EFFECT OF RHENIUM DOPING ON VARIOUS PHYSICAL PROPERTIES OF SINGLE CRYSTALS OF MoSe$_2$

Mihir M. Vora, Aditya M. Vora[*]
Parmeshwari 165, Vijaynagar Area, Hospital Road,
Bhuj – Kutch, 370 001, Gujarat, India

Effect of rhenium doping is examined in the single crystals of MoSe$_2$ viz. MoRe$_{0.005}$Se$_{1.995}$, MoRe$_{0.001}$Se$_{1.999}$ and Mo$_{0.995}$Re$_{0.005}$Se$_2$, which is grown by direct vapour transport (DVT) technique in the laboratory. The grown crystals are structurally characterized with the help of X-ray diffraction, by determining the lattice parameters 'a' and 'c' and X-ray density. Also, the Hall effect and thermoelectric power (TEP) measurements show that, the single crystals are exhibiting semiconducting propertiee. The direct and indirect band gap measurements are also carried out on these semiconducting materials.

1. Introduction

In the last years the materials of the family of transition metal dichalcogenides (TMDC) have received a rapidly growing attention. Many compound of this family having layered structure occupy a central position in the class layered compounds due to their various important applications such as solid lubricants, energy converters, semiconductors, switching devices and model substances for testing and exploring photo-emission methods. Moreover, their polytypic and anisotropic behaviour in the past few years has become an intensively investigated field in the study of the solid state research. These compounds have the general formula TX_2, where T is a transition metal from IV-B,V-B and VI-B group of the Periodic Table and X is one of the chalcogens sulfur, selenium or tellurium. The basic structure of loosely coupled $X - T - X$ sheets make such materials extremely interesting such that, within layer, the bonds are strong, while between the layers they are remarkably weak [1-14].

Some of the TMDCs have recently found applications in the construction as an electrode in photoelectrochamical (PEC) solar ce1l for conversion of solar energy into electrical energy as well as photonic devices in various electronic applications. Intercalated compounds of disulphide and diselenide of molybdenum and tungsten have been extensively studied by various researchers in the literature so far [7-12]. These crystals become superconducting when intercalated with alkali and alkaline earth metals [13].

It has now been decided to carry out the intercalation of MoSe$_2$ either by cation or by anion substitution with elements having more electrons than molybdenum. It maenads that, the compounds will either have the formulae $Mo_{1-X}B_X Se_2$ or $MoB_X Se_{2-X}$ having 'B'as the intercalating metal. For carrying out effective intercalation at the cation site with elements of group higher than that of the molybdenum, a general rule for a solubility defined by Hicks [15] has been followed. According the Hicks [15], not only the intercalating elements must have an ionic radius close to that of the host metal, but also it must come from an adjacent group of the periodic

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table. In the case of MoSe$_2$, two elements 'Mn' and 'Re' available in the group VII-B, which is the next higher group from that of molybdenum, only rhenium (Re) has appreciable solubility, apparently because its ionic radius is closer to that of molybdenum than that of manganese (Mn) [14]. Therefore, we have decided to work on Mo$_{0.995}$Re$_{0.005}$Se$_2$ compounds in the form of the single crystals as an example of intercalation at the cation site and MoRe$_{0.005}$Se$_{1.995}$ and MoRe$_{0.001}$Se$_{1.999}$ compounds in the form of the single crystals as an example of intercalation at the anion site. Therefore, the effect of intercalation at the cation and anion sites by rhenium on the various physical properties has been thoroughly studied and discussed in this article.

2. Experimental details

All rhenium doped single crystals of MoSe$_2$ viz. MoRe$_{0.005}$Se$_{1.995}$, MoRe$_{0.001}$Se$_{1.999}$ and Mo$_{0.995}$Re$_{0.005}$Se$_2$ are grown by direct vapour transport (DVT) technique in the laboratory. The X-ray powder diffractograms recorded with the help of X-ray diffractometer using CuK$_\alpha$ radiation. For this purpose, many small crystals from each group were finely ground with the help of agate mortar and filtered through 106 micrometers sieve to obtain grains of nearly equal size. The X-ray diffractograms of MoRe$_{0.005}$Se$_{1.995}$, MoRe$_{0.001}$Se$_{1.999}$ and Mo$_{0.995}$Re$_{0.005}$Se$_2$ single crystals are displayed in the Figs. 1-3. The values of lattice parameter 'a' and 'c', volume, X-ray density obtained from the diffractograms of the samples of the MoRe$_{0.005}$Se$_{1.995}$, MoRe$_{0.001}$Se$_{1.999}$ and Mo$_{0.995}$Re$_{0.005}$Se$_2$ single crystals are shown in Table 1.

