

Study of Some Physical Parameters of $\text{Se}_{85-x}\text{Sn}_x\text{Te}_{15}$ Chalcogenide Glasses

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Abstract: The effect of adding tin (Sn) on some physical parameters of the glassy alloy $\text{Se}_{85-x}\text{Sn}_x\text{Te}_{15}$ ($x = 1.16, 2.5, 3.84, 6.52, 8.5, 10.2$ at. %) is studied. The studied physical parameters are deviation of stoichiometry R , average coordination number $\langle r \rangle$, floppy number f , lone pair of electrons L , bond energy, heat of atomization H_s , number of constraints N_{con} , glass transition temperature T_g , and mean bond energy $\langle E \rangle$. The average coordination number $\langle r \rangle$ change from 2.02 to 2.20 when this value is smaller than 2.4 when it is under constrained. There are several constraints: N_{con} , the heat of decomposition H_s , and the average bond energy $\langle E \rangle$ increase with increasing Sn, while the proportion of flexible modes in the lattice f decreases, and thus the material becomes rigid. Deviation of stoichiometry R was larger than 1 hence it made material is rich chalcogenide. The lone pair of electrons L drops.

Keywords: Glass transition temperature, Stoichiometry deviation, Physical parameters, Average coordination number Chalcogenides.

1. Introduction

In recent years, chalcogenide glasses have received a lot of attention because of their potential and current use in various solid-state optical and electrical devices. Both selenium and tellurium are expected to be important semiconductor elements, because of their possible application in the fabrication of semiconductor devices.

Currently, interest is being paid to studying glass materials suitable for infrared optical fibers for laser energy delivery (Er: YAG, CO, and CO₂ lasers), active laser fibers, and nonlinear optical elements.

Chalcogenides have many applications due to their specific properties such as solid-state devices, Solar cells that use amorphous thin layers., optical fiber, memory with phase change, photonics, and chalcogenide glasses (CG) [1]. Selenium-rich alloys are the most distinguished today due to their strong nonlinear optical properties, high refractive index, ideal chemical and physical properties, and high transparency in the infrared regions [2,3]. Chalcogenide glasses have a lower phonon energy value and a high refractive index, advantages over other types of glasses, such as halide glasses and oxide glasses [4]. However, they are limited by their low sensitivity, high resistance, and short lifetime, which limits their ability [5].

A suitable element has been added to selenium alloy to overcome and reduce these limitations, and Se-Te binary glass alloys have been found to have several more distinct properties than pure amorphous alloys [6,7]. Due to its exceptional sensitivity to laser writing, Se-based Se-Te glass system alloys are employed in several disciplines such as optical recording media, electrophoresis, and xerography applications such as photoreceptors in laser printing and photolithography [8–10]. Se-Te-Sn has a stronger infrared transmittance due to decreased optical losses and a smaller optical band gap. [11]. When tin (Sn) is added to a Se-Te alloy, it causes formations and compositional

disarray. The addition of Sn to the Te-Se system may alter its electrical and optical characteristics dramatically [12].

We introduced Sn as a third element to the Se-Te binary system in this study to examine the influence of Sn on physical characteristics. Physical factors evaluated included $\langle r \rangle$, f , L , bond energy of distinct bonds, average single bond energy, average bond energy, T_g , and H_s .

2. Samples preparing

For bulk alloying, the melt quench process is utilized $\text{Se}_{85-x}\text{Sn}_x\text{Te}_{15}$ ($x = 1.16, 2.5, 3.84, 6.52, 8.5, 10.2$ at.%) CG. Percentage of atoms (at. %) of the elements' 5N purity, Te, Sn, and Se are weighted atomic ampoules under a 10^{-5} torr vacuum. At 3 °C per minute, the ampoule was heated to 230 °C (MP of Se 221 °C) and held at 221 °C for 6 hours before increasing the temperature to 300 °C (MP of Tin 271 °C), and we maintained That's about 6 hours. Then, the temperature was elevated up to 550 °C, where the MP of tellurium is 450 °C' for 6 h, after that it was fixed at 650 °C for 30 h during which, the ampule was hung by a wire attached to the motor's axis to rotate clock and anti-clockwise for shaking the ampule to check the homogeneity of the result alloy.

