

X-ray studies on microstructural characterization of tantalum substituted tungsten mixed molybdenum diselenide; $W_{0.65}Mo_{35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$)

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Abstract. The wide angle X-ray diffraction on $W_{0.65}Mo_{35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$) 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 $x=0.15$ 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 (TX_2 ; T = group IV, V and VI transition metals, X = S, Se, Te) because of their unique properties and which covered a wide range of spectrum e.g. semi-conducting, 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, $MoSe_2$, WSe_2 and $TaSe_2$ 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 X–T–X, X–T–X. Within each X–T–X layer the T is either in trigonal prismatic coordination or in octahedral coordination. The typical layer type structure of $MoSe_2$ and WSe_2 and identical radii of Mo and W suggested the formation of isomorphous $Mo_xW_{1-x}Se_2$ ($0 \leq x \leq 0.35$) mixed crystals as also reported by Brixner (1963), Revolinsky and Beersten (1964), Agarwal and Wani (1979), Agarwal *et al* (1984) and Hofmann (1988). Similarly, the formation of solid solutions from isostructural WSe_2 and $TaSe_2$ i.e. $W_xTa_{1-x}Se_2$ ($0 \leq x \leq 0.35$) over the entire range is expected. However, it was observed by Brixner (1963) that the $CdCl_2$ structure in $W_xTa_{1-x}Se_2$ is retained up to $x=0.55$ followed by bi-phasic ($0.55 < x < 0.65$) and mono-phasic ($x \geq 0.65$) regions due to $CdCl_2/MoS_2$ and MoS_2 , respectively. The existing literature survey by Brixner and Teufer (1963) showed that very few studies have been reported on the preparation of compounds from $TaSe_2$ and $Mo_{0.5}W_{0.5}Se_2$ in the form of $Mo_{x/2}W_{x/2}Ta_{1-x}Se_2$ with the composition x

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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 $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$) 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, $W_{(2\theta)}$ can be written as

$$W_{(2\theta)} = \frac{\lambda \Delta(2\theta)}{2\pi^2 P_V \cos \theta} + \frac{S\lambda^2}{\cos^2 \theta}, \quad (1)$$

where

$$S = \frac{\langle e^2 \rangle - \beta_d^2 / \pi^2}{d^2}$$

P_V is the apparent crystallite size which is obtained by the method of variance and P_F the true crystallite size as determined by the method of Fourier analysis and both are related as

$$\frac{1}{P_V} = \frac{1}{P_F} + \frac{\beta_d}{d}, \quad (2)$$

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

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

$$g = \frac{1}{\pi l} \cot^{-1} \left(\frac{\pi \Delta}{\beta_d} \right), \quad (3)$$

and

$$\gamma = \frac{\beta_d}{\sin^2 \pi l g}, \quad (4)$$

where, Δ 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, ρ as shown by Williamson and Smallman (1956), can be written as

$$\rho = \frac{2(3\langle e^2 \rangle)^{1/2}}{bp}, \quad (5)$$

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 ρ can be easily calculated.

The stacking fault probability α 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) α can be calculated based on the following equation

$$-\left(\frac{dA_n}{d_n} \right) = \frac{1}{p} + \frac{3\alpha ld}{c^2}, \quad (6)$$

where (dA_n/d_n) is the initial slope of the Fourier coefficient (A_n) versus order (n) of the curve, c the lattice parameter. It may be noted that the probability of growth fault β 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.

For radial distribution analysis (RDF) and differential radial analysis (DRDF) the intensities as observed for each of the samples were corrected for respective background, polarization and absorption following the procedures described by Warren (1968) and Kruh (1967), respectively. The tabulated values of atomic scattering (Cromer and Webber 1971) and incoherent scattering factors (Hazdu 1956) were used to obtain the independent scattering curves. The corrected intensities were scaled to electron units using the techniques already reported by Kruh (1967), Krough-Moe (1956) and Warren (1968). For this purpose a programme was run in a Pentium computer. The overlapped peaks were resolved by fitting a multiple Gaussian functions. The mean square displacements and the coupling constants were calculated by the procedure described by Kaplow *et al* (1968).