Table 1. Structural, electrical and optical data of single crystals.

| Parameters	MoSe$_2$	MoRe$_{0.005}$Se$_{1.995}$	MoRe$_{0.001}$Se$_{1.999}$	Mo$_{0.995}$Re$_{0.005}$Se$_2$
a (Å)	3.287	3.772	3.776	3.766
c (Å)	12.921	13.102	13.140	13.026
Volume (Å)^3	120.90	121.64	121.88	120.65
X-ray density (gm/cm^3)	6.972	6.8247	6.8344	6.9143
Room Temperature Resistivity (Ω- cm)	5.4577	0.1061	1.3590	0.3445
Hall coefficient (cm^3/coul.)	638.22	781.80	2594.47	546.49
Mobility (cm^3/V-s)	117.02	7367.79	1909.08	1586.28
Carrier concentration (cm^{-3})	0.97×10^{16}	7.98×10^{16}	2.41×10^{16}	1.14×10^{16}
Direct band gap (eV)	1.47	1.45	1.425	1.50
Indirect band gap (eV)	1.195	1.215	1.125	1.10
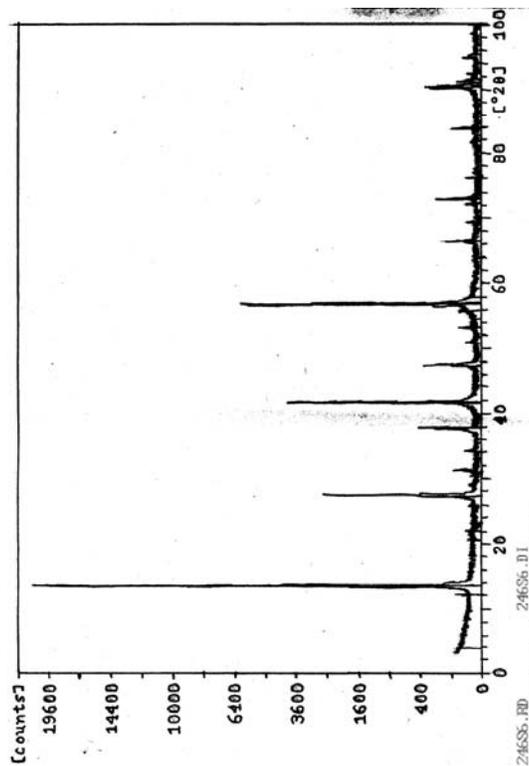
Fig. 1. X-ray diffractograms of MoRe$_{0.005}$Se$_{1.995}$ single crystal.

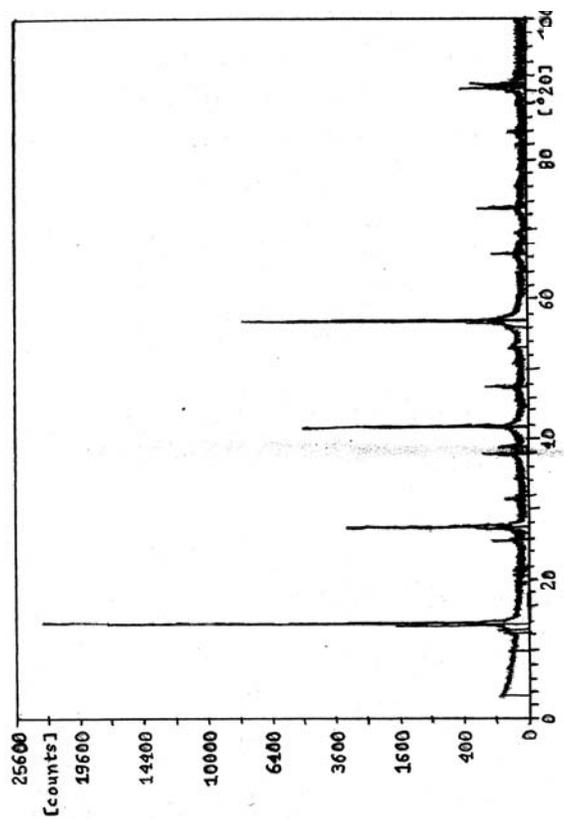

Fig. 2. X-ray diffractograms of MoRe$_{0.001}$Se$_{1.999}$ single crystal.

