# $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$: Halide Flux Growth of Single Crystals and $^{45}$Sc Solid-state NMR

Sarkarainadar Balamurugan[a], Ute Ch. Rodewald[a], Thomas Harmening[a], Leo van Wüllen[b], Daniel Mohr[b], Hellmut Eckert[b], and Rainer Pöttgen[a]

[a] Institut für Anorganische und Analytische Chemie and NRW Graduate School of Chemistry, Universität Münster, Corrensstraße 30, 48149 Münster, Germany
[b] Institut für Physikalische Chemie and NRW Graduate School of Chemistry, Universität Münster, Corrensstraße 30, 48149 Münster, Germany

Reprint requests to R. Pöttgen. E-mail: pottgen@uni-muenster.de

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Single crystals of $Sc_2(TO_4)_3$ with $T$ = Mo and W were synthesized from $Sc_2O_3$, $MoO_3$, and $WO_3$ at 1223 K in NaCl / KCl as solvent. Both structures were refined from X-ray diffractometer data: *Pbcn*, $a$ = 1325.1(1), $b$ = 954.9(1), $c$ = 964.4(1) pm, $wR2$ = 0.0425, 2097 $F^2$, 79 variables for $Sc_2(MoO_4)_3$ and $a$ = 1332.9(9), $b$ = 959.4(7), $c$ = 967.9(2) pm, $wR2$ = 0.0384, 1971 $F^2$, 79 variables for $Sc_2(WO_4)_3$. The structures consist of a three-dimensional network of corner-sharing $ScO_{6/2}$ octahedra and two crystallographically independent $TO_{4/2}$ tetrahedra. $^{45}$Sc MAS NMR spectra show sharp single resonances in accordance with the crystallographic data. The quadrupolar interaction parameters obtained from a simulation of the full $^{45}$Sc MAS NMR spectra are found to be in good agreement with those obtained from DFT calculations of the electric field gradient.

*Key words:* Scandium, Crystal Chemistry, Solid-state NMR

## Introduction

The complex oxides $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$ have been studied intensely for their negative thermal expansion properties and with respect to potential application as trivalent ion-conducting solid electrolytes [1 – 5]. So far more than 200 entries occur in the current SciFinder Scholar version. Single crystals of $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$ can be grown by the Czochralski technique, from precipitation routes followed by firing, or *via* flux techniques, *e. g.* $Bi_2O_3$ / $WO_3$, $Li_2MoO_4$, or $Sc_2(MoO_4)_3$ / $Cs_2MoO_4$ as flux media [6]. These fluxes are expensive and require high temperatures. Herein we present a simple growth of high-quality crystals *via* an NaCl / KCl flux for structure refinement and $^{45}$Sc NMR spectroscopy.

The $^{45}$Sc isotope has 100 % natural abundance. It has an $I$ = 7/2 nuclear spin, a gyromagnetic ratio of $6.50880 \times 10^7$ rad $T^{-1}$ $s^{-1}$, and a moderately large nuclear electric quadrupole moment $Q = 0.22 \times 10^{-28}$ m$^2$. Although these characteristics are excellent prerequisites for solid state NMR experiments, only few NMR spectroscopic reports can be found in the literature, and little is known about the correlation of the $^{45}$Sc NMR parameters with local structural data. Apart from an early work on intermetallic phases [7], which has been recently extended by us to other, more complex scandium-containing intermetallic systems [8 – 11], several laboratories (including our own) have been examining oxidic systems [12 – 24], contributing to the establishment of a comprehensive data base of $^{45}$Sc NMR interaction parameters in inorganic materials. While the experiments of the present study were conducted, a publication by Kim and Stebbins appeared reporting $^{45}$Sc chemical shift data on these materials and their solid solutions [24], however, their study did not address the nuclear electric quadrupolar interactions of the scandium nuclei. In the present study, we present a more complete analysis of the NMR spectra, including both the experimental determination and the quantum mechanical calculation of the nuclear electric quadrupolar coupling constants $C_Q$ and the asymmetry parameters $\eta_Q$, characterizing the size and symmetry of the electric field gradients present at the $^{45}$Sc nuclei in these materials.

