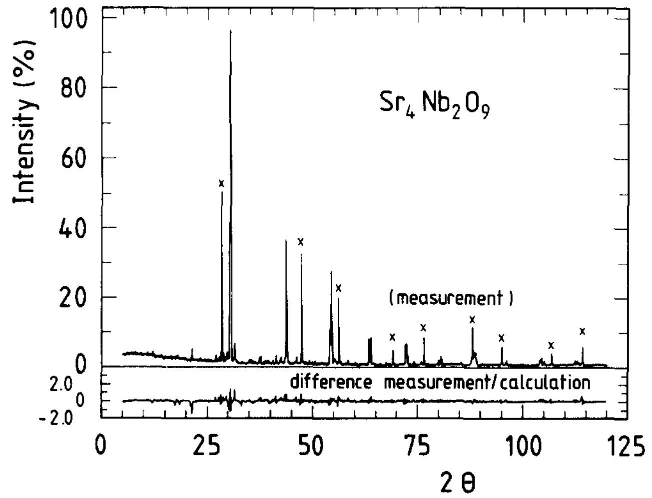

Fig. 1. The measured intensities of $Sr_4Nb_2O_9$ vs. 2θ and the difference of the measured and calculated data. The (*x*) indicate Bragg-reflections originated by the silicon.

temperature dependencies of $\rho(T)$ failed as a result of the very high resistances. The X-ray measurements were carried out on a STOE diffractometer using silicon for internal calibration. The measured Bragg-peaks were identified with the help of a fit program, the Rietveld refinements were performed with a program from Wiles and Young [11,12] until the changes in all parameters became less than 0.05% per cycle.

3. Structural characterization

It was supposed that $Sr_4Nb_2O_9$ would crystallize in a structure similar to that of $Ba_3SrNb_2O_9$, an already known hexagonal compound [13] with unit cell constants $a=5.82$ Å and $c=14.39$ Å. However, refining the assumed structure with the data of $Sr_4Nb_2O_{15}$ showed the necessity to lower the symmetry to P −1, a triclinic unit cell, as all reflections differ slightly from the hexagonal values. The cell constants turned out to be $a=5.820(6)$ Å, $b=14.392(3)$ Å and $c=5.819(6)$ Å, $\alpha=89.827(5)°$, $\beta=119.734(5)°$ and $\gamma=90.221(5)°$. These given lattice constants were the starting point for the Rietveld analysis which then lead to the determination of the fractional atomic coordinates, see Table 1. The measured datapoints and the difference between the observed and calculated data are shown in Fig. 1.

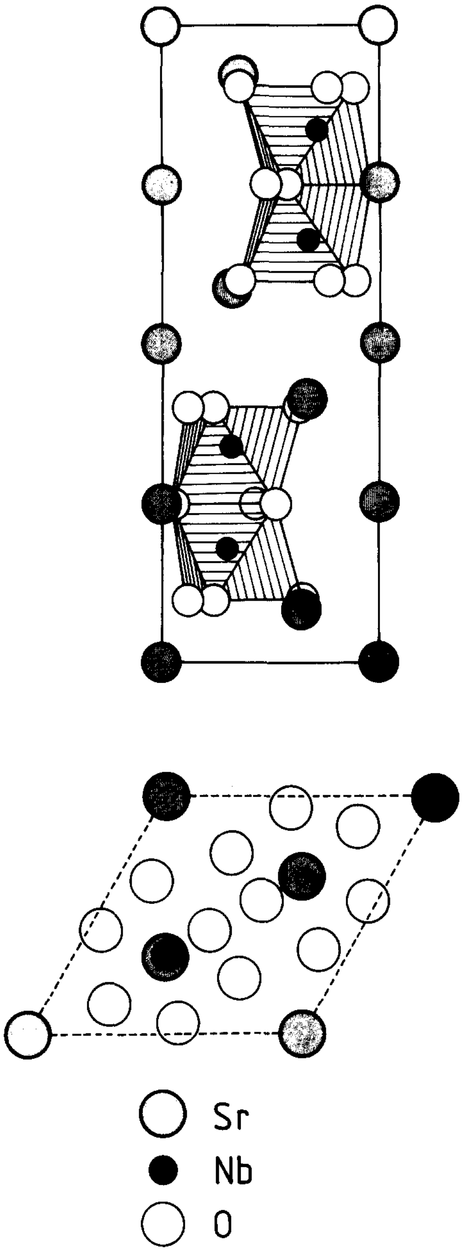

Fig. 2. The crystal structure of $Sr_4Nb_2O_9$. (a) View along the *a*–*c*-plane; (b) view along the *b*-axis. In (a), the Sr–O-layers perpendicular to the *b*-axis can be seen clearly, whereas in (b) the localization of the positive ions on three axes ∥ *b* can be observed. Nb–O-octahedras are indicated by the dashed planes to show the octahedral coordination of the niobium.

