SUPPLEMENTARY INFORMATION

Cation Substitution in Defect Thiospinels: Structural and Magnetic Properties of $\text{GaV}_{4-x}\text{Mo}_x\text{S}_4$ ($0 \leq x \leq 4$)

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S.1 Thermogravimetric Data

S.2 Final Observed, Calculated and Difference Profiles for $\text{GaV}_{4-x}\text{Mo}_x\text{S}_8$ Phases at 300K ($x = 1, 2, 3$) and 150K ($x = 4$) Described in the Space Group $F\bar{4}3m$

S2.1: GaV_3MoS_8 – (a) HRPD backscattering bank; (b) HRPD 90° bank (upper tick marks: minority phase; lower tick marks: majority phase)

S2.2: $\text{GaV}_2\text{Mo}_2\text{S}_8$ – (a) HRPD backscattering bank; (b) HRPD 90° bank

S2.3: GaVMo₃S₈ – (a) HRPD backscattering bank; (b) HRPD 90° bank

S2.4: GaMo₄S₈ (at 150K) – (a) HRPD backscattering bank; (b) HRPD 90° bank (upper tick marks: Mo; lower tick marks: GaMo₄S₈)

S.3 Final Observed, Calculated and Difference Profiles for $\text{GaV}_{4-x}\text{Mo}_x\text{S}_8$ Phases ($x = 1, 3$) at 4.2K Described in the Space Group $F\bar{4}3m$

S3.1: GaV_3MoS_8 – (a) HRPD backscattering bank; (b) HRPD 90° bank (upper tick marks: minority phase; lower tick marks: majority phase)

S3.2: GaVMo₃S₈ – (a) HRPD backscattering bank; (b) HRPD 90° bank

**S4: A Comparison of the Calculated Profile in the Region 1.60-180Å Using a Peak Shape
Incorporating Terms to Account for Strain (top) with that Obtained Omitting these Terms
(bottom)**

S5.1: Final refined parameters for $\text{GaV}_{4-x}\text{Mo}_x\text{S}_8$ ($1 \leq x \leq 3$) phases at 4.2K described in the space group $F-43m^a$.

		x in $\text{GaV}_{4-x}\text{Mo}_x\text{S}_8$		
		1 ^b	2	3
	a/Å	9.67683(4)	9.69596(4)	9.72928(3)
Ga	B/Å ²	0.73(4)	0.54(3)	1.11(5)
B ^c	x	0.5998(2)	0.60129(9)	0.60215(7)
	B/Å ²	0.16(6)	0.35(3)	0.08(2)
S(1)	x	0.3686(2)	0.3673(2)	0.3660(2)
	B/Å ²	0.66(5)	0.87(4)	1.07(2)
S(2)	x	0.8641(2)	0.8646(2)	0.8643(2)
	B/Å ²	0.49(5)	0.64(5)	1.07(2)
R _{wp} /° (neutron)	(2θ = 168°)	3.91	4.27	5.44
	(2θ = 90°)	2.88	3.48	4.14

^aGa on 4(a): (0,0,0); B, S(1) and S(2) on- 16(e): (x,x,x).

^b Parameters are given for the majority phase (weight fraction 61%)

^cSite occupancy factors set at the values determined at room temperature.

S5.2: Bond Lengths (Å) and Angles (°) for the Cubic Form of $\text{GaV}_{4-x}\text{Mo}_x\text{S}_8$ ($1 \leq x \leq 3$) at 4.2K

	x in $\text{GaV}_{4-x}\text{Mo}_x\text{S}_8$		
	1 ^a	2	3
Ga-S(2)	$4 \times 2.278(3)$	$4 \times 2.274(3)$	$4 \times 2.286(3)$
B-S(1)	$3 \times 2.279(2)$	$3 \times 2.309(2)$	$3 \times 2.340(3)$
B-S(2)	$3 \times 2.605(3)$	$3 \times 2.596(2)$	$3 \times 2.592(2)$
B-B	$6 \times 2.732(2)$	$6 \times 2.778(2)$	$6 \times 2.811(2)$
S(2)-Ga-S(2)	$6 \times 109.471(-)$	$6 \times 109.471(-)$	$6 \times 109.471(-)$
S(1)-B-S(1)	$3 \times 104.2(1)$	$3 \times 103.98(7)$	$3 \times 104.06(6)$
S(1)-B-S(2)	$6 \times 88.96(8)$	$6 \times 88.78(7)$	$6 \times 88.65(7)$
S(2)-B-S(2)	$3 \times 73.7(1)$	$3 \times 74.53(8)$	$3 \times 74.72(9)$

^a Parameters are given for the majority phase (weight fraction 61%)