Synthesis, Structure, Magnetic and Electric Transport Properties of $Mo_{0.5}Si_{0.5}Se_{1.94}$

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Abstract

A new phase with the composition $Mo_{0.5}Si_{0.5}Se_{1.94}$ has been synthesised by the standard ceramic method. X-ray diffraction studies show that the phase crystallizes in hexagonal unit cell (a=17.452Å and c=6.463Å). The molar magnetic susceptibility measurements as a function of temperature suggest that the phase is diamagnetic and magnetic susceptibility is temperature independent. The electrical resistivity measurements as a function of temperature suggest that the phase is semi-conductor in nature in the temperature range 300K-500K and the conduction occurs via thermally activated mechanism. Anomaly at around 344 K, shows a variation in the energy of activation. The thermal analysis suggests that above 673 K there is mass loss of about 4% and at low temperature (496.9K), there is phase transformation which results polymerisation process.

Keywords: Mixed binary dichalcogenides, XRD, electrical resistivity, TG-DTA

Introduction:

Binary dichalcogenides of numerous elements with composition MX_2 and their mixed analogues $M_{1-x}M'X_2$ (M and M′ are different transition elements; X=S, Se or Te) are known in the literature [1, 2]. Many dichalcogenides with reduced content of X are also known [3, 4]. It has been reported that structure and physical properties substantially vary with change in composition [1, 2, 3, 4]. It was thought interesting to prepare mixed chalcogenides with composition $M_{0.5}M'_{0.5}X_2$ study of their crystal structure& follow their physical properties as function of temperature.

In the present study, synthesis of a new phase with the composition $Mo_{0.5}Si_{0.5}Se_2$ has been reported. Its crystal structure has been determined from the powder X-ray diffraction data. Magnetic and electric transport properties have been studied in the temperature range 80K-300K and 300K-500K respectively. The phase has been analyzed for thermogravimeteric analysis (TGA) and differential thermogravimeteric analysis (DTGA).

Experiment

Synthesis Aldrich make Molybdenum (Mo) Silicon (Si) and Selenium (Se) elements (purity 99.9%) have been used for synthesis of the new phase. The constituentelements weighed corresponding to the stoichiometry $Mo_{0.5}Si_{0.5}Se_{1.94}$ were mixed and homogenized by grinding in cyclohexane.The dried and homogenized mixture, pressed into pellets in hydraulic press was placed in quartz tube and

evacuated to ~10^{-5} Torr, vacuum sealed and was heat- treated at 1048K for 72 hours. The mixture during the heat treatment was subjected to a number of intermediate grindings, pelletizing and sealing undersame conditions for the completion of the reaction. The final product was pulverized to fine powder for further investigations [5, 6, 7].

Elemental Analysis

The phase was further analyzed by atomic absorption spectrophotometry, which is one of the most prevalent methods for the trace element analysis [8, 9, 10]. The results of chemical elemental analysis [11, 12] and the atomic absorption spectrophotometry are in good agreement. The data are given in Table 1.

Table 1: Analytical data of the phase ($Mo_{0.5}Si_{0.5}Se_{1.94}$).
The theoretical value is given parenthesis.Analysis (%)

Phase	Mo	Si	Se
$Mo_{0.5}Si_{0.5}Se_{1.94}$	21.57 (21.81)	6.26 (6.38)	69.64 (71.80)

X-ray Diffraction studies

Room temperature powder X-ray diffraction data of the product were recorded on a Stoe-powder diffraction system and a Philips diffractometer at a scanning speed of 1deg./minute in the 2θ range using CuKα and FeKα radiations [13, 14 and 15].The X- ray diffraction data are given in the Table 2, while the X-ray pattern, intensity, versus 2θ is drawn in the figure1.

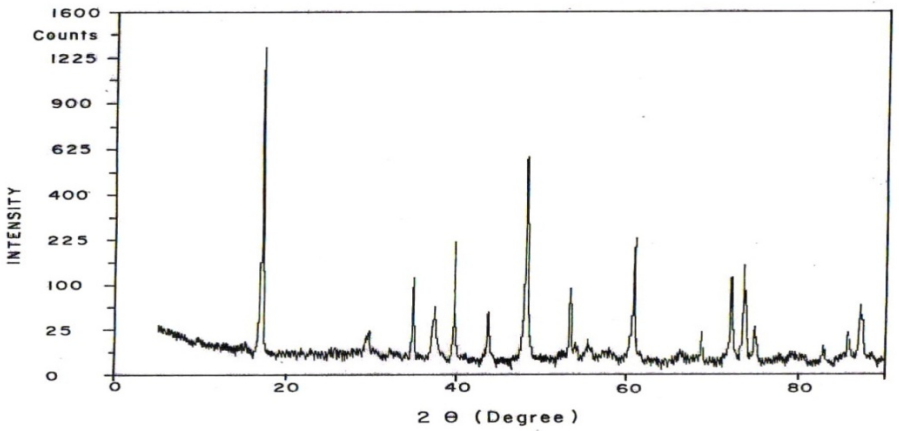

Figure 1: *X-ray Diffraction pattern of $Mo_{0.5}Si_{0.5}Se_{1.94}$*

Magnetic Susceptibility Measurement

Magnetic susceptibility of the powdered phase was recorded in a Faraday balance provided with Polytronic Faraday-type electromagnet and a Mettler microbalance. Specially fabricated Dewar flask of the size which could be adjusted within pole gaps of electromagnet was used for keeping liquid nitrogen, which surrounded the phase crucible [16, 17]. The phase was held hanging in the inner tube of the Dewar

