Semiconductor Physics, Quantum Electronics & Optoelectronics, 2020. V. 23, No 3. P. 267-270.

Semiconductor physics

Study of structural, electrical and optical properties of $MoRe_{0.001}Se_{1.999}$ single crystal

A.M. Vora

Department of Physics, University School of Sciences, Gujarat University, Navarangpura, Ahmedabad 380009, Gujrat, India
E-mail: voraam@gmail.com

Abstract. In the present work, structural, electrical and optical properties of $MoRe_{0.001}Se_{1.999}$ single crystal grown using the direct vapour transport (DVT) method have been reported. The crystal has been structurally characterized by XRD, determining its lattice parameters *a* and *c* and by measuring the X-ray density. The obtained data of the Hall effect and thermoelectric power measurements support that this crystal is of *p*-type in nature. The direct and indirect band gap measurements were also carried out for this semiconducting material. It has been ascertained that the rhenium doping has a considerable effect on the properties of $MoSe_2$ single crystal.

Keywords: single crystal, direct vapour transport (DVT) technique, structural, electrical and optical properties.

https://doi.org/10.15407/spqeo23.03.267
PACS 61.50.-f, 61.66.-f, 72.20.Pa, 78.20.-e

Manuscript received 22.11.19; revised version received 22.01.20; accepted for publication 10.09.20; published online 22.09.20.

1. Introduction

The transition-metal dichalcogenides (TMDCs) are relatively old materials used in the solar cell applications. The TMDCs having a MoS_2 type layered structure are also known as *d*-*d* semiconductors. They were regarded as potential materials for liquid junction photovoltaic solar cell in 1970's. The advantages of using these materials were that they have band gaps (1.1…1.6 eV) that closely match with the solar spectrum and exhibit high conversion efficiencies as single crystals. Besides, they can also achieve long term stability because of the fact that the phototransitions in them are localized in the non-bonding *d*-orbitals. These TMDCs and their intercalated compounds find a wide area of applications, *e.g*., in the field of catalysis, high-temperature and high-pressure lubricants, solid state electrolyte batteries, long-life photoelectrochemical solar cells, hydrogen storage devices, ionic/electronic conductors, SQUID detectors and as superconducting materials [1-22].

A number of researchers have fascinated by the motivating properties of the compounds from this family. The structure of one of the best studied material, *i.e.* MoS_2, was determined back in 1923. Being layered materials, they share similarities with graphite and was mainly used as a dry lubricant, although it also had some 'electronic' applications, *e.g.*, as an anode in lithium-ion batteries. Therefore, TMDCs were a platform to study charge-density waves in low-dimensional solids, which still remains a very challenging research area for experimentalists [1-22]. Despite rather similar structure, TMDCs cover a wide spectrum of properties ranging from insulators to semiconductors and to metals, too. This diversity of properties is a consequence of the existence of non-bonding *d*-bands and the degree to which they are filled with electrons [1-3]. It is clear from the literature survey that the research work on intercalated compounds of $MoSe_2$ is almost insignificant. Hence, in this work, we have decided to study structural, electrical and optical properties of $MoRe_{0.001}Se_{1.999}$ single crystal more precisely than the previously reported works [4-19].

2. Experimental methodology

The $MoRe_{0.001}Se_{1.999}$ crystal was prepared using the direct vapour transport technique (DVT) in the laboratory. It is structurally characterized by X-ray diffraction, by determining its lattice parameters *a* and *c* and by X-ray density. The X-ray diffractograms (XRD) of it were recorded with the help of X-ray diffractometer using CuK_α radiation source and shown in Fig. 1. For this