## Experimental Section

### *Synthesis*

Starting materials used for the syntheses of the $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$ samples were $Sc_2O_3$ (ACROS Organics, > 99.5 %), $MoO_3$ and $WO_3$ (ABCR, > 99.9 %), NaCl (Merck, > 99.5 %), and KCl (Chempur, > 99.9 %). Appropriate amounts of $Sc_2O_3$ and $TO_3$ were thoroughly mixed and ground in an agate mortar under ethanol and acetone in order to obtain homogeneous starting mixtures. Then, small amounts (0.2 g) of these dried fine mixtures were mixed with a dried equimolar mixture of NaCl / KCl (0.8 g). These reaction mixtures were sealed in evacuated silica tubes and slowly heated to 1223 K within 3 h and soaked for 24 h in a muffle furnace (Carbolite RHF 1500). Subsequently the samples were slowly cooled to 773 K at a rate of 8 $\mathrm{K\,h^{-1}}$ and then cooled to room temperature at a rate of 100 $\mathrm{K\,h^{-1}}$. The products consisted of small, well-shaped crystals. They were isolated from the reaction mixtures through extraction of the flux with hot demineralized water.

### *EDX data*

Semiquantitative EDX analyses of the crystals investigated on the diffractometer were carried out with a Leica 420i scanning electron microscope with Sc, Mo, and W as standards. The experimentally observed metal ratios were close to the ideal values of 2 : 3. The oxygen content of the samples could not be determined reliably (detection limit of the instrument). No impurity elements heavier than sodium were found.

### *X-Ray diffraction*

The flux-grown samples were characterized through Guinier patterns (imaging plate detector, Fujifilm BAS-1800) with Cu$K_{\alpha 1}$ radiation and $\alpha$-quartz ($a$ = 491.30, $c$ = 540.46 pm) as an internal standard. The orthorhombic lattice parameters (Table 1) were obtained from least-squares refinements. The correct indexing was ensured through intensity calculations [25].

Well-shaped single crystals of $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$ were selected from the samples and tested by Laue photographs on a Buerger camera using white Mo radiation. Intensity data were collected on a Stoe IPDS II diffractometer (graphite-monochromatized Mo$K_\alpha$ radiation; oscillation mode). Numerical absorption corrections were applied to the data sets. All relevant details concerning the data collections and evaluations are listed in Table 1.

### *Structure refinements*

The systematic extinctions observed for both data sets were compatible with space group *Pbcn*, in agreement with previous investigations [3 – 5]. The atomic parameters from Efremov *et al.* [4] were taken as starting values, and the two structures were refined using SHELXL-97 [26] (full-matrix least-squares on $F^2$) with anisotropic atomic displacement parameters for all atoms. The final difference Fourier syntheses were flat (Table 1). The refined positions and interatomic distances are listed in Tables 2 and 3.

Table 1. Crystal data and structure refinement for $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$, $Al_2(WO_4)_3$ type, space group *Pbcn*, $Z = 4$.

| Empirical formula | $Sc_2(MoO_4)_3$ | $Sc_2(WO_4)_3$ |
|---|---|---|
| Molar mass, g $\mathrm{mol^{-1}}$ | 569.74 | 833.47 |
| *Lattice parameters (Guinier powder data):* | | |
| $a$, pm | 1325.1(1) | 1332.9(9) |
| $b$, pm | 954.9(1) | 959.4(7) |
| $c$, pm | 964.4(1) | 967.9(2) |
| Cell volume $V$, $\mathrm{nm^3}$ | 1.2203 | 1.2377 |
| Calculated density, g $\mathrm{cm^{-3}}$ | 3.10 | 4.47 |
| Crystal size, $\mu\mathrm{m}^3$ | $40 \times 140 \times 240$ | $40 \times 40 \times 100$ |
| Transmission (max/min) | 1.58 | 2.87 |
| Abs. coefficient, $\mathrm{mm^{-1}}$ | 4.1 | 28.9 |
| Exposure time, min | 4 | 8 |
| Detector distance, mm | 80 | 80 |
| $\omega$ range / increment, deg | 0 – 180 / 1.0 | 0 – 180 / 1.0 |
| Integr. parameter A / B / EMS | 14.0 / 4.0 / 0.022 | 14.0 / 4.0 / 0.020 |
| $F(000)$, e | 1056 | 1440 |
| $\theta$ range, deg | 2 – 32 | 2 – 32 |
| Range in *hkl* | −19/16, −14/13, ±14 | −15/19, −11/13, −13/14 |
| Total no. reflections | 12239 | 7678 |
| Independent reflections / $R_{\mathrm{int}}$ | 2097 / 0.0231 | 1971 / 0.0477 |
| Reflections with $I \geq 2\sigma(I)/R_\sigma$ | 1739 / 0.0237 | 1520 / 0.0510 |
| Data / parameters | 2097 / 79 | 1971 / 79 |
| $R1/wR2$ for $I \geq 2\sigma(I)$ | 0.0182 / 0.0417 | 0.0204 / 0.0368 |
| $R1/wR2$ for all data | 0.0256 / 0.0425 | 0.0350 / 0.0384 |
| Goodness-of-fit on $F^2$ | 0.945 | 0.831 |
| Extinction coefficient | 0.0127(3) | 0.0051(1) |
| Largest diff. peak / hole, e $\mathrm{Å^{-3}}$ | 0.67 / −0.80 | 1.22 / −1.97 |

