directional bonds. A valence of four of Ti is expected since one would expect the $3d^24s^2$ electrons to be involved in bonding. The high Ti valences obtained using equation (1) could be due to short non-bonded Ti–Ti distances.

Summary

The bonding of each metal atom in Ti_2S is different and complex; bond order and valence calculations on all metal atoms yield fairly reasonable results. Two descriptions of the sulfur bonding have been presented:

(1) Sulfur coordination of from seven to nine metal atoms, six of which form a distorted trigonal prism with one or more metal atoms removed from the faces of the prism; this description is based on covalent, electron deficient interactions and Pauling bond orders.

(2) Sulfur coordination to six metal atoms in a slightly distorted trigonal prism based on covalent, directional, electron deficient interactions. The second description has been presented in an effort to correlate the sulfur bonding in Ti_2S with that in other lower chalconides.

A distinction between the two bonding alternatives will, it is hoped, be possible when more structural information is available for lower transition metal chalconides.

Note added in proof:- Ti_2S is isostructural with Ta_2P, the crystal structure of which was recently published by Nyland (1966).

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Double Oxides containing Niobium or Tantalum. II. Systems Involving Strontium or Barium

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The binary oxide systems $SrO–Nb_2O_5$, $BaO–Nb_2O_5$, and $SrO–Ta_2O_5$ have been studied. Unit-cell data for most of the previously reported compounds and for four new phases have been determined. Both 'ideal' and 'tripled' forms of the tetragonal bronze structure occur in these systems. $SrNb_2O_6$ is isostructural with the orthorhombic form of $CaTa_2O_6$.

Introduction

The procedure used in investigating these systems was that described earlier (Whiston & Smith, 1965). The relevant literature is reviewed under each section for convenience in presenting our results and comparing them with those of previous workers.

The system $SrO–Nb_2O_5$

Goldschmidt (1960) detected, by means of powder patterns, four phases of approximate compositions

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$SrNb_2O_6$, $Sr_2Nb_6O_{17}$, $SrNb_6O_{16}$, and $SrNb_{24}O_{61}$. The first of these was cubic with a cell edge of 4·131 Å and seems to correspond to the supposed oxygen-deficient perovskite $Sr_6Nb_2O_{11}$, or $Sr(Sr_{0\cdot5}Nb_{0\cdot5})O_{2\cdot75}$, prepared by Galasso, Katz & Ward (1959) and shown by them to have a doubled cubic cell of side 8·34 Å.

Krylov & Alekseev (1954) obtained $SrNb_2O_6$ (m.p. 1225°C) from the hydrated oxide, but the material of this composition prepared by Francombe (1960) from strontium carbonate and niobium pentoxide did not melt up to 1400°C. Francombe also reported the tetragonal bronze phase $Sr_2Nb_{10}O_{27}$ having

$$a=12\cdot34,\ c=3\cdot94\ \text{Å}\ .$$

We prepared $Sr_6Nb_2O_{11}$ at 1400°C and found it to be face-centred cubic with $a=8\cdot3055\pm0\cdot0008$ Å, it being isostructural with the tantalum analogue discovered by Brixner (1958) and with $Ba_6Nb_2O_{11}$, both of which have the ammonium ferrifluoride structure. The observed density of 5·0 $g.cm^{-3}$ agreed with that of 5·1 $g.cm^{-3}$ calculated for $4\times Sr_3NbO_{5\cdot5}$ per unit cell.

Samples of initial composition $Sr_5Nb_4O_{15}$, after reaction for 12 hours at 1400°C, gave powder patterns containing reflexions due to $Sr_6Nb_2O_{11}$, a hexagonal phase, and an orthorhombic one. Crystalline masses obtained from melts at 1800°C consisted of irregular fragments of the hexagonal material and flat plates of the orthorhombic one. The former had

$$a=5\cdot665\pm0\cdot002,\ c=3\times3\cdot827\pm0\cdot001\ \text{Å}$$

and is believed to be $Sr_5Nb_4O_{15}$. It is isostructural with the tantalum analogue characterised by Galasso & Katz (1961). The observed density was 5·3 $g.cm^{-3}$ (calculated for $Z=1$, 5·46 $g.cm^{-3}$).