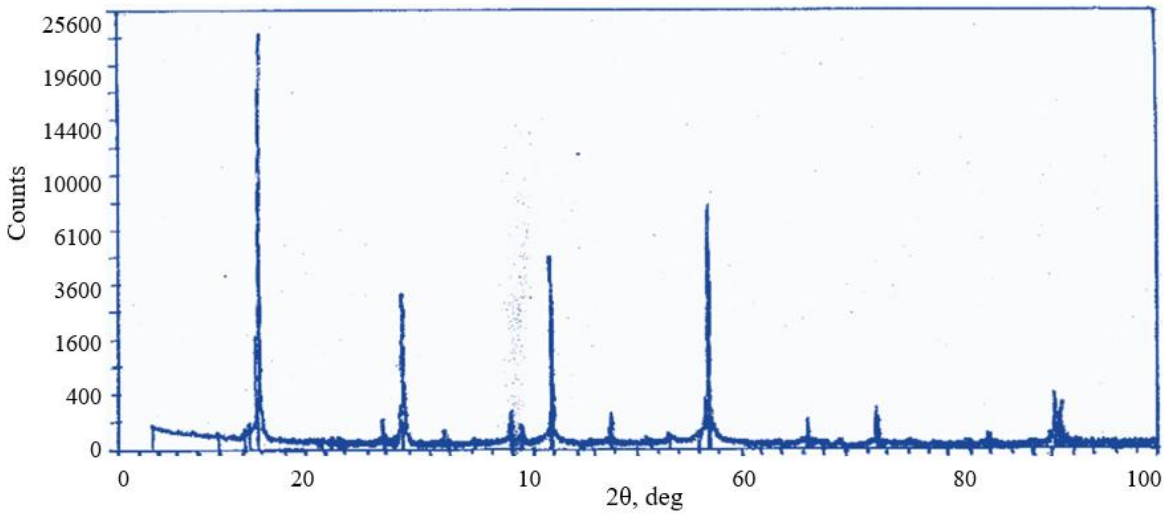

Fig. 1. XRD patterns of $MoRe_{0.001}Se_{1.999}$.

observation, many small crystals are finely crushed in the agate mortar and filtered through 106-μm sieve to obtain grains of nearly equal size. The values of lattice parameters *a* and *c*, volume and X-ray density obtained from the XRD are reported in Table. While, the Hall effect measurement, resistivity, mobility and carrier concentration of such crystal are also determined and summarized in the same table. The thermoelectric power (TEP) measurements were carried out by TEP apparatus within the temperature range from room temperature to 122 °C, which is shown in Fig. 2. Since this crystal is semiconducting in its nature, hence, optical characterization for determining the direct and indirect band gaps are also carried out by using UV-VIS-NIR spectrophotometer in the range of 700 up to 1450 nm, which is also noted in Table.

Table. Structural, electrical and optical properties of $MoRe_{0.001}Se_{1.999}$.

Parameters	$MoSe_2$	$MoRe_{0.001}Se_{1.999}$
a (Å)	3.2921	3.7841
c (Å)	12.9212	13.1424
Volume $(Å)^3$	120.92	121.88
X-ray density (g/cm^3)	6.9713	6.8344
Room temperature resistivity (Ω·cm)	5.4630	1.3621
Hall coefficient (cm^3/C)	638.22	2594.47
Mobility $(cm^3/V·s)$	117.02	1910.07
Carrier concentration (cm^{-3})	$0.97·10^{16}$	$2.45·10^{16}$
Direct band gap (eV)	1.4752	1.4325
Indirect band gap (eV)	1.2025	1.1354

3. Results and discussion

The XRD patterns of $MoRe_{0.001}Se_{1.999}$ shown in Fig. 1 is obtained in the range from 0° to 100°, which clearly displays that (002) reflection is of the maximum intensity, and thus it specifies strong orientation along the *c*-axis. While the broad peaks are indicative of tiny size crystallites. The crystallite size is calculated using the well known Scherrer formula for this peak.

From the study of Table, it is observed that there is a slight amount of rise in the values of the lattice parameters *a* and *c* in comparison with those of pure $MoSe_2$ single crystal, which indicates that rhenium has been doping in between the layers, thereby expanding both the parameters. However, this rise is very small, because the amount of rhenium doped into $MoSe_2$ also has minor contribution in the proportion. Also, as the