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-391467 ($Sc_2(MoO_4)_3$) and CSD-391468 ($Sc_2(WO_4)_3$).

### *Solid-state NMR*

$^{45}$Sc magic-angle spinning (MAS) NMR spectra were recorded at ambient temperature at the resonance frequency of 121.5 MHz on a Bruker DSX-500 spectrometer, using a 2.5 mm MAS NMR probe operated at a rotation frequency of 20 kHz. Typical acquisition parameters were a 0.3 $\mu$s (22° solid flip angle) pulse length and a recycle delay of 0.5 s. The $^{45}$Sc NMR resonance shifts are referenced to 0.2 M aqueous scandium nitrate solution.

Table 2. Atomic coordinates and isotropic displacement parameters ($pm^2$) of $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|---|
| $Sc_2(MoO_4)_3$: | | | | | |
| Sc | 8*d* | 0.11922(3) | 0.25083(4) | 0.46561(4) | 77(1) |
| Mo1 | 8*d* | 0.14441(1) | 0.10446(2) | 0.11728(2) | 82(1) |
| Mo2 | 4*c* | 0 | 0.52747(3) | 1/4 | 87(1) |
| O1 | 8*d* | 0.02694(14) | 0.1765(2) | 0.0744(2) | 239(4) |
| O2 | 8*d* | 0.14189(16) | −0.0775(2) | 0.0920(2) | 221(4) |
| O3 | 8*d* | 0.23772(14) | 0.1788(2) | 0.0112(2) | 237(4) |
| O4 | 8*d* | 0.16999(15) | 0.1394(2) | 0.2927(2) | 197(4) |
| O5 | 8*d* | 0.08844(16) | 0.4210(2) | 0.3345(2) | 236(4) |
| O6 | 8*d* | 0.06320(18) | 0.6331(2) | 0.1298(2) | 280(5) |
| $Sc_2(WO_4)_3$: | | | | | |
| Sc | 8*d* | 0.11905(8) | 0.25078(10) | 0.46644(9) | 70(2) |
| W1 | 8*d* | 0.14410(2) | 0.10539(2) | 0.11678(2) | 78(1) |
| W2 | 4*c* | 0 | 0.52697(3) | 1/4 | 81(1) |
| O1 | 8*d* | 0.0272(4) | 0.1783(5) | 0.0715(5) | 232(10) |
| O2 | 8*d* | 0.1409(4) | −0.0775(4) | 0.0913(4) | 197(9) |
| O3 | 8*d* | 0.2378(4) | 0.1807(5) | 0.0129(4) | 229(10) |
| O4 | 8*d* | 0.1681(4) | 0.1393(4) | 0.2936(4) | 192(10) |
| O5 | 8*d* | 0.0880(4) | 0.4200(4) | 0.3353(5) | 200(10) |
| O6 | 8*d* | 0.0633(4) | 0.6332(5) | 0.1301(4) | 258(11) |

Table 3. Cation-oxygen distances (pm), calculated with the powder lattice parameters of $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$.