Table 2
The fractional atomic coordinates of $Sr_5Nb_4O_{15}$

Atom	*x*	*y*	*z*
Sr1	0.000	0.000	0.000
Sr2	0.838	0.500	0.235
Sr3	0.500	0.500	0.000
Sr4	0.170	0.500	0.448
Sr5	0.332	0.000	0.213
Sr6	0.674	0.000	0.458
Nb1	0.996	0.000	0.306
Nb2	0.666	0.000	0.131
Nb3	0.498	0.500	0.348
Nb4	0.170	0.500	0.118
O1	0.000	0.500	0.000
O2	0.806	0.000	0.209
O3	0.769	0.253	0.000
O4	0.576	0.361	0.214
O5	0.879	0.030	0.414
O6	0.703	0.500	0.416
O7	0.500	0.000	0.000
O8	0.413	0.189	0.382
O9	0.172	0.000	0.399
O10	0.110	0.120	0.171
O11	0.290	0.500	0.199

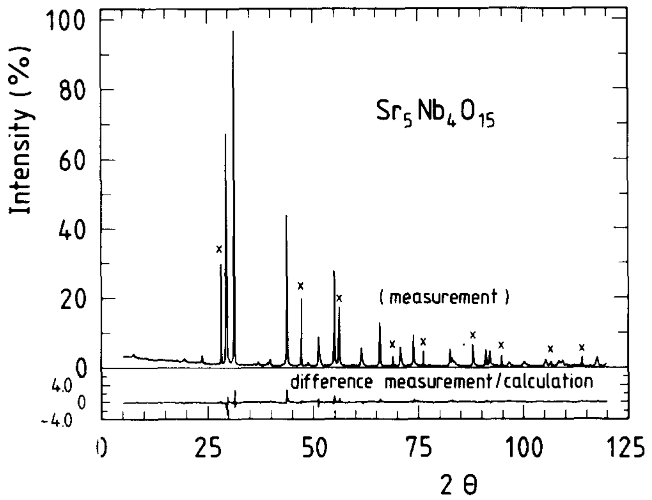

Fig. 3. The measured and difference spectra of $Sr_5Nb_4O_{15}$. The (*x*) indicate silicon reflections.

The elementary cell contains two formula units building up a closest packing of six layers, each consisting of one strontium and three oxygen ions. The niobium ions are located in edge-sharing octahedral holes between the layers, and so are the additional strontium ions. The repeat sequence of these octahedral holes is AAB(AA)'B with A containing niobium, B strontium, and ()' indicating the inverted position of the niobium ions (see Figs. 2(a) and 2(b)). As the Sr^{2+} ions are much larger than the Nb^{5+} ions, they enlarge the distance between the bordering Sr–O-layers.

The structure determination of $Sr_5Nb_4O_{15}$ started with the presumption that $Ba_5Ta_4O_{15}$, a hexagonal compound with lattice constants $a = 5.79$ Å and $c = 11.75$ Å [14], would crystallize in a similar structure. But comparing the presumed structure with the measured data of $Sr_4Nb_2O_9$, we found a monoclinic distortion which leads to a unit cell with symmetry *P*2/*m* with twice the volume of the hexagonal cell. The lattice constants are $a = 9.796(6)$ Å, $b = 5.657(5)$ Å, $c = 11.421(2)$ Å and $\beta = 90.190(4)°$. The procedure of determination of the fractional atomic coordinates was the same as for $Sr_4Nb_2O_9$, which lead to the data shown in Table 2. The measured data and the comparison with the calculation are shown in Fig. 3.

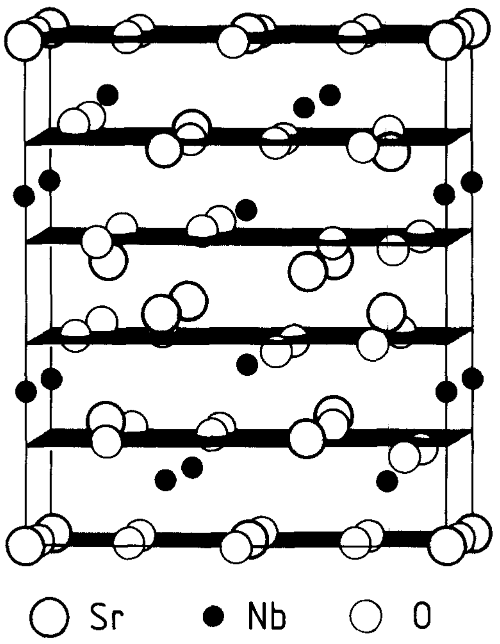

Fig. 4. The crystal structure of $Sr_5Nb_4O_{15}$. View along the *a*–*b*-plane: the Sr^{2+} and the O^{2-} ions do not build exact planes. The Sr^{2+} ions are located below the layers to maximize the distance between the positive Sr^{2+} and the Nb^{5+} ions. The largest distortion of the planes can be found between the third and fourth layers where no niobium is located.