The orthorhombic material mentioned above had

$$a=26\cdot79\pm0\cdot02,\ b=3\cdot991\pm0\cdot010,\ c=5\cdot703\pm0\cdot003\ \text{Å}$$

and space group $C222_1$. Since this compound was never prepared as a pure single phase and the crystals were too small for satisfactory analysis, its composition is uncertain. It appears to be isostructural with a compound, also of unknown composition, in the SrO–Ta_2O_5 system.

Crystals of $SrNb_2O_6$ were prepared by heating the material to 1850°C and quenching the melt. It appears to be isostructural with $CeNbTiO_6$ (Komkov, 1959) and with orthorhombic $CaTa_2O_6$ (Jahnberg, 1963). The experimental density of $SrNb_2O_6$ was 5·1 $g.cm^{-3}$ (calculated for $Z=4$, 5·4 $g.cm^{-3}$).

The powder patterns obtained from compositions $SrNb_6O_{16}$ and $Sr_3Nb_{10}O_{28}$ were indistinguishable and characteristic of the tetragonal bronzes. Melts of both compositions yielded crystals on cooling from 1200°C. The unit cells were both tetragonal, the former showing superlattice reflexions.

Table 1. *Compounds* MR_2O_6

	a	*b*	*c*
$SrNb_2O_6$	11·021 ± 0·007 Å	7·733 ± 0·004 Å	5·604 ± 0·002 Å
$CeNbTiO_6$	10·99	7·56	5·43
$CaTa_2O_6$	11·068	7·505	5·378

$$\begin{array}{ll} SrNb_6O_{16} & a=3\times12\cdot11\ \text{Å} \\ & c=3\cdot791 \\ & \varrho_{\text{obs}}=4\cdot8\ \text{g.cm}^{-3} \\ Sr_3Nb_{10}O_{28} & a=12\cdot11\ \text{Å} \\ & c=3\cdot791 \\ & \varrho_{\text{obs}}=4\cdot9\ \text{g.cm}^{-3}\ . \end{array}$$

The density of the tripled bronze phase agrees better with that calculated for interstitial cations, *viz.* 5·0 $g.cm^{-3}$, than with 4·5 $g.cm^{-3}$ for anion vacancies.

No further niobium-rich mixed oxides were observed when strontium carbonate–niobium pentoxide mixtures were fired at up to 1400°C.

The system BaO–Nb_2O_5

Mixed oxides reported in the literature for this system are summarized in Table 2. We prepared products corresponding to all but the first phase in the table and crystals of the last three.

Table 2. *Literature on barium niobium oxides*

	Melting point		References
$Ba_6Nb_2O_{11}$			GKW, AK
$Ba_5Nb_4O_{15}$	1542°C	congruent	RW, GK
$BaNb_2O_6$	1455	congruent	RW, CK, F
$\sim Ba_6Nb_{14}O_{41}$	1330	incongruent	RW
$Ba_3Nb_{10}O_{24}$	1290	incongruent	RW
$BaNb_6O_{16}$	1315	incongruent	RW

AK, Andreeva & Keler (1964); CK, Coates & Kay (1958); F, Francombe (1960); GK, Galasso & Katz (1961); GKW, Galasso, Katz & Ward (1959); RW, Roth & Waring (1961).

Barium-rich mixtures containing 6 or more $BaCO_3$ per Nb_2O_5, after firing for about 12 hours in platinum at 1400°C, ranged in colour from purple to black. Powder patterns of these products were identical but very faint and could not be indexed. They were not cubic and did not correspond to $Ba_6Nb_2O_{11}$ as reported. White crystals were obtained from melts at 1480°C and gave sharp powder patterns entirely different from those of the coloured materials. During these preparations the platinum containers were severely attacked and it is probable that the white crystals, as well as the coloured products, are ternary mixed oxides containing platinum in addition to barium and niobium. The crystals were body-centered tetragonal with

$$a=4\cdot012\pm0\cdot001,\ c=6\cdot386\pm0\cdot008\ \text{Å}\ .$$

The powder patterns of $BaNb_2O_6$ and $Ba_5Nb_4O_{15}$ were observed but no further work was done on these substances as their structures are already known.