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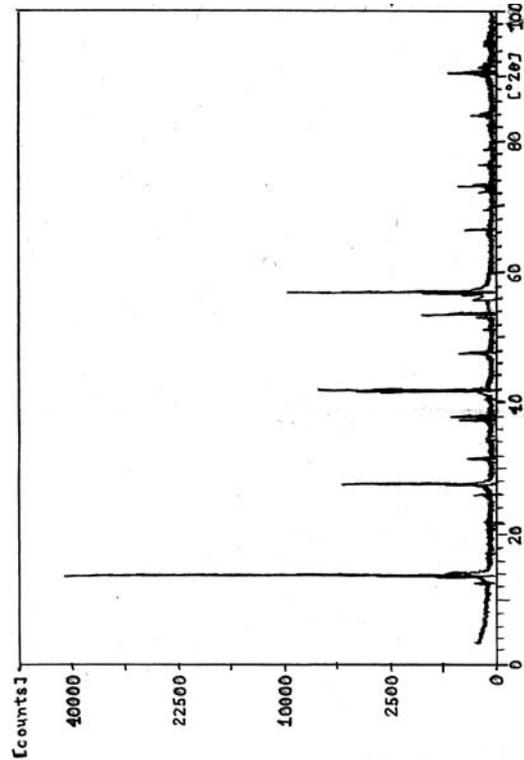*Fig. 3. X-ray diffractograms of $Mo_{0.995}Re_{0.005}Se_2$ single crystal.*

From Hall Effect measurements on each sample, the resistivity, mobility and carrier concentration were determined whose values are also shown in the Table 1. Thermo power measurements of $MoRe_{0.005}Se_{1.995}$, $MoRe_{0.001}Se_{1.999}$ and $Mo_{0.995}Re_{0.005}Se_2$ single crystals were carried out on TEP apparatus in the temperature range room temperature to 140^oC which are shown in the Figs. 4-6.
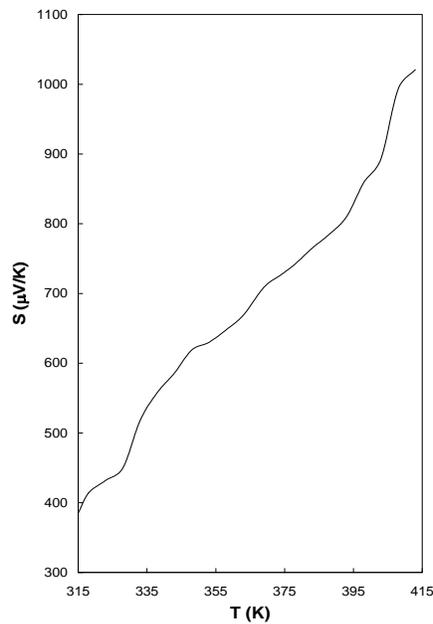

Fig. 4. Temperature dependent Seebeck coefficient (S) (in µV/K) of $MoRe_{0.005}Se_{1.995}$ single crystal.

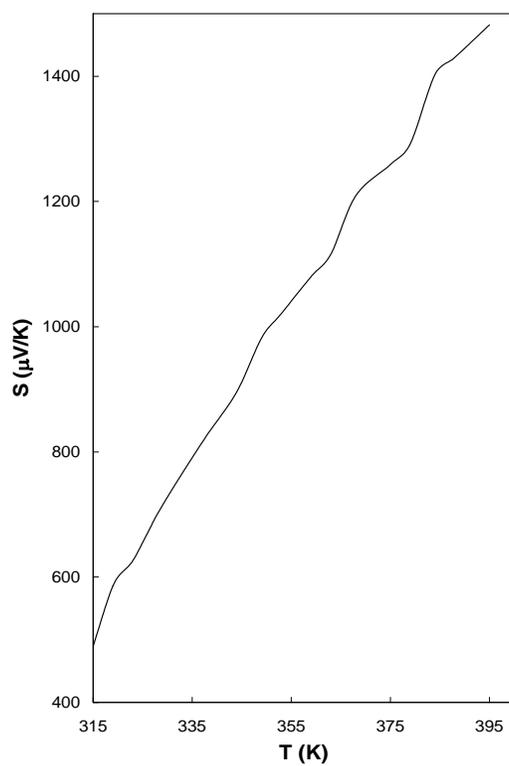*Fig. 5. Temperature dependent Seeback coefficient (S) (in μV/K) of MoRe$_{0.001}$Se$_{1.999}$ single crystal.*

