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Structural Development in Ge-rich Ge-S glasses

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Abstract

The Raman spectra of Ge-S glasses in the Ge-rich region from Ge 33 to 46 % have been investigated in order to know the structural development of the network glasses. From the detailed curve fits, we have found that there is an unassigned peak at 410 cm^{-1} and it becomes larger with increasing Ge composition. To clarify the structural origin of the peak, we virtually constructed the atomic arrangement of the glassy state starting from the crystalline state through the liquid state and changed the composition gradually depleting the medium in sulfur. From the consideration of the structural modeling and the atomic orbital theory, we suggest that single Ge-S chain is a probable structural origin of the peak.

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I. INTRODUCTION

Ge-chalcogenide (Ge-X: X=S, Se) glasses are known as typical network glasses and are of a great interest because of their application potential. To utilize their attractive properties, it is quite important to know the exact structure of the materials. In the past few decades there has been an extensive effort to investigate the structure of the glassy Ge-chalcogenides. Results of several measurements have shown that a structural transition occurs with increasing Ge composition^{1,2}. According to the results of Mössbauer spectroscopy by Boolchand et al.², at high Ge concentration there are three structural phases, A, B and C, in these glasses. A phase has similar structure to the high temperature crystalline phase of GeX_2 , which consists of tetrahedral $\text{Ge}(X_{1/2})_4$ units. B phase consists of the ethane-like $(X_{1/2})_3\text{Ge-Ge}(X_{1/2})_3$ units. C phase has a double layer structure like crystalline(c-) GeX . The relative presence of these phases changes with increasing Ge composition. In recent years, the interest was mainly focused on the region around the critical composition of the rigidity percolation threshold, where the number of the constraints per atom is equal to the degree of freedom. In the composition region, a steep first-order-like transition, from very flexible floppy phase to rigid phase, is observed. The composition in Ge-Se system is Ge 23 % [3]. In addition to that, in very recent years great attention has been paid to a narrow region near the critical composition, the “intermediate phase window”, where specific changes due to a self-organization occur [3, 4]. For Ge-Se system, the region is between Ge 20 and 26 % [3]. On the other hand, in the Ge-rich region from Ge 33 to 43 %, a much qualitative change is observed in the Raman spectra [1]. Indeed, it can be related to the structural transformations from A to B and from B to C phase. However, it is still worth examining the details of the structural development in the composition region because a quantitative analysis of Raman spectra has not been fully made yet. In this paper, we present the results of the detailed analysis of the Raman spectra of Ge-S glasses in the Ge-rich region, including our experimental data of thin films. On the basis of the results, we propose a unified model, which also explains other previous experimental results. Using the concept of the model, we finally provide perspective on the possibilities for applications.

II. EXPERIMENTAL

Thin films of amorphous $\text{Ge}_{46}\text{S}_{54}$ with the thickness of 300 nm were prepared by sputtering.

The composition was measured by the electron probe micro-analyzer in the system of the scanning electron microscope (LEO 1430VP). Raman spectra were recorded using a Raman spectroscopic system of Horiba Jobin Yvon T64000 equipped with liquid-nitrogen-cooled multichannel coupled-charge-device detector, in backscattering geometry. The power?? 441.6 nm He-Cd laser line was used for excitation.