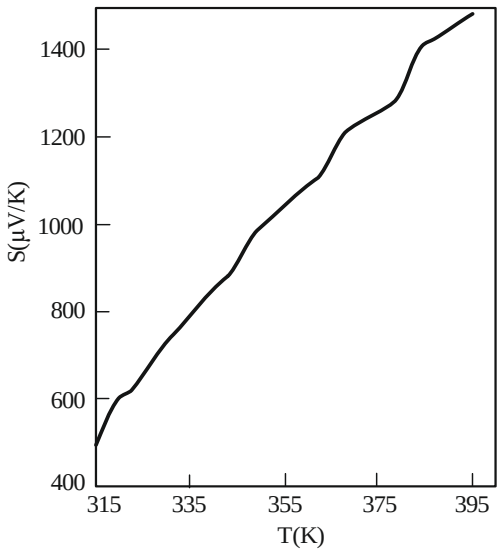

Fig. 2. Seeback coefficient (*S*) (in μV/K) of $MoRe_{0.001}Se_{1.999}$.

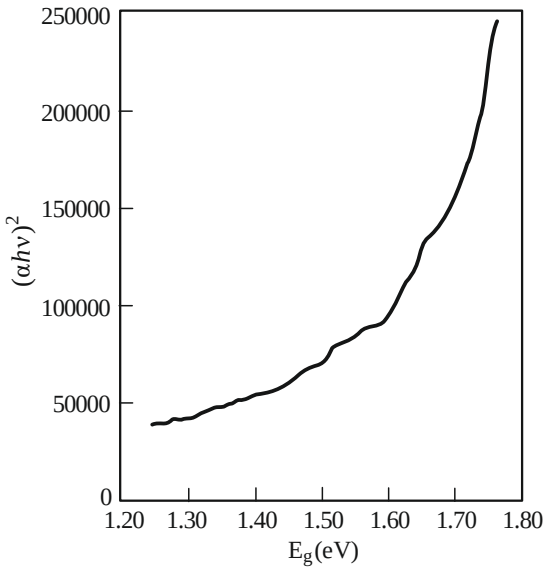

Fig. 3. Spectral dependences of the absorption near the energy gap $(\alpha h\nu)^2 \to E_g$ of $MoRe_{0.001}Se_{1.999}$.

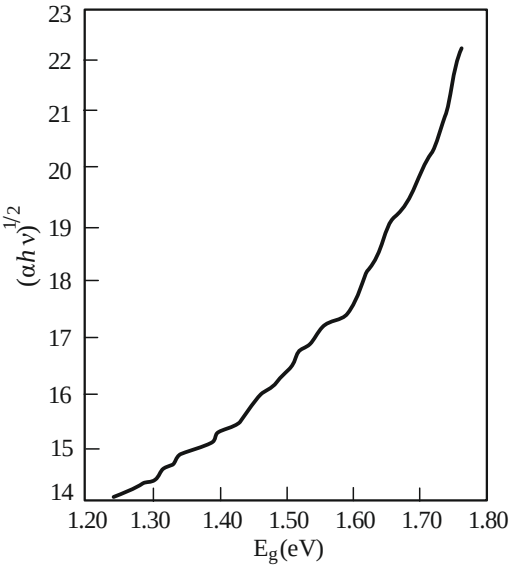

Fig. 4. Spectral dependences of the absorption near the energy gap $(\alpha h\nu)^{1/2} \to E_g$ of $MoRe_{0.001}Se_{1.999}$.

proportion of rhenium added into $MoSe_2$ is increased, its X-ray density decreases, which is noted in Table. It may be because of addition of rhenium atoms to the lattice of $MoSe_2$. The room temperature resistivity obtained from the Hall effect measurements declines after addition of rhenium in comparison with $MoSe_2$ data, which can be associated with the decrease in band gap of this material. The mobility and carrier concentration are also increased as the proportion of rhenium adding into the crystal $MoSe_2$, which indicates the increase in the concentration of charge carriers in this material.