3. Results and Discussion:

3.1 Average coordination, Constraints, and Floppy numbers:

Rigidity theory, popularized by J. C. Phillips [13] and, established by M. F. Thorpe [14] is important in understanding the mechanical and structural features of lattice glasses in terms of the average number of mechanical constraints. Thorpe believed that weak forces like van der Waals forces were negligible, but that interatomic forces were the closest bond-stretching forces, and bond-bending forces were the most crucial in the rigidity of network glasses which is measured by counting

constraints or Maxwell counting, which only involves counting bond stretching and bond bending constraints. Because each bond is shared by two atoms, the number of bond-stretching restrictions for atoms with $\langle r \rangle$ bonds is N_b . Since $\langle r \rangle = 2$ each additional bond provides two new angles, the number of bond-bending restrictions is $N_a = 2\langle r \rangle - 3$. When N_{con} is equal to the total number of degrees of freedom according to Phillips' theorem, glass formation will be maximized. When $\langle r \rangle = 2.4$, ideal mechanical stability is achieved in this case, because the number of interfacial forces that make up the glass will be maximized, and the constraints for each atom are equal to the number of vector degrees of freedom for each atom. On the other hand, if $\langle r \rangle$ is < 2.4 as is the case in this paper, the network is under-constrained- floppy or spongy- and becomes over-(rigid) when $\langle r \rangle$ is > 2.4 . Hence, we find that CG alloys with different compositions have different coordination numbers. Therefore, it is useful to calculate $\langle r \rangle$. The $\langle r \rangle$ was calculated by using the formula [13–15]. For the composition, $Se_{85-x}Sn_xTe_{15}$ $\langle r \rangle$ is given by

$$\langle r \rangle = \frac{aCN_{sn} + bCN_{se} + cCN_{te}}{a + b + c} \quad (1)$$

where a, b & c are concentrations (at. %) of Sn, Se & Te respectively and CN is the coordination number of each element respectively, $CN(Sn) = 4$, $CN(Se) = 2$, $CN(Te) = 2$ they are calculated by 8-N rule [16]. From equation (1). Figure 1 clearly shows that $\langle r \rangle$ increases with increasing Sn content, hence, $\langle r \rangle$ lies in the range from 2.02 to 2.20. In this chalcogenide system $Se_{85-x}Sn_xTe_{15}$, bond bending (N_b), bond stretching (N_a), and the mechanical constraints (N_{con}) are associated with atomic bonding and have impact on covalent bonded networks. All the above parameters can be calculated using the following equations [17].

$$N_b = \frac{\langle r \rangle}{2} \quad (2)$$

$$N_a = 2\langle r \rangle - 3 \quad (3)$$

$$N_{con} = N_b + N_a \quad (4)$$

Also, the number of floppy can be calculated by following the equation [18] According to Maxwell counting or constraints counting.

$$f = 2 - \left(\frac{5}{6}\right) \langle r \rangle \quad (5)$$

Table 1 exhibits the values $\langle r \rangle$, N_a , N_b , N_{con} , and f for the amorphous alloy of $Se_{85-x}Sn_xTe_{15}$. It is clear from Table 1 that as Sn concentration increases; both the $\langle r \rangle$ and thus N_{con} also increase. The $\langle r \rangle$ increases as a result of an increase in the degree of cross-link density X in the network as shown in Figure 2, and is given from:

$$X = N_{con} - 2 \quad (6)$$

where the cross-linking density (X) is defined as a cross-linked chain's $\langle r \rangle$ being less than the beginning chain's [19]. Also, from Figure 3 we find that the floppy number decreases and thus makes the material rigid [20].

3.2 The Stoichiometry of Composition (R)

It is defined as the ratio of the covalent bonding probabilities of the chalcogen atom to the covalent bonding probabilities of

the non-chalcogen atom. The R-value may be used to determine the material type

- 1- If $R = 1$ in this type of material, it becomes Stoichiometric (only heteropolar bonds are present)
- 2- If $R > 1$ chalcogen-rich (chalcogen–chalcogen bonds and heteropolar bonds are present).
- 3- If $R < 1$ chalcogen-poor (hetero-polar bonds and metal–metal bonds are present).

The value for the $Se_{85-x}Sn_xTe_{15}$ system is given by [21–22].

$$R = \frac{bCN_{se} + cCN_{te}}{aCN_{sn}} \quad (7)$$

Figure 4 shows the changes in R concerning the atomic percentage of Sn, where R decreases with increasing Sn content and all compositions are chalcogenide-rich, also values in Table 1.