III. RESULTS

Fig.1 shows the Raman spectra of Ge-rich Ge-S glasses from Ge 33 to 46%. The three Raman spectra, (a)-(c), are from the results of Takebe et al. [5], which were measured for bulk samples. The spectrum at Ge 46% was obtained using thin film prepared by sputtering in the present study. The qualitative change in the spectra is consistent with the results of Lucovsky et al. [1] and Kotsalas and Raptis [6]. A background component has been subtracted for the spectra at Ge 40 and 46 %. We performed curve fits with Gaussians to the spectra, assuming the presence of the peaks, which have already been assigned. Among the peaks, the peak at 340 cm^{-1} is attributed to the symmetric breathing mode of S atoms at $\text{Ge}(\text{S}_{1/2})_4$ tetrahedron [7]. The intensity of the peak decreases with increasing Ge composition. This suggests that the number of the tetrahedral unit decreases with increasing Ge composition. At Ge 36 %, the content of A phase is 0 % [2]. Therefore, the peak at 340 cm^{-1} in the spectrum at Ge 36 % should have other structural origin. According to Lucovsky [8], there is a vibrational frequency at 340 cm^{-1} of the ethane-like units, whose Raman active frequencies are at 240, 340 and 376 cm^{-1} . The presence of the ethane-like units indicates the presence of Ge-Ge bonds, in other words, chemical disorder in the system. The peak at 370 cm^{-1} is interpreted as the stretching motion of the outrigger raft (OR) accompanied by S-S bond, which was suggested by Bridenbaugh et al. [9], or the vibration of S atoms on the edge-sharing double bonds [10, 11]. The vibrational frequency of the ethane-like units is also located near 370 cm^{-1} [8]. Jackson et al. point out from first-principles molecular-dynamics simulations that there are two peaks near 370 cm^{-1} ; a peak at 373 cm^{-1} , the mode of the edge-sharing cluster, and a peak at 366 cm^{-1} , the mode of the ethane-like cluster [12]. Overall, the peak at 370 cm^{-1} contains two components. One arises from ethane-like units. The other arises from and the edge-sharing double bonds or the stretching motion of OR. The peak at 430 cm^{-1} is regarded as the stretching mode of dimerized S atoms on the edge of the OR [9, 13]. This is also a peak indicative of chemical disorder at a stoichiometric composition of Ge 33%. The peak decreases with increasing Ge composition from 33 to 36%, and almost vanishes at Ge 40%. One can expect that the chance for creation of S-S bond declines with decreasing S composition and the result is consistent with the expectation. In $200\text{-}300\text{ cm}^{-1}$, we obtained two peaks located at 220 and 255 cm^{-1} from the curve fit. One of the vibrational frequencies of the ethane-like unit is located near 255 cm^{-1} ; 240 cm^{-1} according to Lucovsky et al. [8] and 255 cm^{-1} according to Jackson et al. [12]. In the spectra of c-GeS₂, there are two intensive peaks at 212 and 238 cm^{-1} , which are the modes of double layer structure [14]. The peak at 220 cm^{-1} is considered to originate from these peaks. So far we made curve fits only using the peaks which have already been assigned. However, in the Ge-rich region more than 35 %, we could not fit the spectra without considering a peak at 410 cm^{-1} , which becomes larger with increasing Ge composition. It is obvious that the peak at 410 cm^{-1} is not formed due to a shift of the peak at 430 cm^{-1} because both peaks were required to fit the spectrum at Ge 36 %. It seems that the increase of the peak at 410 cm^{-1} is related to the increase of C phase. But there is no peak with such high frequency in the spectra of c-GeS₂. We would expect that there exists a structural unit, which has a stronger bond than that in the double layer and gives such high frequency vibration. As far as we know, no one suggests such a structural unit.

IV. DISCUSSION

A. Structural model

In order to find out the structural origin of the vibrational mode at 410 cm^{-1} , we have performed a virtual structural modeling. Fig. 2 shows how amorphous structure is formed from c-GeS₂. High temperature crystalline phase of GeS₂ consists of the tetrahedral units. In the figure, there are two streams of Ge-S chains. The stream can also be regarded as the sequence of corner-sharing tetrahedral units. The edge-sharing tetrahedral units connect the two streams. When c-GeS₂ is heated and molten GeS₂ is obtained from the high temperature crystalline phase, some Ge-S covalent bonds would break. If a bond break occurs as shown in the figure, two neighboring S atoms become free and there is a chance to form a new S-S bond. This corresponds to the S-S dimer on the edge of the OR. After breaking of the Ge-S bonds, the other counterparts of Ge atoms become also free. These atoms can bind each other

and form a new Ge-Ge bond. As a result, the ethane-like unit is formed. Such structure, formed in the liquid phase is supposed to be preserved in the amorphous phase by quenching. This picture provides an answer to the fundamental question, why the chemical disorder exists in the stoichiometric composition and in amorphous phase.

To clarify the structure in Ge-rich Ge-S glasses, we subtracted S atoms from the structure of amorphous (a-) GeS_2 as shown in Fig.3. Here we subtracted S atoms out of the Ge-S chain and we assumed that the Ge-S chain structure is preserved. S atoms are classified into three groups; 1st, 2nd and 3rd column, as shown in the figure. The S atoms in the 1st column are the compositional elements of the Ge-S chain. The S atoms in the 2nd column are at the edges of the corner-sharing tetrahedral units on the Ge-S chain, but not in the Ge-S chain. The S atoms in the 3rd column are in the middle of the two Ge-S chains, and are out of the 2nd column. By subtracting S atoms, the ethane-like unit will lose one S atom and Ge atom will seek other S atom. If there is a neighboring S atom in the 2nd column, the Ge atom will bond with this S atom. If there is no neighboring S atoms in the 2nd column, the Ge atom will bond with a S atom in the 1st column. Through such dynamics, we would expect that the interaction between the two streams of Ge-S chain becomes stronger, resulting in approaching of the two streams. Here, the ethane-like units play a role of glue. In fact, the composition variation of density indicates that there is considerable volume contraction in the region from Ge 33 to 45% [5, 15]. The same tendency is also observed in Ge-Se system [16]. We suggest that the large volume contraction in the region is caused by such an increase of the interaction between the Ge-S(Se) chains.