Variation of Seeback coefficient with temperature is shown in Fig. 2. It is seen that the studied material has *p*-type semiconducting nature, and it is also confirmed by the Hall effect data. The optical absorption spectra have been obtained in the range of 700 to 1400 nm for studying the absorption edge. The direct and indirect band gaps for this crystal obtained taking the slope of the plots $(\alpha h\nu)^2 \to E_g$ and $(\alpha h\nu)^{1/2} \to E_g$ are displayed in Figs 3 and 4. The optical values obtained from these plots are also listed in Table, which shows that there is minor change or fall down in the indirect and direct band gaps of $MoSe_2$ after doping with rhenium, while small variation has been detected. The reason behind that the reduction in the band gaps may be of the impurity levels presented due to the accumulation of rhenium in $MoSe_2$ [4-22]. One of the feasible tools for studying the features of the energy bands can be caused by interlayer low energy membrane rigid phonon modes, verified by Rybak *et al.* [23, 24]. Nowadays, more sophisticated instruments are available for studying the various properties of TMDC materials with minor error corrections. We have corrected our previously reported data with more accurate data generated using the apparatus in this work, with minimum error. The presently reported data shows smaller deviations from the previous one and give good comparison with those data for $MoSe_2$.

4. Conclusion

From examination of the structural, electrical and optical properties of $MoRe_{0.001}Se_{1.999}$ single crystal, we have concluded that rhenium doping affects the above properties of $MoSe_2$ single crystal. Also, the Hall effect and thermoelectric power measurements confirm that this crystal is of *p*-type in its nature. While, the negligible changes are shown in the direct and indirect band gaps of $MoSe_2$ after doping with rhenium. The intercalating component rhenium has considerable solubility, because its ionic radius is very close to that of molybdenum as suggested by Hicks [25]. The studied crystal $MoRe_{0.001}Se_{1.999}$ is an illustration of intercalation through the anion sites. Therefore, various physical and chemical properties have been altered considerably due to this intercalation.

References

1. Kolobov A.V. Tominaga J. *Two-Dimensional Transition-Metal Dichalcogenides*. Springer, Switzerland, 2016.
2. Omkaram I., Hong Y.K., Kim S. *Transition Metal Dichalcogenide Photodetectors.* IntechOpen, UK, 2018.
3. Wonbong C., Choudhary N., Han G.H. *et al*. Recent development of two-dimensional transition metal dichalcogenides and their applications. *Materials Today*. 2017. **20**. P. 116–130. https://doi.org/10.1016/j.mattod.2016.10.002.
4. Vora M.M., Vora A.M. Stacking faults in Re doped $MoSe_2$ single crystals. *Chalcogenide Lett.* 2008. **5**. P. 65–71.
5. Vora M.M., Vora A.M. Effect of rhenium doping on various physical properties of single crystals of $MoSe_2$. *J. Semicond.* 2012. **33**. P. 062001(1–5). https://doi.org/10.1088/1674-4926/33/1/012001.