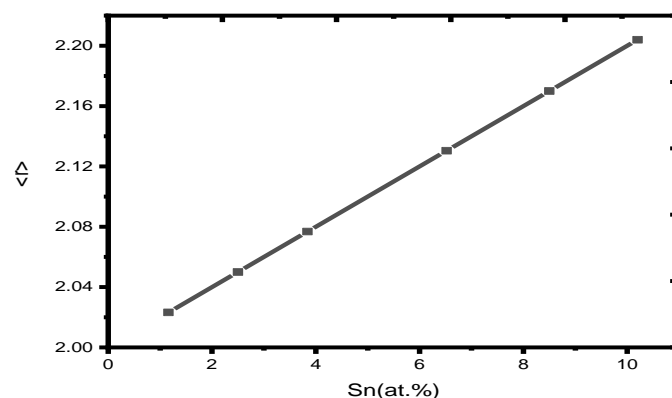


Fig.1: The average coordination number $\langle r \rangle$ of $Se_{85-x}Sn_xTe_{15}$ with the concentration of Sn.

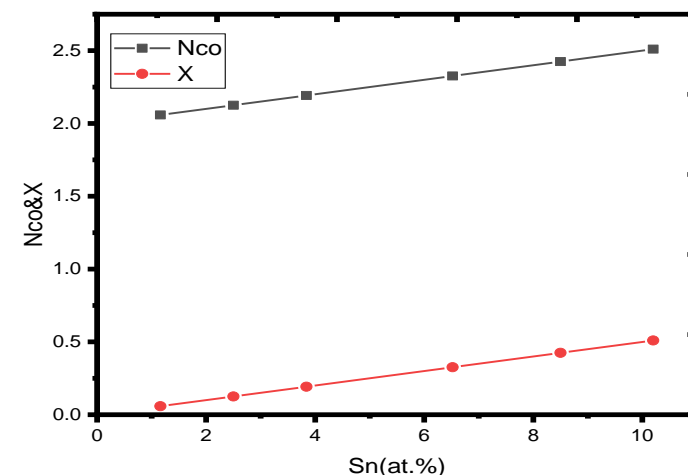


Fig.1: Variations of cross-linking density X and N_{con} with Sn content for $Se_{85-x}Sn_xTe_{15}$ chalcogenide glass

3.3 The function of lone pair electrons and glass forming ability:

The number of lone pair is given by the following equation [23–24]:

$$L = V - \langle r \rangle \quad (8)$$

where L denotes the number of lone pair electrons and V denotes the number of valence electrons. The correlation between lone pair electron content L and Sn content is represented in Figure

5. According to Pauling [25], a lone pair is a pair of valence electrons that do not contribute to forming covalent bonds with adjacent atoms. According to Pauling, a lone pair is a pair of valence electrons that do not participate in forming covalent bonds with adjacent atoms. Thus, when the number of lone pairs of electrons glassy structures decreases. The number of lone pairs that change with the value of the $\langle r \rangle$ is in Table 2.

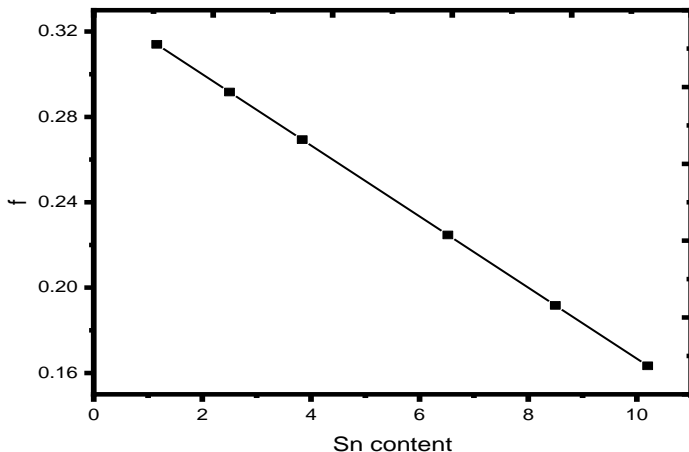


Fig.2: The floppy mode with a concentration of Sn for $Se_{85-x}Sn_xTe_{15}$ chalcogenide glass.

