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Short Communication

Low-Temperature Structural Phase Transition in $SrMo_6S_8$ Studied by X-Ray Powder Diffraction

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Abstract. Lattice parameters as a function of temperature for, and atomic coordinates of the low-temperature phase of, $SrMo_6S_8$ are reported from X-ray powder diffraction. The structure transforms at $T_l = 135(3)$ K from the rhombohedral high-temperature modification ($R\bar{3}$, $a_{rh} = 6.5630(3)$ Å, $\alpha_{rh} = 88.9982(2)°$, $V_{rh} = 282.55(5)$ Å^3 at 298 K) into the triclinic low-temperature modification ($P\bar{1}$, $a_{tr} = 6.481(1)$ Å, $b_{tr} = 6.572(1)$ Å, $c_{tr} = 6.611(1)$ Å, $\alpha_{tr} = 89.246(4)°$, $\beta_{tr} = 89.304(4)°$, $\gamma_{tr} = 88.169(4)°$, $V_{tr} = 281.4(2)$ Å^3 at 20 K). The triclinic distortion is larger than in the Ca analogue, and similar to the Ba and Eu analogues.

Keywords. Chevrel phases; Crystal structure; Phase transition; X-ray analysis; Rietveld refinement; Powder diffraction.

Untersuchung des Tieftemperatur-Phasenübergangs von $SrMo_6S_8$ mittels Röntgenpulverdiffraktometrie (Kurze Mitt.)

Zusammenfassung. Die Temperaturabhängigkeit der Gitterparameter und die Atomlagen der Tieftemperaturphase von $SrMo_6S_8$ wurden mittels Röntgenpulverdiffraktometrie bestimmt. Die rhomboedrische Hochtemperaturmodifikation ($R\bar{3}$, $a_{rh} = 6.5630(3)$ Å, $\alpha_{rh} = 88.9982(2)°$, $V_{rh} = 282.55(5)$ Å^3, $T = 298$ K) wandelt bei $T_l = 135(3)$ K in die trikline Tieftemperaturmodifikation ($P\bar{1}$, $a_{tr} = 6.481(1)$ Å, $b_{tr} = 6.572(1)$ Å, $c_{tr} = 6.611(1)$ Å, $\alpha_{tr} = 89.246(4)°$, $\beta_{tr} = 89.304(4)°$, $\gamma_{tr} = 88.169(4)°$, $V_{tr} = 281.4(2)$ Å^3, $T = 20$ K) um. Die trikline Deformation ist stärker ausgeprägt als in der Ca-Verbindung und ähnlich jener der Ba- and Eu-Verbindung.

Introduction

Evidence for a low-temperature structural phase transition in $SrMo_6S_8$ was first reported from specific-heat measurements by Lachal et al. [1]. The transition occurred at $T_l = 134$ K and led from a rhombohedral high-temperature modification to a presumably triclinic low-temperature modification. Cell parameters for the low-temperature modification were later reported from X-ray single-crystal diffraction by Kalsbach et al. [2], and an X-ray single-crystal structure refinement of the high-temperature modification was reported by Kubel and Yvon [3]. In contrast to the rhombohedral-to-triclinic phase transitions in the analogues $CaMo_6S_8$ [4],

$BaMo_6S_8$ [5, 6, 7] and $EuMo_6S_8$ [7, 8], the structural transition in $SrMo_6S_8$ is not yet well characterized. In this communication we report lattice parameters as a function of temperature from X-ray powder diffraction, and a structure refinement of the triclinic low-temperature modification by the Rietveld profile fitting method [9].