3. Results and discussion

Figure 1 shows the X-ray diffractograms of tantalum substituted molybdenum mixed tungsten diselenide, $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$) compound. They were thoroughly scanned for the presence of X-ray reflections arising from all possible binary phases e.g. $MoSe_2$, WSe_2 and $TaSe_2$, which were found to be absent. It is interesting to note that the diffractograms of these compounds exhibit good resemblance within themselves suggesting thereby that even upon substitution of molybdenum by tantalum in $W_{0.65}Mo_{0.35}Se_2$, the structure of the host, which is of the MoS_2 type, remained unchanged. The 002, 006 and 008 reflections are observed to be of high intensity indicating thereby a strong orientation along the c-axis. The intensities of all the reflections in general are sharp in the ternary compounds. However, in quaternary compounds there is a considerable broadening of the peaks, which gives rise to the overlapping of some of the reflections. This is found to be maximum in case of the $W_{0.65}Mo_{0.20}Ta_{0.15}Se_2$ compound. Moreover, the broadening is observed to be asymmetric with a sharp rise in the low angle side and a gradual fall in the high angle side. This is probably due to the presence of layer disorder which is being introduced in these compounds. The schematic variation of lattice parameter and other crystallographic data with composition for $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$) compounds are displayed in table 1. The data on $W_{0.65}Mo_{0.35}Se_2$ matched well with the already reported values (Brixner 1963). The variation of lattice parameter a (\AA), and cell volume V (\AA^3) showed an increasing trend while that of c (\AA) and c/a showed the opposite behaviour with an increasing amount of tantalum content in $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$).

Table 2 also records the data on crystallite size, mean fractional change in inter layer spacing g , fractions of the planes affected by defects (γ), root mean square

strain ($\langle e^2 \rangle^{1/2}$), dislocation density ρ , crystallite size anisotropy ($\rho_{002}^F/\rho_{103}^F$) and stacking fault probability (α) for $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$) compounds. It is noted from this that the variance crystallite size in general is always lower than that calculated by Fourier for the corresponding compounds respectively. It also showed that there is a gradual fall in the crystallite size values on substitution of tantalum in $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$) with the appearance of a minimum for $W_{0.65}Mo_{0.20}Ta_{0.15}Se_2$ and then again increased up to $W_{0.65}Ta_{0.35}Se_2$. It shows that the magnitude of both $\langle e^2 \rangle^{1/2}$ and ρ gradually increased, attained a maximum at $W_{0.65}Mo_{0.20}Ta_{0.15}Se_2$ and then decreased with increasing tantalum contents. It may be noted here that the crystallite size values obtained by line profile analysis is the size of the crystallite which is surrounded by grain boundaries at the interfaces. With decrease in the crystallite size values, the ratio of the number of atoms lying in the grain boundary region is greater. Since the grain boundaries are formed by dislocation networks which also