Table 1. Average of coordination number, constraints, floppy number, and stoichiometry of composition

Composition	$\langle r \rangle$	N_b	N_a	N_{co}	F	R
$Se_{83.84}Sn_{1.16}Te_1$ 5	2.02 3	1.01 2	1.04 6	2.05 8	0.31 4	42.60 3
$Se_{82.5}Sn_{2.5}Te_{15}$	2.05 0	1.02 5	1.10 0	2.12 5	0.29 2	19.50 0
$Se_{81.16}Sn_{3.84}Te_1$ 5	2.07 7	1.03 8	1.15 4	2.19 2	0.26 9	12.52 1
$Se_{78.48}Sn_{6.52}Te_1$ 5	2.13 0	1.06 5	1.26 1	2.32 6	0.22 5	7.169
$Se_{76.5}Sn_{8.5}Te_{15}$	2.17 0	1.08 5	1.34 0	2.42 5	0.19 2	5.382
$Se_{74.8}Sn_{10.2}Te_{15}$	2.20 4	1.10 2	1.40 8	2.51 0	0.16 3	4.402

Table 2. ACN, number of lone pair electrons for $Se_{85-x}Sn_xTe_{15}$ glassy alloy.

Composition	$\langle r \rangle$	V	L
$Se_{83.84}Sn_{1.16}Te_{15}$	2.023	5.977	3.954
$Se_{82.5}Sn_{2.5}Te_{15}$	2.050	5.950	3.900
$Se_{81.16}Sn_{3.84}Te_{15}$	2.077	5.923	3.846
$Se_{78.48}Sn_{6.52}Te_{15}$	2.130	5.870	3.739
$Se_{76.5}Sn_{8.5}Te_{15}$	2.170	5.830	3.660
$Se_{74.8}Sn_{10.2}Te_{15}$	2.204	5.796	3.592

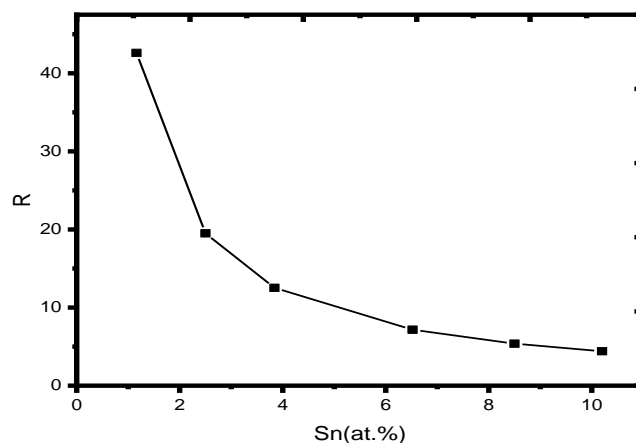


Fig.3: The value of R parameter versus Sn concentration.

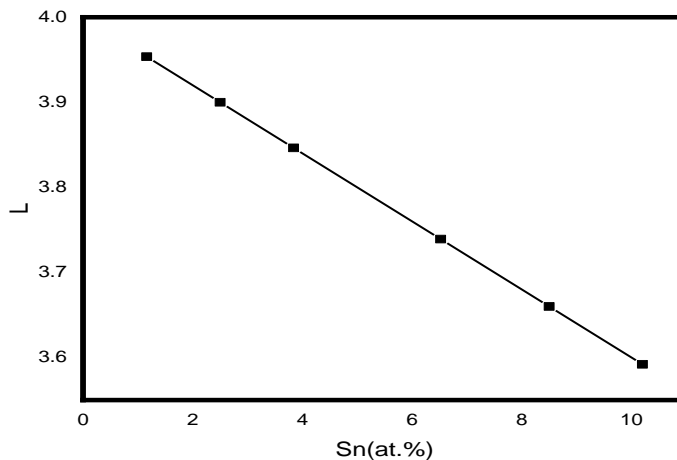


Fig.4: L Vs. Sn content for $Se_{85-x}Sn_xTe_{15}$ CG.

