EDGARITE, FeNb$_3$S$_6$, FROM THE KHIBINA ALKALINE COMPLEX, RUSSIA: SOLUTION OF THE CRYSTAL STRUCTURE

Luca BINDI[§]

Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy and CNR – Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via G. La Pira 4, I-50121 Firenze, Italy

Robert F. MARTIN

Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, Québec, H3A 0E8, Canada

Abstract

The crystal structure of edgarite, a rare Fe-Nb sulfide mineral, was solved using intensity data collected from a crystal from the Khibina alkaline massif, Russia. The study revealed that the structure is hexagonal, space group $P6_3$, with cell parameters *a* 5.912(1), *c* 12.675(2) Å, and *V* 383.7(1) Å^3. Refinement of an anisotropic model led to an *R* index of 0.0392 for 580 independent reflections. One Fe and three Nb sites occur in the crystal structure of edgarite. Edgarite is shown to have the formula FeNb$^{3+}_2$Nb^{4+}S$_6$. Niobium can be expected to be chalcophile in unusually reducing crustal assemblages and to be trivalent and tetravalent in the mantle.

Keywords: edgarite, crystal structure, Nb sulfide, Khibina massif, Russia.

Introduction

The discovery of a natural occurrence of a sulfide of niobium, edgarite (Barkov *et al*. 2000), was a shock to many geochemists, to whom niobium and tantalum are quintessential lithophile elements, with a strong attraction to oxygen and generally considered to be present in the pentavalent state in crustal environments (*e.g*., Černý & Ercit 1989). As reviewed by Martin & Wülser (2014), some geochemists have even proposed that Nb^{5+} is prevalent in the mantle and that it coexists with Nb^0 in the Earth's core. In this context, it is important to document the crystal structure of edgarite, FeNb$_3$S$_6$, from its type locality, the Khibina (Khibiny) alkaline complex, Kola Peninsula, Russia, and to establish the valence state of its niobium atoms.

Crystal-Structure Solution and Refinement

A small crystal fragment ($40 \times 55 \times 70$ μm^3) was selected for the single-crystal X-ray diffraction study from a sample from the type locality, which was kindly donated to the Natural History Museum of the University of Florence by Evgeniy Semenov (Fersman Museum) in 2004. The collection of intensity data (see Table 1 for details) was carried out by means of an Oxford Diffraction Xcalibur 3 single-crystal diffractometer (enhanced X-ray source, X-ray radiation Mo*K*α, λ = 0.71073 Å) equipped with a Sapphire 2 CCD detector. A total of 1598 frames of data were collected at room temperature as six sets of omega runs, with an exposure time of 50 s per frame and a frame width of 1.00°. This afforded an overall data collection of 4413 reflections (580 unique). The refined hexagonal unit-cell parameters are *a* 5.912(1), *c* 12.675(2) Å, and *V* 383.7(1) Å^3, which are similar to those originally reported by Barkov *et al*. (2000) for the holotype and those measured for synthetic FeNb$_3$S$_6$ by Anzenhofer *et al*. (1970).

Data frames were processed using the *CrysAlis* software package (Oxford Diffraction 2006) running on the Xcalibur 3 control PC. The program ABSPACK (Oxford Diffraction 2006) was used for the absorption correction. The merging *R* for the data set decreased

---
§ *Corresponding author e-mail address*: luca.bindi@unifi.it

TABLE 1. CRYSTAL DATA AND EXPERIMENTAL DETAILS FOR THE SELECTED
EDGARITE CRYSTAL

Crystal data	
Formula	$FeNb_3S_6$
Crystal size (mm^3)	$0.040 \times 0.055 \times 0.070$
Form	block
Color	black
Crystal system	hexagonal
Space group	$P6_3$ (#173)
a (Å)	5.912(1)
c (Å)	12.675(2)
V ($Å^3$)	383.7(1)
Z	2
Data collection	
Instrument	Oxford Diffraction Xcalibur 3
Radiation type	Mo$K\alpha$ ($\lambda = 0.71073$)
Temperature (K)	293(3)
Detector to sample distance (cm)	6
Number of frames	1598
Measuring time (s)	50
Maximum covered 2θ (°)	59.38
Absorption correction	multi-scan (Oxford Diffraction 2006)
Collected reflections	4413
Unique reflections	580
Reflections with $F_o > 4\sigma(F_o)$	316
R_{int}	0.0525
R_σ	0.0783
Range of h, k, l	$-8 \leq h \leq 0$, $0 \leq k \leq 10$, $0 \leq l \leq 13$
Refinement	
Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4\sigma(F_o)$]	0.0340
Final R_1 (all data)	0.0392
S	1.02
Number refined parameters	31
$\Delta\rho_{max}$ (e $Å^{-3}$)	0.55
$\Delta\rho_{min}$ (e $Å^{-3}$)	-0.58