Experimental

The preparation of the sample was described previously [1]. The powder contained the known rhombohedral $SrMo_6S_8$ phase and traces of the monoclinic Mo_2S_3 phase [12]. It was investigated on a Guinier diffractometer (CuKα_1 radiation) equipped with a low-temperature helium closed-cycle cryostat [10]. Cell parameters were determined at 25 different temperatures in the temperature interval between 295 K and 20 K from least-squares refinements of measured diffraction angles for about 50 reflections in the 2θ interval between 6° and 97°. The results are represented in Fig. 1. Atomic coordinates of the rhombohedral high-temperature and the triclinic low-temperature modification were refined from diffraction patterns recorded in the 2θ intervals 6°–90° at 298 K, and 8°–97° at 20 K [counting time: 10 s/step, step width: 0.02° (2θ)], by using a profile fitting routine [11]. The

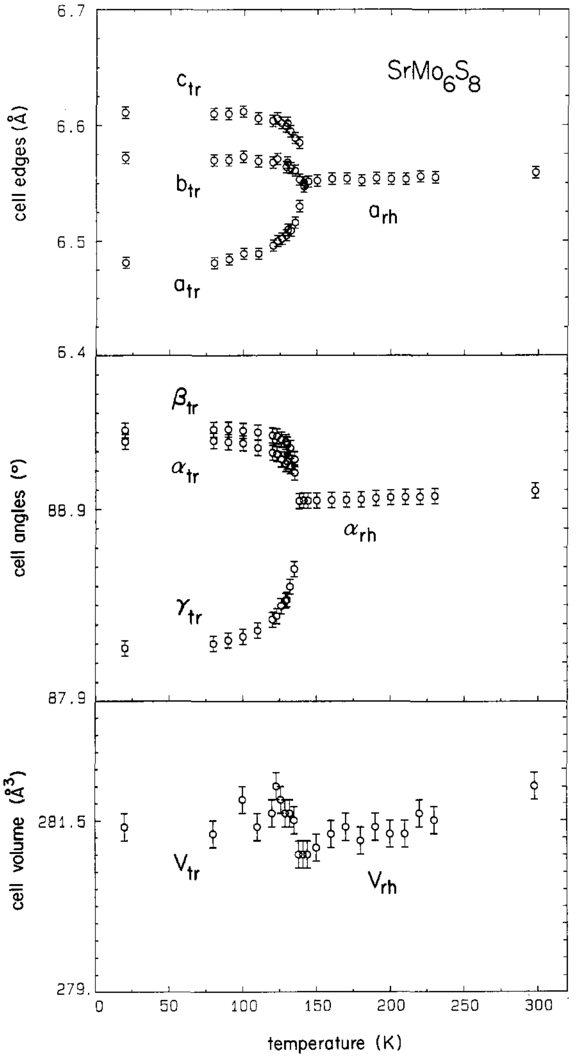

Fig. 1. Cell parameters of $SrMo_6S_8$ powder as a function of temperature; error bars: 2σ, volume: 1σ