B. Formation of layer structure

To know further about the structural nature of the Ge-S glasses close to Ge 50 %, the diffraction study is useful. Using the results of the neutron diffraction study for Ge-Se system by Salmon's group [17, 18], we obtained that the bond angles of Se-Ge-Se are 111.01° in a- GeSe_2 , and 101.57° in liquid (l-) GeSe_2 , which are close to 109.47° , while the bond angle is 94.82° in l- GeSe , which is close to 90° . Recent *ab initio* molecular-dynamics simulations by Van Roon et al. support these bond angles [19]. The change in the bond angle from Ge 33 to 50 % can be explained in terms of the atomic orbital theory. The outermost electronic configuration of Ge is $(4s)^2(4p)^2$ and that of Se is $(4s)^2(4p)^4$. In Se atom, two *s* electrons are low in energy and they do not participate in bonding. Two electrons among four *p* electrons are used to form covalent bond with other two atoms. Hence, Se atom makes twofold coordination. The remaining two *p* electrons do not participate in bonding and form a pair called "lone-pair electrons". For Ge atom, there are two cases depending on the composition. When the Se composition is large enough, a tetrahedral structure will be formed centering a Ge atom. In this case, sp^3 hybridization occurs in the Ge atom by the promotion of one *s* electron to *p* level. The formation of four sp^3 orbitals results in the four equivalent covalent bonds. Thus, the bond angle is close to 109.47° , which is the value for a perfect tetrahedron. When the Ge composition becomes 50 %, twofold coordinated Ge-Se chains are formed, as depicted in Fig. 4(a), as a result of the subtraction of Se atoms. In order to form twofold coordination in Ge atom, two *p* electrons would participate in bonding, leaving *s* electrons in bonding without forming hybridization. Since two *p* orbitals have normal orientation to each other, the bond angle of Se-Ge-Se is fixed to be 90° . In Fig.4(b), we illustrate how a double layer structure can be formed from the Ge-Se chains. The Ge-Se chains are alternatively aligned along *b*-axis at different height in *c* axis. They are connected to each other having a third bond. This is the way how a layer structure is formed from the chains and the layer becomes 'double'. The formation of the third bond can also be explained in terms of the atomic orbital theory. In Se atom, two *p* electrons are used for covalent bonds and two *p* electrons remain as lone-pair electrons. In Ge atom, two *p* electrons are used for covalent bonds and one *p* orbital is empty. As it is well known in the formation of ammonium ion NH_4^+ , a coordinate bond is formed between a lone-pair orbital and an empty orbital. Applying this concept to this situation, we can expect that a new coordinate bond could be formed between a Ge atom and a Se atom, which are in different neighboring chains.

C. Origin of the peak at 410 cm^{-1}

The important point in the third bond formation is that the bond formation is possible only for hetero-polar pair. According to the neutron diffraction study, there exist homo-polar bonds in l- GeSe [18]. The homo-polar bonds should only exist in the Ge-Se chain composed of covalent bonds. This leads to the situation that some atoms in the chain face homo-polar atoms in a neighboring chain. At the portion, the atoms do not bond with the faced atoms and the chains can fail to form double layer. In the region, the Ge-Se chain is left as a single chain without being involved in the layer. The structure in the liquid might be quenched in amorphous phase. Although we dealt with Ge-Se system in the above discussion, the situation could be the same in Ge-S system since the atomic organization and chemical bonding are very similar. Therefore, such single chain in Ge-S system would be a possible structural origin of the peak at 410 cm^{-1} .

V. CONCLUSION

We have made an analysis of Raman spectra of Ge-rich Ge-S glasses and found that there is an unassigned peak, which is located at 410 cm^{-1} , in the region from Ge 36 to 46 %. In order to know the structural origin of the peak, we considered the structural development in the atomic arrangement starting from the crystal structure of GeS_2 and proposed a structural model of Ge-rich Ge-S glasses. The model explains why the ethane-like units appear in the glasses. The interaction between the two Ge-S chains becomes stronger with increasing Ge composition due to the role of the ethane-like units. This is consistent with the data of the density measurements. We have also demonstrated that a new type of bond, which bridges the two Ge-S chains to form double layer structure, is supposed to appear in Ge-rich region close to 50 % using a concept of atomic orbital theory. From these our considerations, we have speculated that there is incomplete portion in the double layer structure in Ge-rich Ge-S glasses close to 50 % and proposed the structural origin of the Raman peak at 410 cm^{-1} as single Ge-S chain. Although we could not give direct evidence in the present study, such possibility will be examined by first-principles molecular-dynamics simulations. Our model emphasizes the uniqueness of amorphous structure. The concept of our model can provide a useful guideline to find a new functionality in Ge-S glasses in Ge-rich region. The unique nature in the interaction between Ge-S chains can affect optoelectronic response and photodiffusion of silver. In addition, the low dimensionality in the structure may be utilized in producing a new type of nano-structures. It would be interesting to examine these possibilities in further studies.