flask with a fine thread. Magnetic susceptibility in the temperature range 77K-300K could be measured by this arrangement.

Electrical Resistance study

Electrical Resistivity of thin pellet of the phase as a function of temperature in a continues flow of nitrogen was recorded by four probe method in a four probe cell, using Keithley programmable constant current supply source model 224 and nanovoltmeter model 181 for the purpose of current source and voltage measurement respectively [18,19]. The bottom surface of the pellet was kept non-conducting. The data of specific resistance (ρ) as a function of temperature are given in Table 4, while the log ρ versus 1/T data are plotted in the figure2.

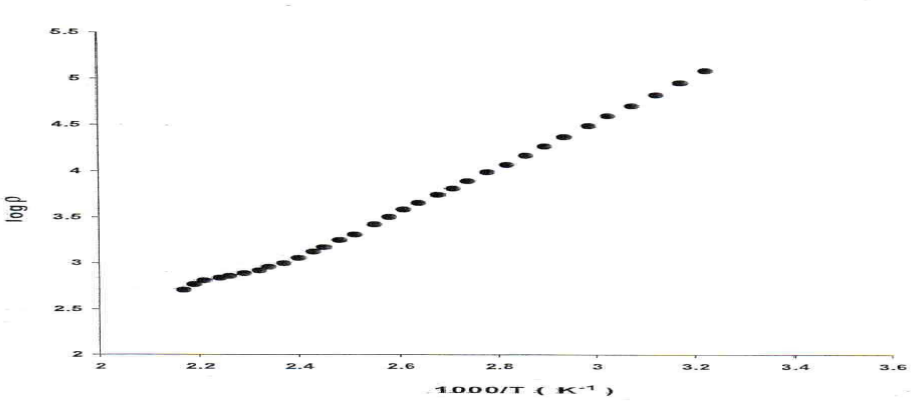

Figure 2: Log ρ versus1/T plot of $Mo_{0.5}Si_{0.5}Se_{1.94}$

Thermal Analysis

The phase has been thermally analyzed for thermogravimeteric (TG) and differential thermal analysis (DTA) by Rigaku Thermal Analysis System 8150, provided with a microprocessor, in the temperature range 300K-873K at the heating rate of 10 deg./min in continuous flow of nitrogen [20, 21]. The TG and DTA plot is given in figure 3.

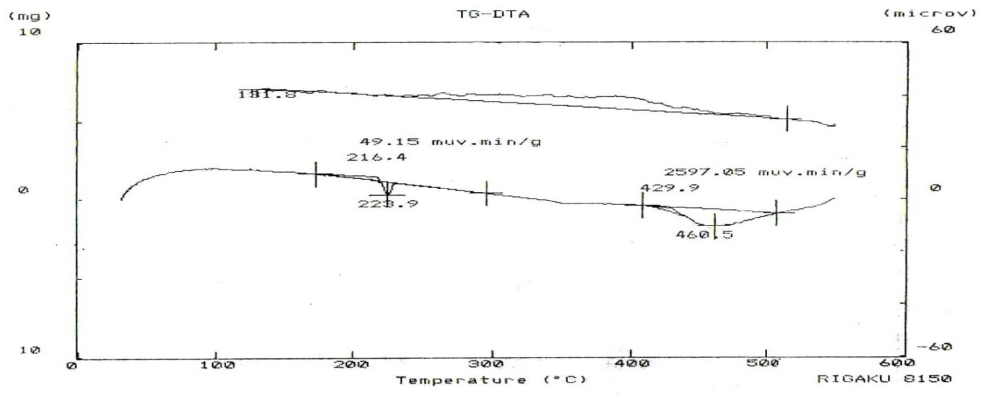

Figure 3: TG-DTA Curves of $Mo_{0.5}Si_{0.5}Se_{1.94}$

Results and Discussion

Crystal Structure

The unit cell parameters of the phase were calculated from X-ray diffraction data (Table 2). The indexing of the data shows that it crystallises in hexagonal unit cell (a=17.452Å and c=6.463Å). In order to determine the crystal structure, the theoretical X-ray diffraction data were generated by Treor and Lazy-Pulverix analysis. The $\mathbf{d_{cal}}$ values computed from data are in good agreement with the experimental interplanar distances. The data along with the assigned **h k l** values are given in the Table 2.