Crystals of '$Ba_6Nb_{14}O_{41}$' were grown from a melt at 1330°C. The lattice was orthorhombic with

$$a=20\cdot86,\ b=36\cdot27,\ c=3\cdot878\ \text{Å}\ .$$

The density observed was 5·25 $g.cm^{-3}$, which gives $Z=3\cdot5$. It seems much more satisfactory to write the formula as $Ba_5Nb_{12}O_{35}$, when the calculated density for $Z=4$ becomes 5·34 g.cm^{-3}.

The powder patterns of $Ba_3Nb_{10}O_{28}$ and $BaNb_6O_{16}$ could not be distinguished though Roth & Waring (1961) report small differences in lattice parameters and superstructure. Crystals of $BaNb_6O_{16}$ grown from a melt at 1350 °C were tetragonal (tripled bronze type) with

$$a = 3 \times 12\cdot43,\ c = 3\cdot965\ \text{Å}\ .$$

The observed density was 4·8 g.cm^{-3}, which is in agreement with the calculated value of 4·8 g.cm^{-3} for interstitial cations. Melts of initial composition $Ba_3Nb_{10}O_{28}$ gave crystals of two kinds; platy ones with the same pseudo-cell as the above tetragonal bronze phase, and irregular ones of $Ba_5Nb_{12}O_{35}$.

The system $SrO–Ta_2O_5$

The strontium tantalum oxides previously reported are summarized in Table 3. We obtained products from solid-state reactions corresponding to the first three phases but found no evidence for $Sr_2Ta_2O_7$.

Table 3. *Literature on strontium tantalum oxides*

	Unit cell	References
$Sr_6Ta_2O_{11}$	Cubic $a=8\cdot34$ Å	B, GKW
$Sr_5Ta_4O_{15}$	Hexagonal $a=5\cdot67$ $c=11\cdot42$	GK
$SrTa_2O_6$	Tetragonal $a=12\cdot41$ $c=3\cdot90$	GKW, I
$Sr_2Ta_2O_7$	Tetragonal $a=10\cdot628$ $c=10\cdot908$	I

B, Brixner (1958); GK, Galasso & Katz (1961); GKW, Galasso, Katz & Ward (1959); I, Ismailzade (1958, 1960).

$Sr_6Ta_2O_{11}$ and $Sr_5Ta_4O_{15}$ were both formed at 1200 °C. The cubic powder pattern of the former phase was refined to $a=8\cdot323\pm0\cdot002$ Å but the pattern of $Sr_5Ta_4O_{15}$ was too weak to permit of accurate measurement.

Products from mixtures which ranged in composition from $2SrCO_3+Ta_2O_5$ to $SrCO_3+3Ta_2O_5$ showed powder patterns characteristic of the tetragonal bronze structure together with small quantities of a second phase. Crystalline material was obtained from melts of initial composition $SrTa_2O_6$ on cooling from 1800 °C. Two crystals were further studied: that of the major component had the tetragonal bronze structure with

$$a = 12\cdot304 \pm 0\cdot003,\ c = 3\cdot926 \pm 0\cdot002\ \text{Å}$$

while the other, corresponding with the minor component observed in the powder patterns of lower temperature preparations, was orthorhombic with

$$a = 27\cdot228 \pm 0\cdot007, b = 3\cdot939 \pm 0\cdot007, c = 5\cdot702 \pm 0\cdot002\text{Å}.$$

It does not appear to be related to Ismailzade's $Sr_2Ta_2O_7$ phase, but has the space group $C222_1$.

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