3.4 Measure the bond energy and glass transition temperature:

The following relation may be used to determine the bond energies of heteronuclear bonds [25]:

$$D_{(A-B)} = (D_{A-A} \times D_{B-B})^{0.5} + 30(\chi_A - \chi_B)^2 \quad (9)$$

where $D_{(A-B)}$ is the bond energy of hetero-nuclear bond, and $D_{(A-A)}$ and $D_{(B-B)}$ are the bond energies of homo-nuclear bonds. The $D_{(A-A)}$ values for Sn, Se, and Te are $34.2 \text{ Kcal mol}^{-1}$, 44 Kcal mol^{-1} , 33 Kcal mol^{-1} . χ_A and χ_B are the electronegativity values of atoms A and B, where electronegativities values of Sn, Se and Te are 1.96, 2.55, 2.1 respectively [11]. Table 3 shows the values of bond energy of different bonds.

Table 3 Bond energy of $Se_{85-x}Sn_xTe_{15}$ CG.

Bonds	bond (Kcal/mol)	bond (KJ/mol)	bond(ev)
Se-Se	44.000	184.096	1.908
Te-Te	33.000	138.072	1.431
Sn-Sn	34.200	143.093	1.483
Se-Te	48.548	203.125	2.105
Se-Sn	44.867	187.722	1.946
Te-Sn	34.183	143.020	1.482

Tichy and Ticha models can be used to get the T_g . The most important parameter to characterize the glassy state is T_g . The T_g is proportional to mean bond energy $\langle E \rangle$, and mean bond energy depends on factors such as bond energy, nature of bonds, and coordination number, so the relationship between $\langle E \rangle$ and T_g is [26]:

$$T_g = 311[\langle E \rangle - 0.9] \tag{10}$$

Where $\langle E \rangle$ is

$$\langle E \rangle = E_c + E_{(rm)} \tag{11}$$

Where E_c represents the total contribution of strong hetero polar bonds to the bond energy and $E_{(rm)}$ describes the contribution of weaker bonds after strong bonds have been maximized. According to Tichy and Ticha [21-22] there are two cases (1) chalcogenide rich and (2) chalcogenide poor and since this paper $R > 1$ we should use the equation which belongs to chalcogenide rich which appears in equation 11 and 12 and thus the values of T_g with increasing Sn concentration. Table 4 shows the average bond energy and glass transition values.

$$E_c = 3cE(sn - se) + 4aE(se - Te) \tag{12}$$

$$E_{(rm)} = \left[\frac{2b-4c-3a}{z} \right] E(se - se) \tag{13}$$

Table 4 Mean bond energy and T_g of $Se_{85-x}Sn_xTe_{15}$ CG

Composition	$E_{(rm)}$ (ev)	E_c (ev)	$\langle E \rangle$ (ev)	T_g (K)
$Se_{83.84}Sn_{1.16}Te_{15}$	0.983	1.050	2.032	352.138
$Se_{82.5}Sn_{2.5}Te_{15}$	0.908	1.152	2.059	360.671
$Se_{81.16}Sn_{3.84}Te_{15}$	0.834	1.255	2.089	369.808
$Se_{78.48}Sn_{6.52}Te_{15}$	0.693	1.460	2.153	389.802
$Se_{76.5}Sn_{8.5}Te_{15}$	0.594	1.612	2.205	405.965
$Se_{74.8}Sn_{10.2}Te_{15}$	0.511	1.742	2.253	420.731

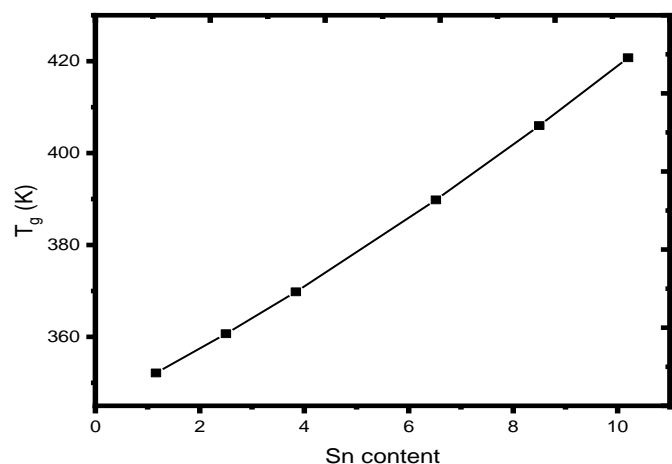


Fig.5:The glass transition temperature (T_g) vs. Sn content (at.%).