| | $Sc_2(MoO_4)_3$ | | | $Sc_2(WO_4)_3$ | | |
|---|---|---|---|---|---|---|
| Sc: | 1 | O3 | 205.9(2) | 1 | O3 | 206.8(5) |
| | 1 | O6 | 207.0(2) | 1 | O6 | 207.4(4) |
| | 1 | O2 | 207.7(2) | 1 | O2 | 207.6(4) |
| | 1 | O4 | 209.0(2) | 1 | O4 | 209.0(4) |
| | 1 | O1 | 209.8(2) | 1 | O1 | 210.2(5) |
| | 1 | O5 | 209.9(2) | 1 | O5 | 210.3(4) |
| *T*1: | 1 | O1 | 175.2(2) | 1 | O3 | 175.9(4) |
| | 1 | O3 | 175.5(2) | 1 | O1 | 176.4(5) |
| | 1 | O2 | 175.5(2) | 1 | O4 | 177.2(4) |
| | 1 | O4 | 175.7(2) | 1 | O2 | 177.2(4) |
| *T*2: | 2 | O6 | 175.0(2) | 2 | O6 | 176.0(4) |
| | 2 | O5 | 175.2(2) | 2 | O5 | 176.3(5) |

## Results and Discussion

### *Crystal chemistry*

Our present study has shown that the growth of small, high-quality single crystals of $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$ is also possible *via* a simple eutectic NaCl / KCl halide flux at moderate temperature. The present structure refinements fully confirm the previous data [3–5], but with slightly higher precision and well-behaved anisotropic displacement parameters, especially for the weakly scattering oxygen sites. We have refined both structures with the standard setting, space group *Pbcn*, similar to the work of Efremov *et al.* [4].

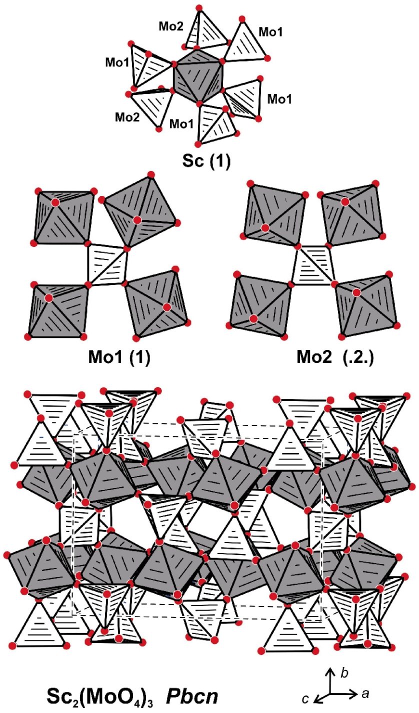

Fig. 1. (color online) The crystal structure of $Sc_2(MoO_4)_3$. A view of the unit cell approximately along the *c* axis is presented at the bottom. The connectivity patterns of the $ScO_{6/2}$ and the two crystallographically independent $MoO_{4/2}$ tetrahedra are shown in the top drawings. The site symmetries are given.

As emphasized in Fig. 1, the $Sc_2(TO_4)_3$ structures consist of a three-dimensional network of corner-sharing $ScO_{6/2}$ octahedra and two crystallographically independent $TO_{4/2}$ tetrahedra. The polyhedral connectivity patterns of the three metal sites are presented at

