X-ray studies on microstructural characterization of tantalum substituted tungsten mixed molybdenum diselenide;\ W_{0.65}Mo_{0.35-x}Ta_{x}Se_{2} \ (0 \leq x \leq 0.35)

DEBASHIS PALIT*, S K SRIVASTAVA* and B K SAMANTAY RAY*
Department of Chemistry, * Department of Physics, Indian Institute of Technology, Kharagpur 721 302, India
* Present address: Department of Chemistry, University of Chittagong, Bangladesh

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Abstract. The wide angle X-ray diffraction on \W_{0.65}Mo_{0.35-x}Ta_{x}Se_{2}\ (0 \leq x \leq 0.35)\ compounds have been used for calculation of the crystallite size by method of variance and Fourier technique and for microstructural parameters purposes. The crystallite size showed the decreasing trend with increasing composition up to \textit{x}=0.15\ and after that it increased sharply. On the contrary, mean fractional change in interlayer spacing, fractions of the planes affected by defects, dislocation density, and root mean square strain showed the opposite trend. The crystallite size anisotropy and stacking fault probability showed 1:1 correspondence in their variation with composition. The radial distribution analysis have also been employed to find out the information about the inter atomic distances, coupling constants and mean square displacements for different pairs of atoms. These results have been interpreted in terms of difference in packing of layers in these compounds.

Keywords. Tungsten diselenide; tantalum diselenide; microstructure parameters.

1. Introduction

During the past few years there has been a great deal of research in the study of the properties of materials having layered type of structure. Probably the greatest attention has been focussed on transition metal dichalcogenides (\textit{TX}_{2}; \textit{T} = group IV, V and VI transition metals, \textit{X} = S, Se, Te) because of their unique properties and which covered a wide range of spectrum e.g. semiconducting, insulators, metallic and superconducting (Wilson and Yoffe 1969; Subba Rao and Schafer 1979; Srivastava and Avasthi 1981, 1985, 1993; Srivastava 1989; Young and Frindt 1996; Srivastava et al 1997).

The distinctive feature of these two dimensional materials is their easy cleavage along the planes parallel to layers. This feature implies that the chemical binding within each layer is much stronger than the binding between layers and that some, but not necessarily all, physical properties of layered crystals have two-dimensional character. In addition, their layer structure also facilitates the process of intercalation allowing thereby a convenient method for altering structure and properties of the host crystals (Whittingham 1979). Recently, Bissessur et al (1993) reported the synthesis of materials based on encapsulation of organic polymers, etc into these layered hosts. These layered transition metal dichalcogenides and their intercalation compounds are useful as high temperature and high pressure lubricants, electrode materials and in secondary batteries, solar energy conversion purposes and in the field of catalysis etc. In this regard, MoSe\textsubscript{2}, WSe\textsubscript{2} and TaSe\textsubscript{2} constitutes structurally and chemically well defined family of compounds which find various applications for modern purposes (Srivastava and Avasthi 1981, 1985). Their crystal structure results from the hexagonally packed atoms in the sequence \textit{X}–\textit{T}–\textit{X}, \textit{X}–\textit{T}–\textit{X}. Within each \textit{X}–\textit{T}–\textit{X} layer the \textit{T} is either in trigonal prismatic coordination or in octahedral coordination. The typical layer type structure of MoSe\textsubscript{2} and WSe\textsubscript{2} and identical radii of Mo and W suggested the formation of isomorphic \textit{Mo}_{\textit{x}}\textit{W}_{1-\textit{x}}\textit{Se}_{2} \ (0 \leq \textit{x} \leq 0.35)\ mixed crystals as also reported by Brixner (1963), Revolinsky and Beernsten (1964), Agarwal and Wani (1979), Agarwal \textit{et al} (1984) and Hofmann (1988). Similarly, the formation of solid solutions from isostructural \textit{WSe}_{2} and \textit{TaSe}_{2} i.e. \textit{W}_{\textit{x}}\textit{Ta}_{1-\textit{x}}\textit{Se}_{2} \ (0 \leq \textit{x} \leq 0.35)\ over the entire range is expected. However, it was observed by Brixner (1963) that the CdCl\textsubscript{2} structure in \textit{W}_{\textit{x}}\textit{Ta}_{1-\textit{x}}\textit{Se}_{2}\ is retained up to \textit{x}=0.55\ followed by bi-phasic (0.55 < \textit{x} < 0.65) and mono-phasic (\textit{x} \geq 0.65) regions due to CdCl\textsubscript{2}/MoS\textsubscript{2} and MoS\textsubscript{2}, respectively. The existing literature survey by Brixner and Teuef, (1963) showed that very few studies have been reported on the preparation of compounds from TaSe\textsubscript{2} and \textit{Mo}_{0.5}\textit{W}_{0.5}\textit{Se}_{2}\ in the form of \textit{Mo}_{\textit{0.5}}\textit{W}_{0.5}\textit{Se}_{2} with the composition \textit{x}
ranging from 0.90 to 0.99. Further studies by Palit et al. (1997) have shown that \( W_{0.65}Mo_{0.35}Se_2 \) and \( W_{0.65}Ta_{0.35}Se_2 \) with MoS\(_2\) structure could be combined together advantageously in the form of a single phase \( W_{0.65}Mo_{0.35}Ta_{0.35}Se_2 \) (0 \( \leq x \leq 0.35 \)) solid solutions. The unique feature common to these materials is their weak interlayer bonding. This introduces the structural anisotropy which directly affects their properties. In addition, it results in the variability of interlayer spacing of some of the planes. Because of these peculiarities the study of microstructure parameters like mean fractional change in interlayer spacing, fractions of the planes affected by defects, dislocation density, root mean square strain, crystallite size anisotropy and stacking fault probability of these compounds using X-ray diffraction have been made in the present investigation. The calculation of the interatomic distances, mean square displacements and coupling constants for different pairs of atoms (M–M, M–X and X–X intra- and interlayer) based on radial distribution analysis is presented.