from 12.63% before the absorption correction to 5.25% after the correction. The statistical tests on the distribution of $|E|$ values strongly indicate the absence of an inversion center ($|E^2 - 1| = 0.746$). This information, together with the observed systematic absences (i.e., $000l = 2n + 1$), suggested space groups $P6_3$ or $P6_322$. Given that $P6_322$ is the space group reported by Anzenhofer et al. (1970), van Laar et al. (1971), and Drábek et al. (2010) for synthetic $FeNb_3S_6$, the first attempt to refine the structure was done in that space group using the atomic coordinates reported by Anzenhofer et al. (1970). The refinement of this model led to a high R index of ∼15%. At this point, a thorough analysis of the structure (based mainly upon the observation of the very large atomic displacement parameters for Nb and S atoms) suggested that the diad axes symmetry elements of

the $P6_322$ space group should be removed. The atomic position data set was then adapted to the $P6_3$ space group and the structure refined. A least-squares refinement on F^2 using the program SHELXL

TABLE 2. ATOMS, FRACTIONAL ATOM
COORDINATES, AND EQUIVALENT ISOTROPIC
DISPLACEMENT PARAMETERS ($Å^2$) FOR THE
EDGARITE CRYSTAL INVESTIGATED

Atom	x	y	z	U_{eq}
Fe	1/3	2/3	0.2397(7)	0.0450(7)
Nb1	0	0	0.0018(3)	0.0346(4)
Nb2	1/3	2/3	0.0030(4)	0.050(1)
Nb3	2/3	1/3	0.9766(4)	0.049(1)
S1	0.3196(14)	0.0163(13)	0.3693(6)	0.059(3)
S2	0.0013(11)	0.3262(12)	0.6301(8)	0.058(2)

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS OF THE ATOMS FOR THE
EDGARITE CRYSTAL INVESTIGATED

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe	0.0472(8)	0.0472(8)	0.0406(19)	0.0236(4)	0.000	0.000
Nb1	0.0347(3)	0.0347(3)	0.0344(12)	0.0173(4)	0.000	0.000
Nb2	0.0495(14)	0.0495(14)	0.052(3)	0.0247(7)	0.000	0.000
Nb3	0.0511(16)	0.0511(16)	0.044(3)	0.0255(8)	0.000	0.000
S1	0.059(3)	0.062(3)	0.057(6)	0.031(3)	0.001(2)	0.001(2)
S2	0.056(3)	0.057(3)	0.060(6)	0.027(2)	0.0012(17)	0.003(2)

(Sheldrick 2008) resulted in an R factor of $\sim$9%. The occupancy of all the sites was left free to vary (Fe *versus* vacancy, Nb *versus* vacancy, and S *versus* vacancy). All the sites were found to be consistent with full occupancy by Fe, Nb, and S, respectively, and then fixed. Neutral scattering curves for Fe, Nb, and S were taken from the *International Tables for X-ray Crystallography* (Ibers & Hamilton 1974). At the final stage, with anisotropic atomic displacement parameters for all atoms and without constraints, the residual value settled at $R1 = 3.40\%$ for 316 observed reflections [$F_o > 4\sigma(F_o)$ level] and 31 parameters and at $R1 = 3.92\%$ for all 580 independent reflections. Inspection of the difference-Fourier map revealed that maximum positive and negative peaks were 0.55 and 0.58 e$^-$/Å^3, respectively.