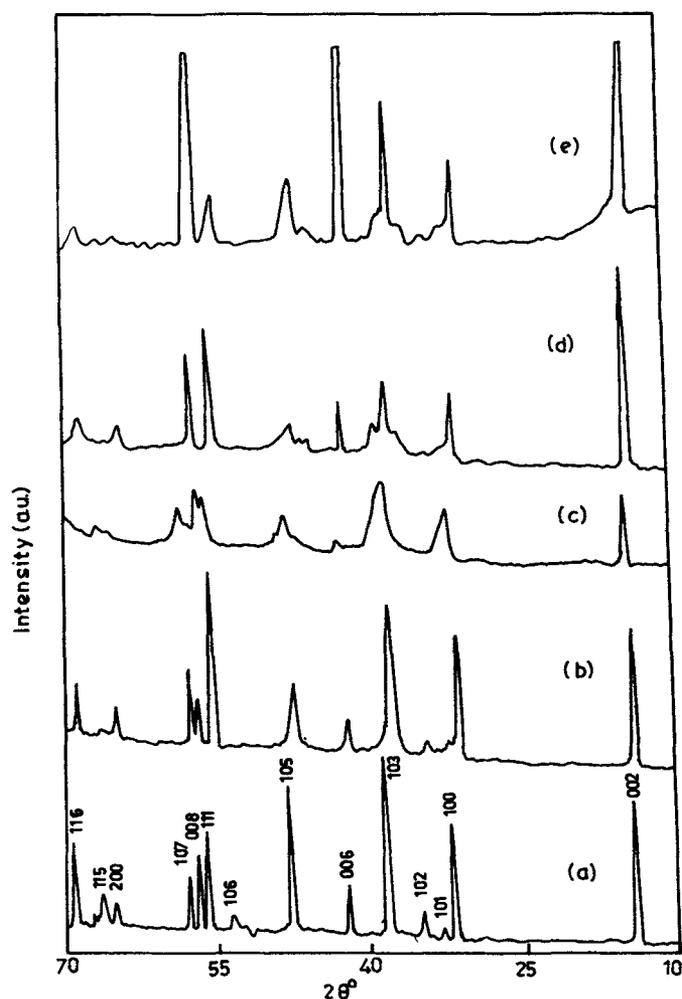


Figure 1. X-ray diffractograms of $W_{0.65}Mo_{0.35-x}Ta_xSe_2$: (a) $x=0$, (b) $x=0.05$, (c) $x=0.15$, (d) $x=0.25$ and (e) $x=0.35$.

give rise to large inhomogeneous strain, it is expected that both $\langle e^2 \rangle^{1/2}$ and ρ would increase with increasing x and become maximum at $W_{0.65}Mo_{0.20}Ta_{0.15}Se_2$. From this it may be concluded that for $x=0.15$ there is a break up of the crystallites which leads to the corresponding increase in the strain and dislocation density. The layer disorder parameters g and γ also show a maximum value at $x=0.15$ indicating the presence of maximum layer disorder for this composition.

The variation of crystallite size anisotropy p_{002}^F/p_{103}^F and stacking fault probability α for $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$) showed almost similar type of variation. Both increased with increasing composition up to $W_{0.65}Mo_{0.20}Ta_{0.15}Se_2$. Thereafter, it remained constant nearly up to $W_{0.65}Mo_{0.10}Ta_{0.25}Se_2$ followed by a sharp increase for $W_{0.65}Ta_{0.35}Se_2$. The exact reason for the crystallite size anisotropy with polycrystalline aggregate is hard to find (Mathur 1977). Even if there exists a real particle shape anisotropy, this will be blurred by the random orientation of the crystallites if all possible orientations have equal probability of occurrence. If, however, there is a slight preference for some of the orientations, the average size in one direction may be different from the other. The other reason for apparent crystallite size anisotropy may be the occurrence of the stacking faults. As has been shown by Warren (1968) and Wagner *et al* (1962) X-ray diffraction broadening of the 111 and 200 reflections of a f.c.c polycrystal are affected by the presence of stacking faults, the apparent crystallite sizes are different in the two directions. The fact that the crystallite size anisotropy as observed in the present course of investigations is almost invariably accompanied by stacking faults indicates that the preferred

orientation plays a very little role in giving rise to this anisotropy. It also appears from this data that the increasing faulting type introduced the breaking of the crystallites in a particular direction. This may lead to a crystallite size anisotropy as observed in the $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$) system.