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Figure captures

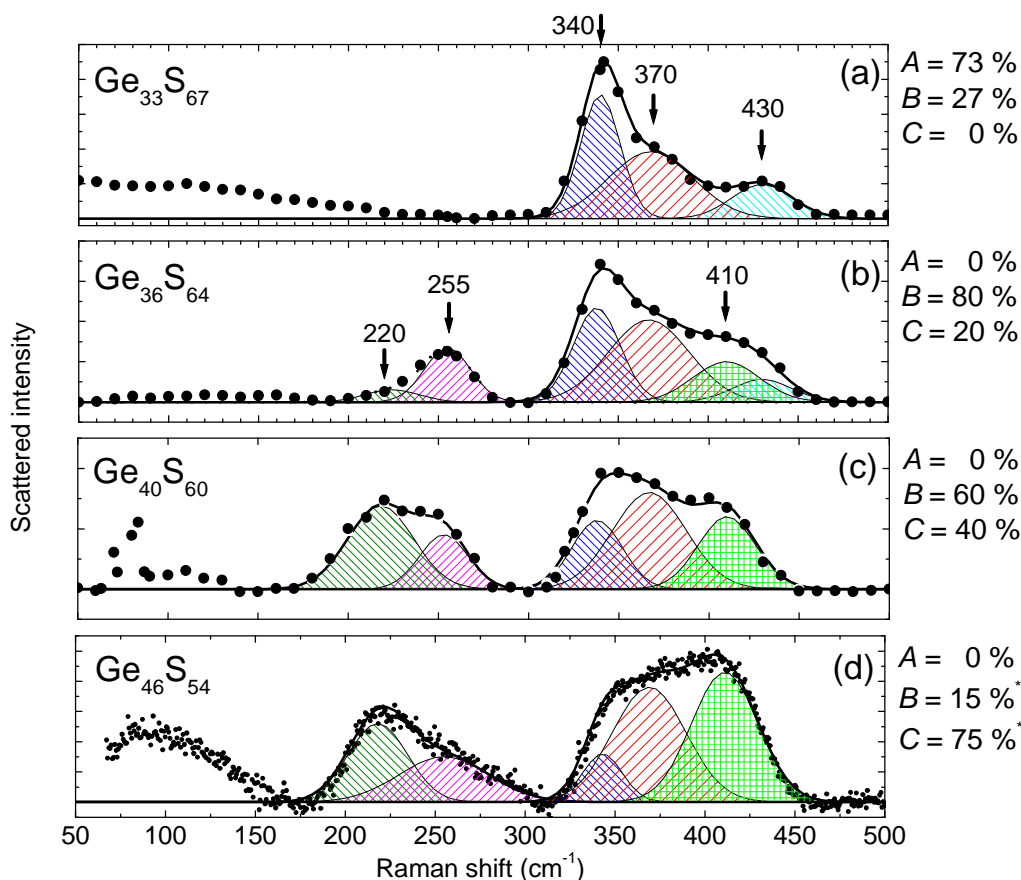


Fig. 1 Raman spectra of Ge-S glasses and the results of the curve fit. The dots show the experimental Raman spectra. The solid curves show the results of fitting, which are the sum of the indicated peaks. The contents of A, B and C phase, which were obtained from Mössbauer spectroscopy [2], are also indicated. The values at Ge 46 % (*) were estimated from the extrapolation of the results.