Experimental details and R indices are given in Table 1. Fractional atomic coordinates and isotropic displacement parameters are reported in Table 2, and the anisotropic displacement parameters are given in Table 3. A list of the observed and calculated structure-factors is available from the Depository of Unpublished Data on the MAC website [document Edgarite CM56_10.3749/canmin.1800019].

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

In the crystal structure of edgarite (Fig. 1), there are four symmetrically independent metal sites (one Fe and three Nb) and two S sites, with $Z = 2$. Fe is coordinated by six sulfur atoms, with distances ranging from 2.425 to 2.673 Å (Table 4). The Nb atoms have a distorted six-fold coordination (Fig. 2) closely resembling the trigonal prisms observed in Nb-bearing misfit-layer chalcogenides (Lafond *et al*. 1999, Deudon *et al*. 2000). Nb–S distances are in the range 2.493–2.782 Å. The most distorted site is Nb3 ($\sigma^2 = 98.82$; Robinson *et al*. 1971), whereas the Nb1 and Nb2 sites ($\sigma^2 = 56.63$ and 53.46, respectively) show values close to those observed for the two Nb positions in the structure of synthetic FeNb$_3$S$_6$ ($\sigma^2 = 54.18$ and 55.09; Anzenhofer *et al*. 1970). The highest σ^2 value

for Nb3 reflects on the cation coordination, which can actually be better described as 3+3.

We note an important difference in the unit-cell volume between edgarite (384 Å^3) and synthetic FeNb$_3$S$_6$ (351 Å^3; Anzenhofer *et al*. 1970, Drábek *et al*. 2010). We do not have a plausible explanation for the 9% increase in the unit-cell volume observed for the natural material. A qualitative chemical analysis of the edgarite crystal studied did not reveal any element beside Fe, Nb, and S. Barkov *et al*. (2000) did report the presence of 0.36% V as the main minor element, presumably present as V^{3+}, and not likely a contributing factor. Drábek *et al*. (2010) carried out a mineralogical and crystallographic study of the products synthesized in the system Fe–Nb–S. They observed an increase of the unit-cell volume as a function of the Fe/(Fe + Nb) ratio in the phases crystallizing with a hexagonal unit-cell. Synthetic phases with Fe/(Fe + Nb) $\approx$ 0.25 (the composition of edgarite) were also found to exhibit a smaller unit-cell volume, close to 350 Å^3.

The main difference with respect to synthetic FeNb$_3$S$_6$ is the fact that edgarite was solved and refined in the space group $P6_3$, whereas the synthetic compounds had been refined in the space group $P6_322$ (Anzenhofer *et al*. 1970, Drábek *et al*. 2010). Although the two structures are topologically very similar, the reduction of symmetry in edgarite allows the existence of three independent Nb sites, instead of the two (with different multiplicity) observed in the synthetic compounds. Such a diversification has important consequences for the ordering of Nb atoms with