Figure 2A shows the radial distribution function (RDF) curves of $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$) compounds. Table 1 records the inter atomic distances corresponding to different peaks in RDF curve. It is observed that the first peak appeared at about 2.80 Å in all the compounds followed by another peak at 3.40 Å. In the corresponding binary chalcogenides e.g. $MoSe_2$, WSe_2 and $TaSe_2$, however, Gamble (1974) showed that the Mo–Se, W–Se and Ta–Se bond distances are 2.49 Å, 2.51 Å and 2.59 Å, respectively. Thus in the present case too the bond distances at 2.80 Å and 3.40 Å could be well accounted for intra and interlayer Se–Se bonding. It is also seen from this data that Se–Se distances are slightly higher in magnitude in comparison to the corresponding MSe_2 ($M = Mo, W, Ta$). The peaks at higher interatomic distances similarly are more likely due to inter layer metal–selenium or selenium–selenium distances. Figure 2B shows the differential radial distribution function (DRDF) curves which showed that the peaks are well resolved.

The coupling constants and mean square displacements corresponding to various interatomic distances are recorded in table 3. It showed that the coupling constant is lowest for M–Se bond (first peak) in all the $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$) compounds indicating thereby a stronger nature of this intralayer bond. The earlier studies on isostructural $MoSe_2$ and WSe_2 also

Table 1. Lattice parameters and other crystallographic data for $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$).

$W_{0.65}Mo_{0.35-x}Ta_xSe_2$	a (Å)	c (Å)	c/a	V (Å) ³
$x=0.00$	3.269 ± 0.001	12.959 ± 0.002	3.959	119.85
$x=0.05$	3.279 ± 0.001	12.904 ± 0.003	3.934	120.19
$x=0.15$	3.294 ± 0.002	12.843 ± 0.001	3.899	120.68
$x=0.25$	3.305 ± 0.003	12.832 ± 0.002	3.882	121.39
$x=0.35$	3.345 ± 0.002	12.802 ± 0.001	3.827	124.05

Table 2. Microstructural and layer disorder parameters of $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$).

$W_{0.65}Mo_{0.35-x}Ta_xSe_2$	P_V	P_F	$\langle (e^2) \rangle^{1/2}$ (10 ⁻³)	ρ (10 ¹⁵) lines m ⁻²	g	γ	p_{002}^F/p_{103}^F	α
$x=0.00$	280	295	2.69	0.96	0.04	0.001	2.10	0.02
$x=0.05$	260	280	3.27	1.40	0.05	0.003	3.11	0.04
$x=0.15$	220	250	4.80	2.20	0.10	0.004	4.44	0.08
$x=0.25$	275	295	3.09	1.11	0.05	0.002	4.83	0.07
$x=0.35$	280	310	5.83	1.95	0.02	0.007	11.0	0.18

