Synthesis, Structure, and Magnetic Properties of $La_3Cd_2S_{6.45}$

SHARMA P. K.[1] AND SHARMA INDU B. [2]

[1]Govt. Degree College Sarh Bagga, Mahore, Reasi, 182315, India.
[2]ISCAS, Institute of Solid State and Material Science, Jammu University Campus, Jammu.
Corresponding author: drpksharma59@gmail.com

Abstract

A new phase with the composition $La_3Cd_2S_{6.45}$ has been synthesized by the standard ceramic method. X-ray diffraction studies show that the phase crystallizes in the RP-type (n=3) structure with tetragonal unit cell (a=4.938Å and c=25.806Å). The phase is diamagnetic and magnetic susceptibility is temperature independent.

Keywords: $La_3Cd_2S_{6.45}$, RP-type, XRD studies, Magnetic Properties.

Introduction

Ruddlesden-Popper-type sulphide phases have been subject matter of intense studies for their wide range of properties. These phases are represented by the composition $A_{n+1}B_nS_{3n+1}$ where usually B-site is occupied by one or more transition metal ion (s). Phases of Zr and Hf with n=1, 2 and 3 are known in literature [1-5]. It has been observed that these phases, generally crystallize in the phase group 14/mmm or Fmmm with tetragonal or orthorhombic unit cell. As compared to the corresponding oxides of Ruddlesden-Popper type phases, the cell dimensions of sulphides are much extended and transition metal atoms are unusually in distorted octahedral geometries with varying M-S distances. $Ba_3Zr_2S_7$ is reported to have space group Cccm with orthorhombic unit cell, while Ba-Zr-S (n=3) phase crystallizes in the space group Fmmm with orthorhombic unit cell [2].

In the present paper, synthesis of a new RP-type phase with the composition $La_3Cd_2S_{6.45}$ has been reported. The deficiency in sulphur is the result of loss of S (3) with position co-ordinates (0, 0.5, and 0.096). However the other S-position remains unaffected as a result of this structural deformation. Its crystal structure has been determined from the power X-ray diffraction data.

Experiment

Synthesis

Aldrich makes Lanthanum (La) Cadmium (Cd) and Sulphur (S) elements (purity 99.9%) have been used for synthesis of the new phase. The constituent elements weighed corresponding to the stoichiometry $La_3Cd_2S_{6.45}$, 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 $\sim 10^{-5}$ Torr, vacuum sealed and was heat- treated at 1273K for 72 hours. The mixture during the heat treatment was subjected to a number of intermediate grindings, pelletizing and sealing under same conditions for the completion of the reaction. The final product was pulverized to fine powder for further investigations [6-8].

Elemental Analysis

The phase was further analyzed by atomic absorption spectrophotometry, which is one of the most prevalent methods for the trace element analysis [9-11]. The results of chemical elemental analysis [12, 13] and the atomic absorption spectrophotometry are in good agreement. The data are given in Table 1.

Table 1: Analytical data of the phase ($La_3Cd_2S_{6.45}$).
The theoretical value is given parenthesis. Analysis (%)

Phase	La	Cd	S
$La_3Cd_2S_{6.45}$	47.99 (48.13)	25.81 (25.96)	23.87 (25.91)

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 [14-18]. The X- ray diffraction data are given in the Table 2, while the X-ray pattern, intensity, versus 2θ is drawn in the figure1.