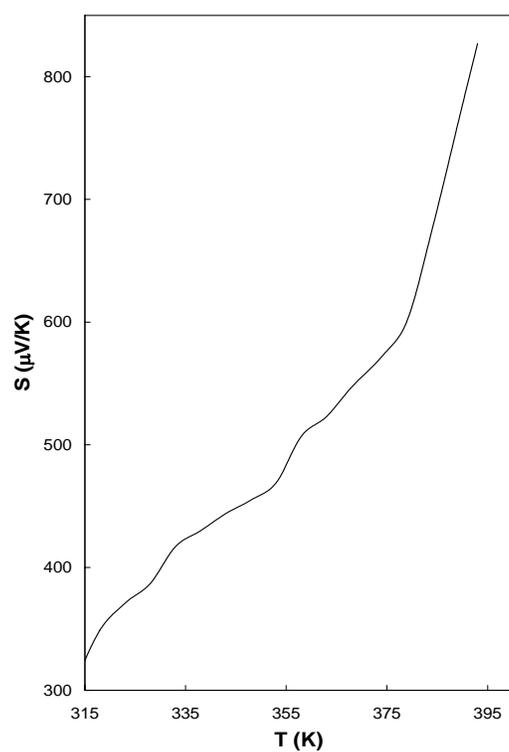*Fig. 6. Temperature dependent Seebeck coefficient (S) (in μV/K) of Mo$_{0.995}$Re$_{0.005}$Se$_2$ single crystal.*

Since these crystals are semiconducting in nature, the optical characterization for determining the direct and indirect band gap is carried out on UV-VIS-NIR spectrophotometer in the wavelength range 700 - 1450 nm.

3. Results and discussion

A comparison of the Figures 1-3 reveals that, the direction patterns of the intercalated compound have a marked resemblance with the diffraction pattern of 2H-MoSe$_2$. The defecation peaks are visible as seen in the MoSe$_2$. This enables us to index the intercalated compounds on a hexagonal unit cell basis and it is possible to assign index nearly all peaks in the diffractograms. Also, (002) reflection is of maximum intensity and thereby indicates strong orientation along the c-axis. The diffractograms for MoRe$_{0.005}$Se$_{1.995}$, MoRe$_{0.001}$Se$_{1.999}$ and Mo$_{0.995}$Re$_{0.005}$Se$_2$ single crystals are similar to those of MoSe$_2$ compounds. The lattice parameter 'a' remains constants for all the samples while there is a slight increase in 'c' parameter indicating that rhenium took the position in between the layers thereby expanding the 'c' parameter. This increase is very small because the amount of rhenium in MoSe$_2$ is small. When rhenium addition is increased in MoSe$_2$, its X-ray density also increases, which can be seen from Table 1. This may be due to rhenium atoms added to the lattice of MoSe$_2$. Room temperature resistivity obtained from Hall effect decreases by addition of rhenium, which fact can be correlated to the decrease in band gap. Mobility and carrier concentration also increases as the proportion of rhenium increases in MoSe$_2$ crystal, which indicates the increase in the charge carriers.

The variation of Seebeck coefficient with temperature for MoRe$_{0.005}$Se$_{1.995}$, MoRe$_{0.001}$Se$_{1.999}$ and Mo$_{0.995}$Re$_{0.005}$Se$_2$ single crystals is shown in the Figures 3-6. It is observed that the samples are semiconducting and p-type in nature, which feature is also confirmed from Hall measurements.

The optical absorption spectra have been obtained in the range 700 – 1400 nm because the absorption edge is situated in this region. The direct and indirect band gap for MoRe$_{0.005}$Se$_{1.995}$ are obtained from the graph of $(\alpha h \upsilon)^2$ Vs. $h\upsilon$ and $(\alpha h \upsilon)^{1/2}$ Vs. $h\upsilon$. The values obtained are shown in Table 1, which shows that there is no change in the indirect band gap of MoSe$_2$ after doping of rhenium while small variation in the direct band gap has been observed. The decrease in the band gap may be because of the impurity levels introduced due to the addition of rhenium in MoSe$_2$ [1-6]. One possible mechanism determining the features of the energy bands may be related to the inter-layer low-energy membrane rigid phonon modes, which fact was demonstrated by Rybak *et al.* [16].

4. Conclusions

The analysis of the accurate measurements of the structural, electrical and optical properties of MoRe$_{0.005}$Se$_{1.995}$, MoRe$_{0.001}$Se$_{1.999}$ and Mo$_{0.995}$Re$_{0.005}$Se$_2$ single crystals has shown that rhenium doping affects the physical properties of MoSe$_2$ single crystals. Also the Hall effect and thermoelectric power measurements show that MoRe$_{0.005}$Se$_{1.995}$, MoRe$_{0.001}$Se$_{1.999}$ and Mo$_{0.995}$Re$_{0.005}$Se$_2$ single crystals are p-type in nature and exhibit semiconducting properties. There is no change in the indirect band gap of MoSe$_2$ after doping with rhenium while small variation in the direct band gap has been observed.

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