TABLE 4. BOND DISTANCES (IN Å) IN THE
STRUCTURE OF EDGARITE

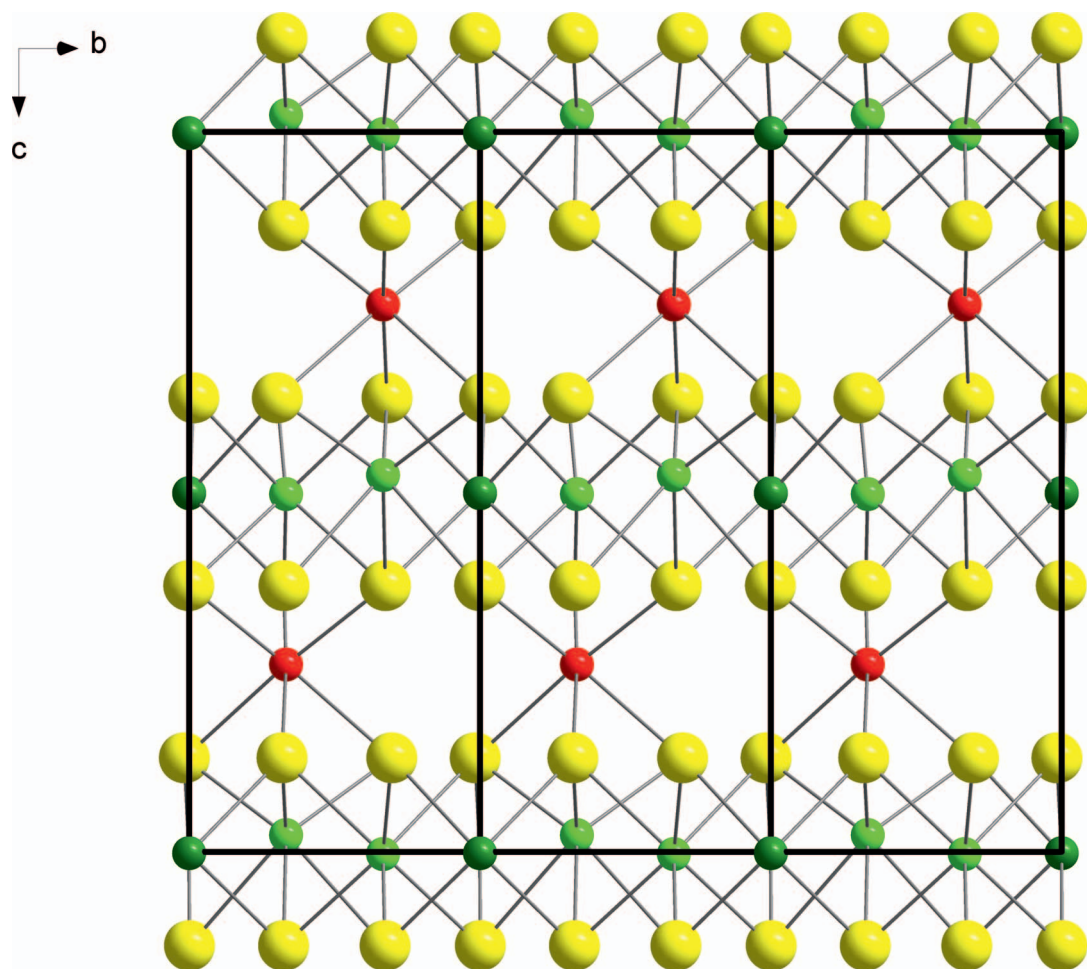|			
Fe–S1 (×3)	2.673(10)	Nb2–S1 (×3)	2.598(9)
Fe–S2 (×3)	2.435(10)	Nb2–S2 (×3)	2.568(10)
mean	2.554	mean	2.583
Nb1–S1 (×3)	2.493(9)	Nb3–S1 (×3)	2.509(9)
Nb1–S2 (×3)	2.520(9)	Nb3–S2 (×3)	2.782(11)
mean	2.507	mean	2.646

FIG. 1. The crystal structure of edgarite projected down [100]. Dark green, light green, red, and yellow spheres indicate Nb^{4+} (Nb1), Nb^{3+} (Nb2 and Nb3), Fe, and S atoms, respectively. The unit cell and the orientation of the Figure are outlined.

different valence states. Barkov *et al.* (2000) proposed the formula $Fe^{2+}Nb^{3+}_2Nb^{4+}S_6$ for edgarite. Mössbauer studies (Katada & Herber 1980, Sundararajan *et al.* 1983) revealed that the formal charge of Fe is 2+ in synthetic $FeNb_3S_6$. Barkov *et al.* (2000) proposed the above formula to obtain a charge balance to compensate for the 12 negative charges of the six sulfur atoms. Martin & Wülser (2014) considered another variant of the formula. If we calculate the bond-valence sums (using the parameters reported by Brese & O'Keeffe 1991) using the structural data reported for synthetic $FeNb_3S_6$ (Anzenhofer *et al.* 1970, Drábek *et al.* 2010), unrealistic values are obtained. The Fe atom exhibits 2.90 *v.u.* (valence units), suggestive of a trivalent state, whereas the two Nb atoms show 4.60 and 4.45 *v.u.*, indicating Nb^{5+} or a mixture of Nb^{4+} and Nb^{5+}. Such a

scenario impacts the valence state of S, which jumps to an unrealistic 2.73 *v.u.*. The bond-valence sums for edgarite, in contrast, give very reasonable values (Table 5). The values obtained for Nb2 and Nb3 (3.35 and 3.02 *v.u.*, respectively) indicate trivalent Nb at these positions. On the other hand, Nb1, with a bond-