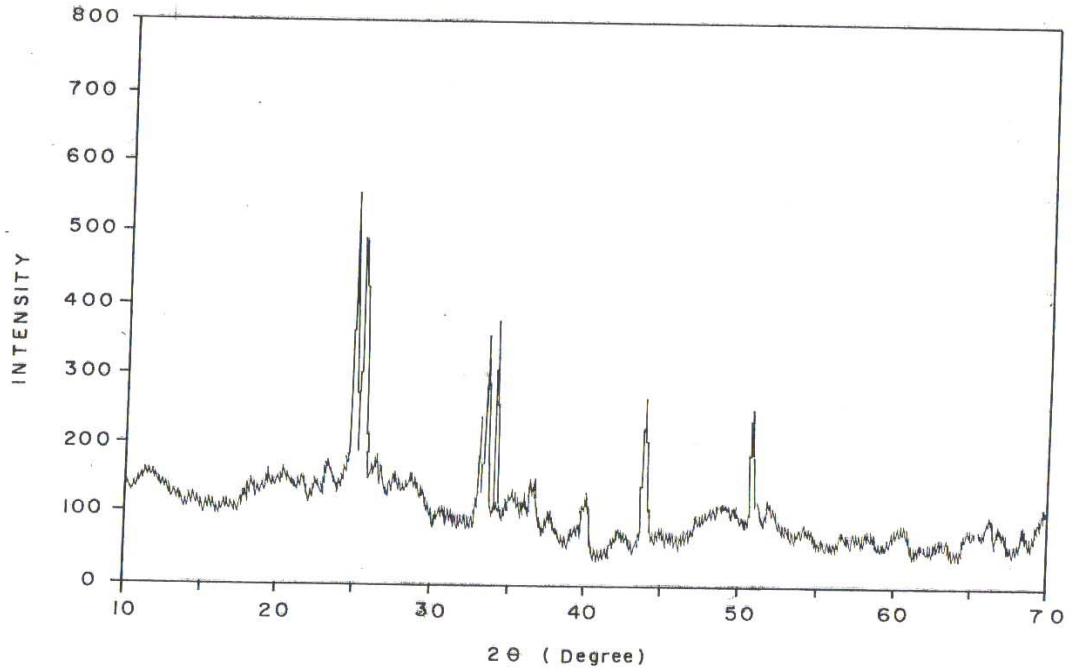

Figure 1: X-ray Diffraction pattern of $La_3Cd_2S_{6.45}$

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.

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 crystallizes in the tetragonal unit cell with **a=4.938Å and c=25.806Å**. 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 $La_3Cd_2S_{6.45}$

h	k	l	d_{obs} (Å)	d_{cal}(Å)	I_{obs}	I_{cal}
0	0	6	4.301	4.301	20	3
1	0	5	3.568	3.568	100	100
1	1	0	3.492	3.491	75	81
1	1	2	3.388	3.370	23	1
0	0	8	3.226	3.225	15	1
1	1	6	2.701	2.710	38	16
0	0	10	2.584	2.580	10	20
2	0	0	2.465	2.469	21	50
2	1	3	2.137	2.319	20	1
1	0	11	2.117	2.119	11	1
1	1	10	2.063	2.075	36	25
2	1	5	2.022	2.030	59	43
2	0	8	1.952	1.960	10	1
2	1	7	1.895	1.894	37	3
2	0	10	1.795	1.784	39	26
2	2	2	1.730	1.730	15	1
2	2	4	1.691	1.685	10	1
1	0	15	1.624	1.624	8	5
2	1	11	1.599	1.608	6	1
3	1	2	1.552	1.550	5	1
2	2	8	1.540	1.535	6	1
3	1	4	1.519	1.517	7	1
0	0	18	1.438	1.433	6	1
3	0	9	1.428	1.427	8	1
3	1	8	1.408	1.405	18	1
2	1	12	1.355	1.355	9	3
3	0	11	1.349	1.347	14	1

Space group: 14/mmm

a=4.938Å, c=25.806Å

Table Positional Coordinates for $La_3Cd_2S_{6.45}$

Atom	X	Y	Z	Occupancy
La (1)	0	0	0.5	1
La (2)	0	0	0.3148	1
Cd	0	0	0.0971	1
S (1)	0	0	0	1
S (2)	0	0	0	1
S(3)	0	0.5	0.096	0.6

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.

Conclusion

A new phase with the composition $La_3Cd_2S_{6.45}$ has been synthesized by the standard ceramic method. X-ray diffraction studies show that the phase crystallizes in the RP-type (n=3) structure with tetragonal unit cell. The molar magnetic susceptibility measurements as a function of temperature suggest that the phase is diamagnetic and magnetic susceptibility is temperature independent.

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