2. Sample preparation and characterization

In the present work, \( W_{0.65}Mo_{0.35-x}Ta_xSe_2 \) (0 \( \leq x \leq 0.35 \)) compounds were synthesized directly from the elements and the method of preparation was quite similar to that already reported by Palit et al. (1997). Appropriate amounts of molybdenum, tungsten, tantalum and selenium (all 99.99% pure and from Aldrich) powders were weighed accurately to give the desired composition, mixed intimately to give a homogeneous mixture and then placed inside a quartz tube and vacuum sealed. The heating of the sample was carried out at 400°C and 750°C for 96 h and 48 h, respectively. A loose product resulted having a considerably larger volume than the reacting elements. This was mixed well mechanically and subsequently placed inside the furnace and heated at 1000°C for 40 h followed by slow cooling to room temperature.

All these compounds were ground at room temperature and passed through 200 mesh sieve. However, it is to be noted that by grinding of the samples one introduces additional strains and lattice imperfections in the crystallites. For this reason all the sample powders were annealed in evacuated ampoules at 1000°C for 24 h. X-ray diffractograms of all the samples were recorded on a Philips 1729 diffractometer using CuK\( \alpha \) radiations. Accurate lattice parameters were obtained by least square method. The microstructural parameters have been calculated while considering 002 reflection in the diffraction pattern. Assuming that the broadening of the X-ray line profile is due to the presence of size broadening and broadening arising in the variance of interlayer spacing (Mitra 1964) the variance of the line profile, \( W_{20} \) can be written as

\[
W_{20} = \frac{\lambda A(2\theta)}{2\pi^2 \beta_v \cos \theta} + \frac{SI^2}{\cos^2 \theta},
\]

where

\[
S = \frac{\langle \varepsilon^2 \rangle - \beta_v^2/\pi^2}{d^2}.
\]

\( \beta_v \) is the integral width of the defect profile. Thus a plot of \( W_{20} \) versus \( \Delta(2\theta) \) will be linear and the slope will give apparent crystallite size \( \beta_v \) and the intercept, \( \langle \varepsilon^2 \rangle - \beta_v^2/\pi^2 \). Thus knowing the values of \( \beta_v \) and \( \beta_p \), the value of \( \beta_d \) can be obtained.

If \( g \) be the mean fractional change in the interlayer spacing in the direction of \( d_{002} \) and \( \gamma \) is the proportion of the planes affected by such disorder, then one can write,

\[
g = \frac{1}{\pi l \cot^{-1}\left(\frac{\pi A}{\beta_d}\right)},
\]

and

\[
\gamma = \frac{\beta_d}{\sin^2 \pi lg},
\]

where, \( \Delta \) is the measure of peak shift from the centroid of the diffraction profile and is determined following the method described by Mitra (1964).

The dislocation density, \( \rho \) as shown by Williamson and Smallman (1956), can be written as

\[
\rho = \frac{2(3\langle \varepsilon^2 \rangle)^{1/2}}{bp},
\]

where \( b \) is the Burger’s vector associated with Burger’s circuit. If it is assumed that \( b = a \), the lattice parameter of the sample, then \( \rho \) can be easily calculated.

The stacking fault probability \( \alpha \) is the fraction of the layers undergoing stacking sequence faults in a given crystal and hence one fault is expected to be found in \( 1/\alpha \) layers. Thus according to Warren (1968) \( \alpha \) can be calculated based on the following equation

\[
\left(\frac{dA_r}{d_s}\right) = \frac{1 + 3\alpha ld}{p^2 c^2},
\]

where \( (dA_r/d_s) \) is the initial slope of the Fourier coefficient \( (A_r) \) versus order \( (n) \) of the curve, \( c \) the lattice parameter. It may be noted that the probability of growth fault \( \beta \) is negligible.

The crystallite size anisotropy for all these compounds was calculated by finding out the relative change in the true crystallite size i.e. Fourier for 002 and 103 reflections.