TABLE 5. BOND VALENCE (*v.u.*) ARRANGEMENT FOR EDGARITE

	Fe	Nb1	Nb2	Nb3	Σ S
S1	$0.258^{\times 3\downarrow}$	$0.712^{\times 3\downarrow}$	$0.536^{\times 3\downarrow}$	$0.682^{\times 3\downarrow}$	2.188
S2	$0.492^{\times 3\downarrow}$	$0.662^{\times 3\downarrow}$	$0.582^{\times 3\downarrow}$	$0.326^{\times 3\downarrow}$	2.062
	2.250	4.122	3.354	3.024	

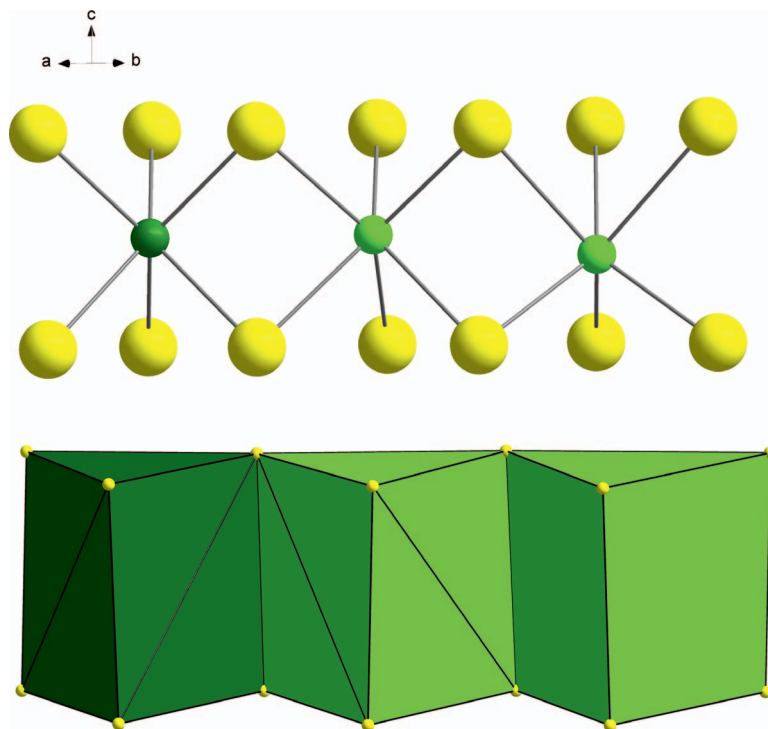Note: Calculated from the bond-valence curves of Brese & O'Keeffe (1991)

Fig. 2. A fragment of the edgarite structure showing the linking of the Nb polyhedra (top: balls and sticks; bottom: coordination polyhedra). Colors as in Figure 1. The unit cell and the orientation of the Figure are outlined.

valence sum of 4.12 *v.u.*, is in the tetravalent state in the edgarite structure. The sums for the two S atoms are 2.19 and 2.06 *v.u.*, as typically observed in sulfide structures.

PARTING REMARK

Edgarite contains Nb^{3+} and Nb^{4+} ions. Its presence in a metasomatized roof-pendant in the Khibina complex establishes the local existence in the Earth's crust of unusually reducing conditions. These presumably reflect the influence of a rising mantle-derived reducing aqueous-carbonic fluid phase (Beeskow *et al.* 2006). In the case of the Khibina complex, the assemblage contains other oddities, such as Ti-rich pyrrhotite, Fe-rich alabandite, a graphite-like material, and a tungstenite–molybdenite solid solution. Chalcophile niobium can be expected in other unusually reducing crustal environments and, of course, in the mantle. It is unfortunate that the Nb_2O_3–NbO_2 and NbO_2–Nb_2O_5 buffer curves remain uncharted territory.

ACKNOWLEDGMENTS

REFERENCES

ANZENHOFER, K., VAN DEN BERG, J.M., COSSEE, P., & HELLE, J.N. (1970) The crystal structure and magnetic susceptibilities of $MnNb_3S_6$, $FeNb_3S_6$, $CoNb_3S_6$, and $NiNb_3S_6$. *Journal of Physics and Chemistry of Solids* **31**, 1057–1067.