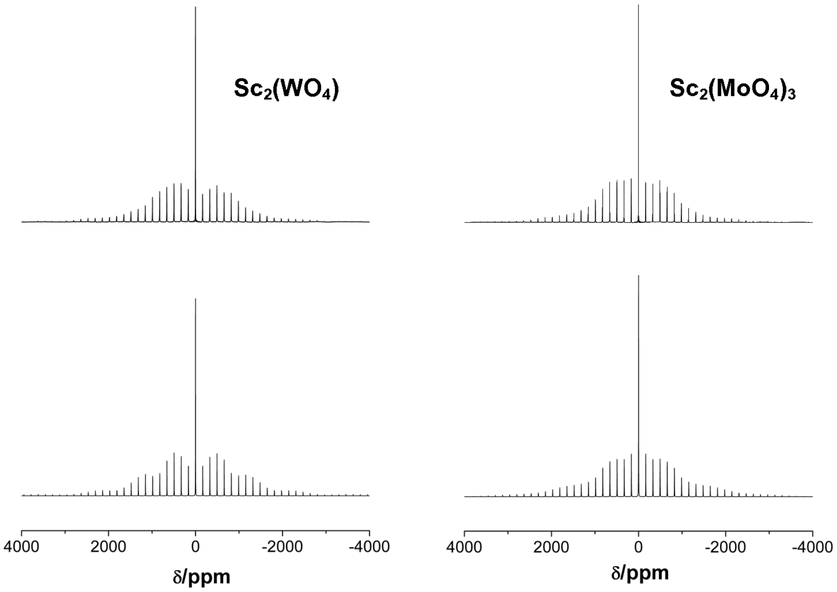

Fig. 2. top: $^{45}$Sc MAS NMR spectra of $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$; bottom: simulations of the spectra using quadrupole parameters of $C_Q$ = 2.4 MHz, $\eta_Q$ = 0.3 and $C_Q$ = 2.1 MHz; $\eta_Q$ = 0.6 for $Sc_2(WO_4)_3$ and $Sc_2(MoO_4)_3$, respectively.

the top of Fig. 1. For a more detailed crystal chemical desciption we refer to the original work [1 – 5].

The symmetry perfection of the scandium coordination is important for the $^{45}$Sc solid state NMR spectra. The $ScO_{6/2}$ octahedra are almost regular in both oxides with very small ranges in the Sc–O distances of 205.9 – 209.9 pm (Mo) and 206.8 – 210.3 pm (W).

### *$^{45}$Sc solid-state NMR*

Fig. 2 (top) shows the full width $^{45}$Sc MAS NMR spectra of $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$. The spectra are characterized by central $|1/2\rangle > \langle - \rangle | - 1/2\rangle$ transitions at 10.1 and 15.6 ppm, respectively. The NMR results are in very good agreement with those reported recently by Kim and Stebbins [24]. The unstructured, narrow resonances (having full widths at half maximum of 300 Hz (Mo) and 400 Hz (W)) indicate second order quadrupolar perturbation effects on the central transition to be negligible at 11.7 T. However, first order quadrupolar perturbations are clearly manifested by the presence of spinning sideband manifolds arising due to the effect of MAS upon the anisotropically broadened satellite Zeeman transitions. While the overall spectral region over which these sideband patterns are observed serves to estimate the magnitude of the quadrupolar coupling constant $C_Q$, the intensity distribution of the sidebands *relative to each other* contains information about the asymmetry parameter $\eta_Q$.

For a quantitative determination of these parameters, the spinning sideband patterns were simulated (Fig. 2, bottom) with the SIMPSON program package [27]. The best match (judged visually) between the experimental and the calculated sideband patterns was observed for the following quadrupolar coupling parameters: $C_Q$ = 2.4 MHz, $\eta_Q$ = 0.3 for $Sc_2(WO_4)_3$ and $C_Q$ = 2.1 MHz, $\eta_Q$ = 0.6 for $Sc_2(MoO_4)_3$. For comparison, DFT calculations, which were conducted with the WIEN2K program package [28] using the procedure and parameters described in ref. [8], yielded the following quadrupolar coupling parameters: $C_Q$ = 2.4 MHz, $\eta_Q$ = 0.4 for $Sc_2(WO_4)_3$ and $C_Q$ = 2.1 MHz, $\eta_Q$ = 0.8 for $Sc_2(MoO_4)_3$.

Systematic simulations conducted over the full range of $\eta_Q$ values ($0 \leq \eta_Q \leq 1$) (data not shown) indicate that the $\eta_Q$ values can be estimated from the experimental intensity profiles within a precision of ±0.1. Considering this error limit, the agreement between the experimental and theoretically calculated quadrupolar coupling parameters is excellent, providing validation to our crystal structure solution. The small experimental $C_Q$ values can be well understood on the basis of the high (nearly octahedral) local symmetry of the scandium atoms. The present study illustrates that for such highly symmetric Sc compounds with relatively small $C_Q$ values an analysis of first order spinning sideband manifolds is the method of choice for the experimental determination of the nuclear electric quadrupolar coupling parameters.

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