6. Vora A.M. Effect of indium intercalation on various properties of $MoSe_2$ single crystals. *Cryst. Res. Tech*. 2007. **42**. P. 286–289. https://doi.org/10.1002/crat.200610814.
7. Vora M.M., Vora A.M. Anisotropy of the optical absorption in layered single crystals. *Cryst. Res. Tech.* 2006. **41**. P. 803–806. https://doi.org/10.1002/crat.200510673.
8. Vora M.M., Vora A.M. Anisotropy of the optical absorption in layered single crystals of $MoRe_{0.001}Se_{1.999}$. *Cryst. Res. Tech.* 2007. **42**. P. 50–53. https://doi.org/10.1002/crat.200610769.
9. Vora M.M., Vora A.M. Intercalation and anisotropy of optical absorption of $MoRe_{0.005}Se_{1.995}$ single crystal. *Cryst. Res. Tech.* 2007. **42**. P. 186–189. https://doi.org/10.1002/crat.200610794.
10. Vora M.M., Vora A.M. Electrical properties measurements of In_xMoSe_2 $(0 \le x \le 1)$ single crystal. *Chalcogenide Lett.* 2007. **4**. P. 77–83.
11. Vora M.M., Vora A.M. Intrinsic stacking fault in single crystal of In_xMoSe_2 $(0 \le x \le 1)$. *Chalcogenide Lett.* 2007. **4**. P. 85–88.
12. Vora M.M., Vora A.M. Effect of rhenium doping on various properties of $MoSe_2$ single crystal. *Chalcogenide Lett.* 2007. **4**. P. 97–100.
13. Vora M.M., Vora A.M. Stacking faults in Re doped $MoSe_2$ single crystals. *Chalcogenide Lett.* 2008. **5**. P. 35–37.
14. Vora A.M. Effect of rhenium doping on various properties of $MoRe_{0.001}Se_{1.999}$ single crystal. *Chalcogenide Lett.* 2008. **5**. P. 17–20.
15. Vora M.M., Vora A.M. Stacking faults in the single crystals. *Semiconductor Physics, Quantum Electronics and Optoelectronics.* 2009. **12**. P. 421–423. https://doi.org/10.15407/spqeo12.04.421.
16. Vora A.M. Electrical properties measurements of Re doped $MoSe_2$ single crystals. *African Phys. Rev.* 2011. **6**. P. 129–135.
17. Vora M.M., Vora A.M. Stacking faults in the single crystals. *African Phys. Rev.* 2011. **6**. P. 137–141. https://doi.org/10.15407/spqeo12.04.421.
18. Vora M.M., Vora A.M. Stacking faults in the single crystals. *J. Electron. Dev.* 2012. **12**. P. 719–724.
19. Vora A.M. *Effect of Rhenium Doping on Various Properties of Single Crystals of $MoSe_2$.* LAP LAMBERT Academic Publishing, Germany, 2015.
20. Agarwal M.K., Patel P.D., Gupta S.K. Effect of doping $MoSe_2$ single crystals with rhenium. *J. Cryst. Growth.* 1993. **129**. P. 559–562. https://doi.org/10.1016/0022-0248(93)90491-E.
21. Agarwal M.K., Gupta S.K. Energetic band location of rhenium doped $MoSe_2$ single crystals to assess their usefulness in PEC solar cell fabrication. *Cryst. Res. Tech.* 1993. **28**. P. 567–571. https://doi.org/10.1002/crat.2170280428.
22. Hu S.Y., Liang C.H., Tiong K.K., Huang Y.S. Effect of Re dopant on the electrical and optical properties of $MoSe_2$ single crystals. *J. Alloys Comp.* 2007. **442**. P. 249–251. https://doi.org/10.1016/j.jallcom.2006.08.360.
23. Rybak O.V., Lun' Y.O., Bordun I.M., Omelyan M.F. Crystal growth and properties of PbI_2 doped with Fe and Ni. *Inorgan. Mater.* 2005. **41**. P. 1124–1127. https://doi.org/10.1007/s10789-005-0271-1.
24. Rybak O., Blonskii I.V., Bilyi Y.M. *et al.* Luminescent spectra of PbI_2 single crystals doped by 3d-metal impurities. *J. Lumin.* 1998. **79**. P. 257–267. https://doi.org/10.1016/S0022-2313(98)00041-6.
25. Hicks W.T. Semiconducting behaviour of substituted tungsten diselenide and its analogues. *J. Electrochem. Soc.* 1964. **111**. P. 1058–1065. https://doi.org/10.1149/1.2426317.

Author and CV

Aditya M. Vora. PhD in Physics, Associate Professor of the Department of Physics at the University School of Sciences, Gujarat University, Navrangpura, Ahmedabad 380009, Gujarat, India. The area of scientific interests covers condensed matter physics and computational materials science. He is the author of more than 200 publications.

Вивчення структурних, електричних та оптичних властивостей монокристала $MoRe_{0.001}Se_{1.999}$

A.M. Vora

Анотація. У цій роботі повідомлено про структурні, електричні та оптичні властивості монокристала $MoRe_{0.001}Se_{1.999}$, вирощеного методом прямого пароперенесення. Структуру кристала проаналізовано методом рентгенівської дифракції, визначено його параметри решітки *a* і *c* та виміряно рентгенівську густину. Отримані дані з вимірювання ефекту Холла та термоелектричної потужності підтверджують, що цей кристал є *p*-типу. Для цього напівпровідного матеріалу також проводилися прямі та непрямі вимірювання забороненої зони. Було встановлено, що легування ренієм значно впливає на властивості монокристала $MoSe_2$.

Ключові слова: монокристал, метод прямого пароперенесення, структурні, електричні та оптичні властивості.