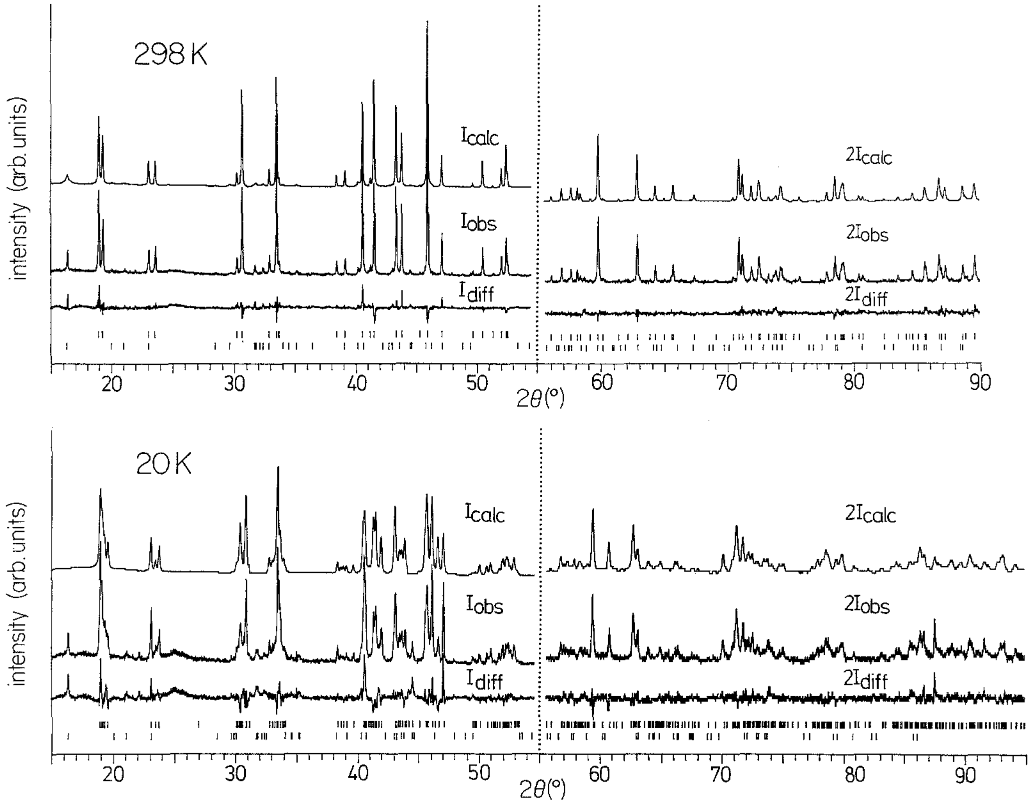

Fig. 2. Calculated, I_{calc}, versus observed, I_{obs}, and difference $I_{diff} = I_{obs} - I_{calc}$, patterns for the rhombohedral high-temperature modification at 289 K (top) and the triclinic low-temperature modification at 20 K (bottom) of $SrMo_6S_8$. Reflections of $SrMo_6S_8$, and of the Mo_2S_3 impurity phase are marked by the top and bottom rows of lines, respectively. Notice the different intensity scales for the patterns with $2\theta > 55°$

number of refined parameters for the 298 K data was 46 (26 atomic, 2 scale, 10 profile, 6 cell parameters, zero point, sample height), and for the 20 K data 58 (32 atomic, 2 scale, 10 profile, 12 cell parameters, zero point, sample height), including those of the secondary phase Mo_2S_3 that also shows a low-temperature phase transition [12]. The observed and calculated diffraction patterns are represented in Fig. 2, and the results of the refinements are summarized in Table 1[1].

Results and Discussion

The temperature dependence of the cell parameters (Fig. 1) confirms the rhombohedral-to-triclinic phase transition. The transition temperature, $T_1 = 135(3)$ K, is consistent with the results of previous specific-heat ($T_1 = 139$ K [1]) and electric conductivity ($T_1 = 134$ K [2]) measurements. The increase of the triclinic cell volume at T_1 ($\delta V = 0.5(3)$ Å^3) is similar to that of the Ca and Eu congeners, and the triclinic lattice splitting ($\delta a_{tr} = 0.12$ Å, $\delta \alpha_{tr} = 1.0°$ at 20 K) is similar to that of the Eu and Ba congeners (for data see Table 1 of Ref. [4]). The triclinic distortion of

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[1] Lists of intensity data and bond distances may be obtained from the Fachinformationszentrum Energie-Physik-Mathematik (CSD-54589), D-7514 Eggenstein-Leopoldshafen, Germany

Table 1. Structure parameters and refinement results for $SrMo_6S_8$

$T = 298$ K

Space group $R\bar{3}$ (rhombohedral setting)

Cell parameters	
	$a_{rh} = 6.5630(3)$ Å
	$\alpha_{rh} = 88.9982(2)°$
	$V_{rh} = 282.55(5)$ Å^3

Coordinates	x	y	z
Sr	0.000	0.000	0.000
Mo	0.2290(4)	0.4192(2)	0.5631(3)
S 1	0.379(2)	0.1308(4)	0.7357(1)
S 2	0.2410(2)	0.2410(2)	0.2410(2)

Agreement indices $R_p = 0.14$, $R_{wp} = 0.18$, $R_I = 0.10$

$T = 20$ K

Space group $P\bar{1}$

Cell parameters	a	b	c
	6.481(1) Å	6.572(1) Å	6.611(1) Å
	α	β	γ
	89.246(4)°	89.304(4)°	88.169(4)°
	V		
	281.4(2)°		