BARKOV, A.Y., MARTIN, R.F., MEN'SHIKOV, Y.P., SAVCHENKO, Y.E., THIBAULT, Y., & LAAJOKI, K.V.O. (2000) Edgarite, $FeNb_3S_6$, first natural niobium-rich sulfide from the Khibina alkaline complex, Russian Far North: Evidence of chalcophile behavior of Nb in a fenite. *Contributions to Mineralogy and Petrology* **138**, 229–236.

BEESKOW, B., TRELOAR, P.J., RANKIN, A.H., VENNEMANN, T.W., & SPANGENBERG, J. (2006) A reassessment of models for hydrocarbon generation in the Khibiny nepheline syenite complex, Kola Peninsula, Russia. *Lithos* **91**, 1–18.

BRESE, N.E. & O'KEEFFE, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica* **B47**, 192–197.

ČERNÝ, P. & ERCIT, T.S. (1989) Mineralogy of niobium and tantalum: crystal chemical relationships, paragenetic

aspects and their economic implications. *In* Lanthanides, Tantalum and Niobium. Mineralogy, Geochemistry, Characteristics of Primary Ore Deposits, Prospecting, Processing and Applications (P. Möller, P. Černý, & F. Saupé, eds.). Springer Verlag, Berlin, Germany (27–79).

DEUDON, C., LAFOND, A., LEYNAUD, O., MOËLO, Y., & MEERSCHAUT, A. (2000) Quantification of the interlayer charge transfer, via bond valence calculation, in 2D misfit compounds: The case of $(Pb(Mn,Nb)_{0.5}S_{1.5})_{1.15}NbS_2$. *Journal of Solid State Chemistry* **155**, 1–8.

DRÁBEK, M., HYBNER, J., RIEDER, M., & BÖHMOVÁ, V. (2010) The system Fe–Nb–S and its geological implications. *Canadian Mineralogist* **48**, 1059–1068.

IBERS, J.A. & HAMILTON, W.C., Eds. (1974) *International Tables for X-ray Crystallography*. Volume IV, Kynoch Press, Dordrecht, Netherlands, 366 pp.

KATADA, M. & HERBER, R.H. (1980) Lattice dynamics and hyperfine interactions of the intercalation compounds Fe_xTiS_2 (x = 1/4, 1/3, and 1/2) and $Fe_{1/3}NbS_2$ from ^{57}Fe Mössbauer spectroscopy. *Journal of Solid State Chemistry* **33**, 361–369.

LAFOND, A., DEUDON, C., MEERSCHAUT, A., PALVADEAU, P., MOËLO Y., & BRIGGS, A. (1999) Structure determination and physical properties of the misfit layered compound $(Pb_2FeS_3)_{0.58}NbS_2$. *Journal of Solid State Chemistry* **142**, 461–469.

MARTIN, R.F. & WÜLSER, P.-A. (2014) Niobium and tantalum in minerals: siderophile, chalcophile or lithophile, and polyvalent. *Journal of Geochemical Exploration* **147**, 16–25.

OXFORD DIFFRACTION (2006) *CrysAlis RED (Version 1.171.31.2) and ABSPACK in CrysAlis RED*. Oxford Diffraction Ltd., Abingdon, Oxfordshire, England.

ROBINSON, K., GIBBS, G.V., & RIBBE, P.H. (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science* **172**, 567–570.

SHELDRICK, G.M. (2008) A short history of SHELX. *Acta Crystallographica* **A64**, 112–122.

SUNDARARAJAN, M.D., NARAYANASAMY, A., NAGARAJAN, T., SUNANDANA, C., SUBBA RAO, G.V., NIARCHOS, D., & SHENOY, G.K. (1983) Mössbauer studies of Fe_xNbS_2 (x = 0.25, 0.33 and 0.5). *Journal of Physics and Chemistry of Solids* **44**, 773–777.

VAN LAAR, B., RIETVELD, H.M., & IJDO, D.J.W. (1971) Magnetic and crystallographic structures of Me_xNbS_2 and Me_xTaS_2. *Journal of Solid State Chemistry* **3**, 154–160.