The cell contains two formula units. As in $Sr_4Nb_2O_9$, the structure consists of a closest packing of five Sr–O-layers with the niobium ions located in corner-sharing octahedral holes. Between the third and the fourth layer, no niobium can be found. This has to be expected, as the holes between these two layers are smaller than between any of the others (see Fig. 4). The average distance between the Sr–O-layers is smaller than in $Sr_4Nb_2O_9$; there are no Sr^{2+} ions in between the layers which enlarge the distance.

4. Discussion

The high-precision X-ray measurements combined with Rietveld-analysis allowed the determination of the symmetry, the lattice constants, and the atomic coordinates of $Sr_4Nb_2O_9$ and $Sr_5Nb_4O_{15}$. The crystalline structure of both compounds can be described as a closest packing of layers containing one strontium and three oxygen ions, whereas the niobium ions are located in octahedral coordination with the oxygen. Both structures are similar to those of related compounds which built of barium and tantalum, except for the distortions; but this might be caused by the strontium which is known to often distort the perfect crystal symmetry [16]. As all investigations were carried out on polycrystalline samples, the determination of the fractional atomic coordinates, especially of the oxygen ions, may be questioned; but owing to the good agreement between measured and calculated intensities we consider the presented structures to be correct.

Attempts to prepare $Sr_xNb_yO_{x+2.5y}$ compounds with a ratio $x/y>2$ failed. These samples are consisting of $Sr_4Nb_2O_9$ and SrO_2 or SrO, respectively. In comparison, $Sr_2Nb_2O_7$ and the bronzes with the ratio $x/y<1$ have a perovskite-type structure [9,10]. Therefore we consider the two compounds $Sr_4Nb_2O_9$ and $Sr_5Nb_4O_{15}$ as the only ones in the system Sr–Nb–O with the ratio $x/y>1$.

Acknowledgements

We wish to thank Dr. Christoph Geibel for discussions and help. This work was supported by the Deutsche Forschungsgemeinschaft under the auspices of the Sonderforschungsbereich (SFB) 252 Darmstadt/Frankfurt/Mainz.

References

[1] J.G. Bednorz and K.A. Müller, *Z. Phys. B – Condensed Matter, 64* (1986) 189.

[2] E.M. Savitskii, V.V. Baron, Y.V. Efimov, M.J. Bychkova and L.F. Myzenkovajn, *Superconducting Materials,* Plenum Press, 1981, p. 123.

[3] M.J. Geselbracht, T.J. Richardson and A.M. Stacy, *Nature, 345* (1990) 324.

[4] D.C. Johnston, *J. Low Temp. Phys., 25* (1976) 145.

[5] A.W. Sleight, J.L. Gillson and P.E. Bierstedt, *Solid State Commun., 17* (1975) 27.

[6] R.J. Cava, B. Batlogg, J.J. Krajewski, R. Farrow, L.W. Rupp, Jr., A.E. White, K. Short, W.F. Peck and T. Komitani, *Nature, 332* (1988) 814.

[7] R.W. McCallum, D.C. Johnston, C.A. Luengo and M.B. Maple, *J. Low Temp. Phys., 25* (1976) 177.

[8] W.W. Schulz, L. Forro, C. Kendziora, R. Wentzcovitch, D. Mandrus, L. Mihaly and P.B. Allen, *Phys. Rev. B, 46* (1992) 14001.

[9] D. Ridgley and R. Ward, *J. Am. Chem. Soc., 77* (1955) 6132.

[10] N. Ishizawa and F. Marumo, *Acta Crystallogr., B31* (1975) 1912.

[11] D.B. Wiles and R.A. Young, *J. Appl. Crystallogr., 14* (1981).

[12] C.J. Howard and R.J. Hill, *AAEC Report,* No. M112, 1986.

[13] H.W. Zandbergen and D.J.W. Ijdo, *Acta Crystallogr., C39* (1983) 829.

[14] F. Galasso and L. Katz, *Acta Crystallogr., 14* (1961) 647.

[15] F. Lichtenberg, T. Williams, A. Reiler, D. Widmer and J.G. Bednorz, *Z. Phys. B-Condensed Matter, 84* (1991) 369.

[16] H. Weitzel, personal communication.