3.5 Average Heat of Atomization

The average Heat of Atomization H_s is the amount of energy needed to convert one mole of an element in its normal state at environmental temperature into the gaseous state. H_s according to Pauling [25] the number of heats of formation ΔH at of atomization H_s^A and H_s^B which correspond to the average

nonpolar bond energies of the two atoms is the H_s (A-B).

$$H_s = \Delta H + \frac{1}{2}(H_s^A + H_s^B) \tag{14}$$

The square of the difference between the two atoms' electro negativities χ_A and χ_B is proportional to ΔH as follows:

$$\Delta H \propto (\chi_A - \chi_B)^2 \tag{15}$$

The value of ΔH is approximately 10% of the H_s and it can be ignored. Hence

$$H_s = \frac{1}{2}(H_s^A + H_s^B) \tag{16}$$

Average H_s is a compound description. $A_a B_b C_c$ is considered a direct measure of cohesive energy and thus average bond strength, as

$$H_s = \frac{aH_s^A + bH_s^B + cH_s^C}{a + b + c} \tag{17}$$

The H_s value obtained using the H_s value of Sn, Se, and Te (the H_s values in KJ/mole are 302, 227, and 197 KJ/mole[11], respectively,) are recorded in Table 5. The H_s increases with increasing Sn content (at. %) that shows in Table 5. The average single bond energy $H_s/\langle r \rangle$, the measure of cohesive energy, decreases with increasing Sn content as shown in Table 5. It also causes an increase in the optical band gap from Figure 7, as the Sn (at. %) rises, H_s also increases.

Table 5 H_s (ev) and $H_s/\langle r \rangle$ of $Se_{85-x}Sn_xTe_{15}$ CG.

Composition	H_s (ev/bond)	$H_s/\langle r \rangle$ (ev/bond)
$Se_{83.84}Sn_{1.16}Te_{15}$	2.315	1.144
$Se_{82.5}Sn_{2.5}Te_{15}$	2.325	1.134
$Se_{81.16}Sn_{3.84}Te_{15}$	2.336	1.124
$Se_{78.48}Sn_{6.52}Te_{15}$	2.357	1.106
$Se_{76.5}Sn_{8.5}Te_{15}$	2.372	1.093
$Se_{74.8}Sn_{10.2}Te_{15}$	2.385	1.082

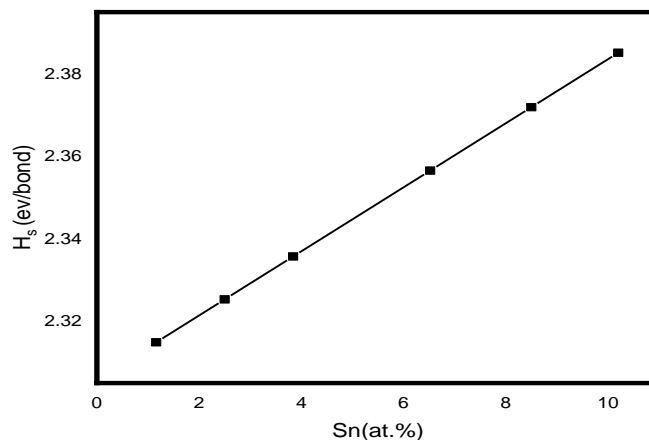


Fig.6:The heat of atomization versus concentration of Sn%.

4. Conclusion

The addition of Sn to Se-Te glassy alloys causes changes in all physical characteristics like making it more rigid. Theoretical calculations have been made for $\langle r \rangle$, lone-pair, mean bond energy, T_g , and average H_s for various combinations. In the $Se_{85-x}Sn_xTe_{15}$ system, the $\langle r \rangle$ increases from 2.02 to 2.2 with Sn

content, also number of constraints, average H_s , mean bond energy, and T_g rise with increasing Sn content. The quantity of lone pair electrons and floppy mode of Se-Te glass decrease with Sn addition. The phase change can be reversibly switched between the amorphous and crystalline state and find applications in rewritable optical recording.

CRedit authorship contribution statement

Amany G. Abdeen specializes in software, formal analysis, investigation, writing (review and editing), and visualization. **M.M. Abd El-Raheem's** responsibilities include supervision, conceptualization, methodology, formal analysis, investigation, resources, data curation, original draft writing, review and editing, and project management. **A. M. Ahmed:** Conceptualization, Resource Management, Original Draft Writing, and Project Administration. **H.F. Mohamed:** Methodology, Software, and Visualization.

Data Availability Statement

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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