Table 2: Powder X-ray Diffraction Data of $Mo_{0.5}Si_{0.5}Se_{1.94}$

h	k	l	d_{obs} (Å)	d_{cal}(Å)	I_{obs}
0	0	1	6.463	6.468	100.0
4	0	0	3.778	3.781	1.2
0	0	2	3.232	3.234	8.4
5	0	0	3.014	3.025	3.9
4	2	0	2.849	2.858	17.8
4	2	1	2.607	2.614	3.1
0	0	3	2.154	2.156	7.0
1	0	3	2.134	2.134	0.8
5	1	2	2.080	2.080	0.7
3	1	3	1.914	1.917	19.2
7	1	1	1.910	1.913	11.6
7	2	1	1.775	1.776	0.3
4	2	3	1.718	1.721	1.5
9	0	0	1.679	1.680	0.2
7	3	1	1.645	1.645	8.4
6	3	2	1.641	1.641	6.3
0	0	4	1.616	1.617	13.2
3	2	4	1.464	1.465	0.6
5	0	4	1.424	1.426	1.5
7	2	3	1.402	1.403	2.9

a = b= 17.452Å $\quad\quad$ $\alpha = \beta = 90^0$

c = 6.463Å $\quad\quad$ $\gamma = 120^0$

Magnetic susceptibility studies

The molar magnetic susceptibility measurements as a function of temperature suggest that the phase is diamagnetic and magnetic susceptibility is temperature independent.

Electric Transport Properties

The electrical resistivity of the phase ($Mo_{0.5}Si_{0.5}Se_{1.94}$), as function of temperature, is plotted (*log ρ versus1/T*) in figure 2. The negative temperature co-efficient of resistivity and the values of the specific resistance (Table.3) suggest that the phase is semi-conductor in nature and the electrical conduction occurs via thermal activated mechanism. However, as a result of change in slope at around 344 K the energy of activation (E_a) shows variation.

Table 3: Specific resistance (log ρ) of $Mo_{0.5}Si_{0.5}Se_{1.94}$ as function of temperature (K).

Temperature (K)	Specific resistance ρ (ohm cm)
309	1.276×10^{5}
314	9.437×10^{4}
319	7.009×10^{4}
324	5.257×10^{4}
329	4.081×10^{4}
334	3.233×10^{4}
339	2.454×10^{4}
344	1.926×10^{4}
349	1.521×10^{4}
354	1.221×10^{4}
359	1.013×10^{4}
364	8.00×10^{3}
368	6.759×10^{3}
373	5.632×10^{3}
378	4.590×10^{3}
383	3.980×10^{3}
387	3.304×10^{3}
392	2.696×10^{3}
397	2.102×10^{3}
402	1.834×10^{3}
407	1.524×10^{3}
411	1.368×10^{3}
416	1.156×10^{3}
421	1.021×10^{3}
426	9.168×10^{2}
431	8.453×10^{2}
436	7.785×10^{2}
441	7.246×10^{2}
446	7.043×10^{2}
451	6.459×10^{2}
456	6.008×10^{2}
460	5.182×10^{2}

Table4: Magnetic and Electric Transport Parameters of ($Mo_{0.5}Si_{0.5}Se_{1.94}$) phase.

Phase	μ_{eff} (B.M)	μ_{theo}(B.M)	E_a(eV)
$Mo_{0.5}Si_{0.5}Se_{1.94}$	Diamagnetic	-	0.50 **(309-421 K)** 0.30 **(426-460K)**

Thermal Analysis:

The thermogravimeteric analysis (TGA) of $Mo_{0.5}Si_{0.5}Se_{1.94}$ fig. 3 suggests that the phase is almost stable between 403K and 673K and above 673K and above 673 K there is mass loss of about 4%. In the temperature range 489.4K – 498.8K there is an endothermic peak with peak temperature 496.9 K in the differential analysis (DTA) curve. The peak is attributed to phase transformation process which in this case is considered to be polymerization process.

Conclusion

A new phase with the composition $Mo_{0.5}Si_{0.5}Se_{1.94}$ has been synthesised by the standard ceramic method. On the basis of Lazy-Pulverix analysis of the X-ray diffraction data it is concluded that the phase crystallises in hexagonal unit cell. The molar magnetic susceptibility measurements as a function of temperature suggest that the phase is diamagnetic and magnetic susceptibility is temperature independent. The study of electrical resistivity in the temperature range 300K-500K shows that the compound is an electrical semi-conductor and conduction occurs via thermal activated mechanism, however an anomaly at around 344 K shows a variation in the energy of activation (E_a). The thermal analysis suggests that there is mass loss of about 4% above 673 K and at low temperature (496.9K), there is phase transformation which results polymerisation process.

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