Coordinates	x	y	z
Sr	0.0000	0.0000	0.0000
Mo 1	0.231(1)	0.564(1)	0.417(1)
Mo 2	0.418(1)	0.232(1)	0.568(1)
Mo 3	0.567(1)	0.418(1)	0.226(1)
S 1	0.126(3)	0.385(4)	0.765(1)
S 2	0.232(3)	0.255(3)	0.225(3)
S 3	0.373(3)	0.718(3)	0.123(3)
S 4	0.748(4)	0.144(3)	0.359(3)

Agreement indices $R_p = 0.15$, $R_{wp} = 0.19$, $R_I = 0.11$

the Mo_6 octahedra in all these compounds is very similar and rather small. In the Sr compound, for example, the Mo-Mo bond distances in the triclinic low-temperature modification at 20 K differ by only up to 0.04 Å from those in the rhombohedral modification at room temperature. Such small displacements are presumably responsible for the strongly reduced electronic density of states in that compound [1], and for the observed semi-conducting behaviour in the Eu compound [13]. In the Ca compound the situation is not yet clear because of a possible influence of non-stoichiometry [14]. A triclinic lattice distortion was reported at $T_t = 50$ K in a nearly stoichiometric and presumably non-superconducting crystal [4], whereas superconductivity was reported in a Ca-deficient crystal ($Ca_{0.94}Mo_6S_8$: $T_c = 9.5$ K at ambient pressure [14]). Stoichiometric Eu, Sr and Ba compounds become superconducting only under pressure (above 1 GPa for $EuMo_6S_8$ [15]; above 2 GPa for $BaMo_6S_8$ [15]; above 11 kbar for $SrMo_6S_8$ [16]). The suppression of the low-temperature structural phase transition by pressure in these compounds is likely but not yet proven.

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References

[1] Lachal B., Baillif R., Junod A., Muller J. (1983) Sol. State Commun. **45**: 849

[2] Kalsbach W. A., Freiburg Ch., Poppe U., Takabatake T., Pobell F. (1983) Phys. Lett. **98 A**: 364

[3] Kubel F., Yvon K. (1987) Acta Cryst. **C 43**: 1655

[4] Kubel F., Yvon K. (1989) Sol. State Commun. **72**: 1219

[5] Jorgensen J. D., Hinks D. G. (1986) Physica **136 B**: 485

[6] Jorgensen J. D., Hinks D. G., Felcher G. P. (1987) Phys. Rev. **B 35**: 5365

[7] Kubel F., Yvon K. (1990) Acta Crystallogr. **C 46**: 181

[8] Kubel F., Yvon K., Ihringer J., Werner P.-E. (1988) Phys. Rev. **B 37**: 5814

[9] Rietveld H. M. (1967) Acta Cryst. **22**: 151; (1969) J. Appl. Crystallogr. **2**: 65

[10] Ihringer J. (1982) J. Appl. Crystallogr. **15**: 1

[11] Joung R. A., Wiles D. B. (1982) J. Appl. Crystallogr. **15**: 430, modified by Sakthivel, A. (version DBW 3.2 S-8804)

[12] De Jonge R., Popma T. J. A., Wiegers G. A., Jelinek F. (1970) J. Sol. State Chem. **2**: 188; see also Deblieck et al. (1983) Phys. Stat. Sol. (a) **77**: 249

[13] Peña O., Horyn R., Geantet C., Gougeon P., Padiou J., Sergent M. (1986) J. Sol. State Chem. **63**: 62

[14] Geantet C., Padiou J., Peña O., Sergent M., Horyn R. (1987) Sol. State Comm. **64**: 1363

[15] Yao Y. S., Guertin R. P., Hinks D. G., Jorgensen J., Capone II D. W. (1988) Phys. Rev. **B 37**: 5032

[16] Kalsbach W. A., McCallum R. W., Poppe U., Pobell F., Shelton R. N., Klavins P. (1982) In: (Buckel W., Weber W., eds.) Proc. IVth Conf. Superconductivity in d- and f-Band Metals. Kernforschungszentrum Karlsruhe, p. 185

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