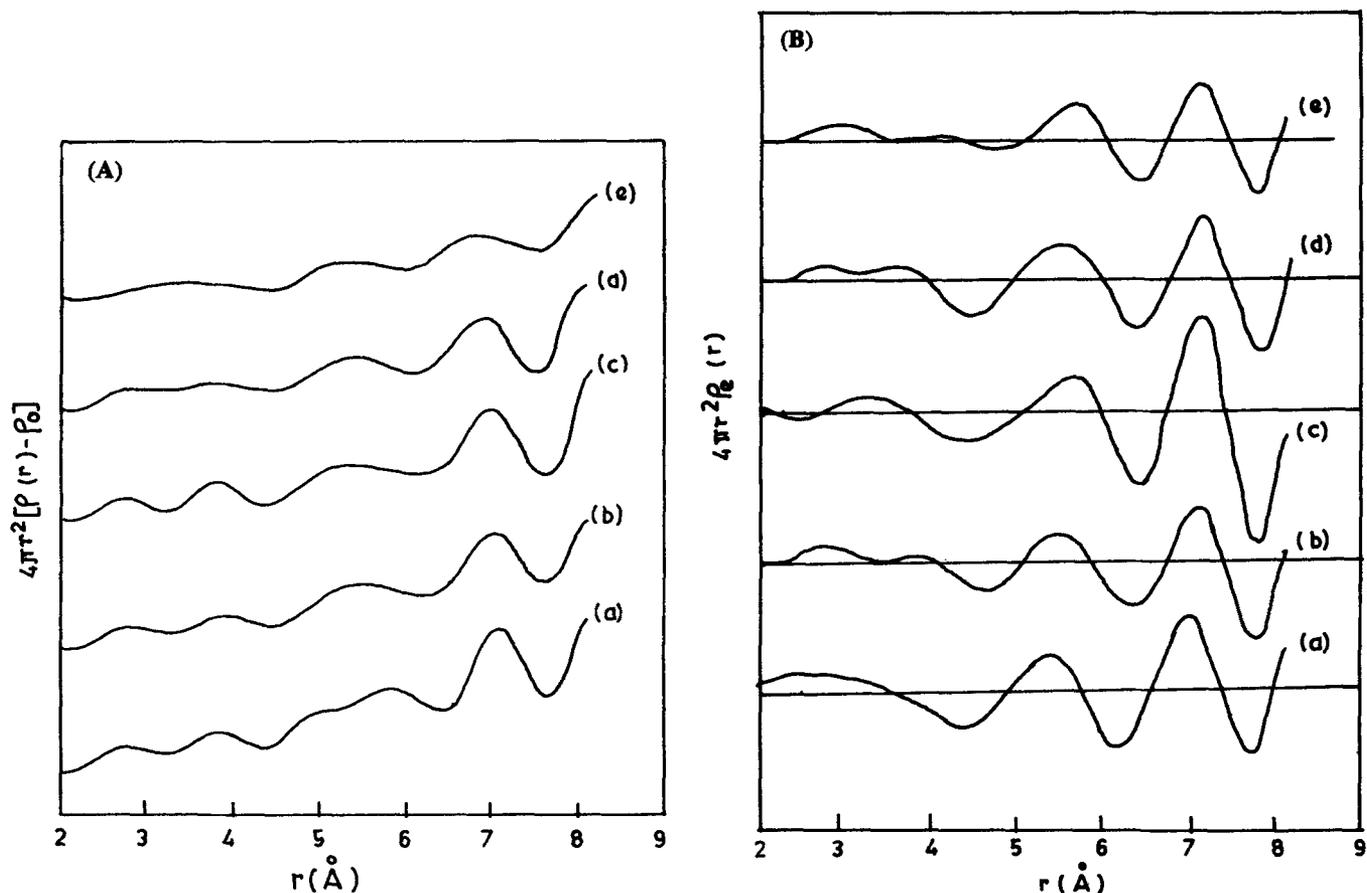


Figure 2. (A) Radial distribution function (RDF) and (B) differential radial distribution function (DRDF) curves for $W_{0.65}Mo_{0.35-x}Ta_xSe_2$; (a) $x=0$, (b) $x=0.05$, (c) $x=0.15$, (d) $x=0.25$ and (e) $x=0.35$.

Table 3. Coupling constant and mean square displacement data of $W_{0.65}Mo_{0.35-x}Ta_xSe_2$ ($0 \leq x \leq 0.35$).

$W_{0.65}Mo_{0.35-x}Ta_xSe_2$	c.c. peak					\bar{u}^2 (Å) peak				
	1	2	3	4	5	1	2	3	4	5
$x=0.00$	0.21	0.32	0.35	0.58	1.00	1.73	2.76	1.08	1.08	1.38
$x=0.05$	0.20	0.38	0.54	0.60	1.00	1.08	1.55	3.00	3.24	5.54
$x=0.15$	0.25	0.36	0.56	0.56	1.00	1.08	1.55	2.43	2.43	4.32
$x=0.25$	0.25	0.56	0.56	0.61	1.00	1.08	2.43	2.43	2.65	4.32
$x=0.35$	0.20	0.43	0.52	0.62	1.00	1.38	3.00	3.63	4.32	6.93

confirmed that the M-Se bond corresponding to this interatomic distance according to White and Lucovsky (1972) is strong and covalent. The coupling constant values are relatively much greater corresponding to M-Se and Se-Se bonds for the second and third peaks in RDF curves suggesting thereby a weak interlayer bonding. These studies also further supported the suggestion of White and Lucovsky (1972) that there exists a Se-Se interlayer bonding.

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