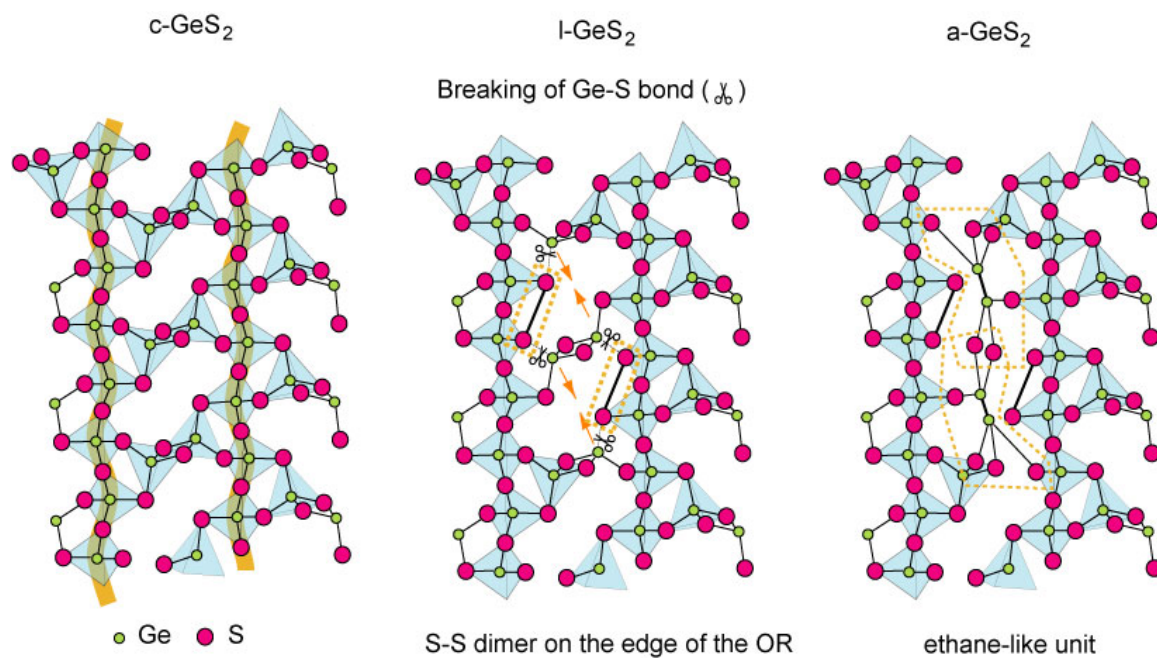


Fig. 2 A structural model, which explains how chemical disorder is formed in amorphous GeS_2 from crystalline GeS_2 through the liquid phase.

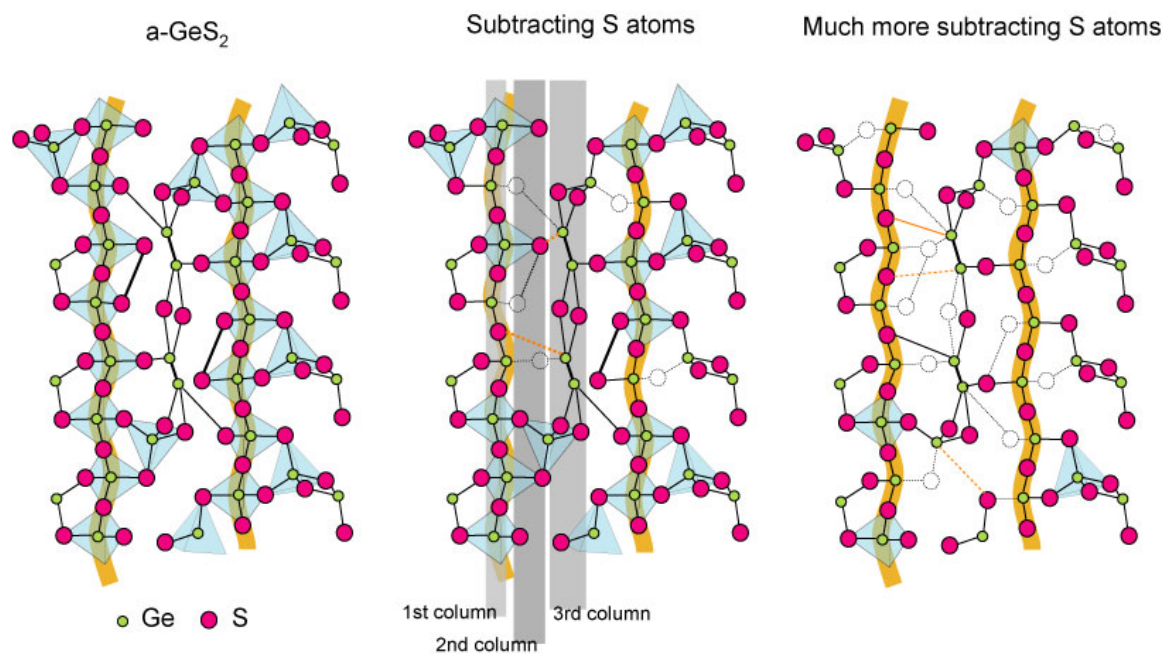
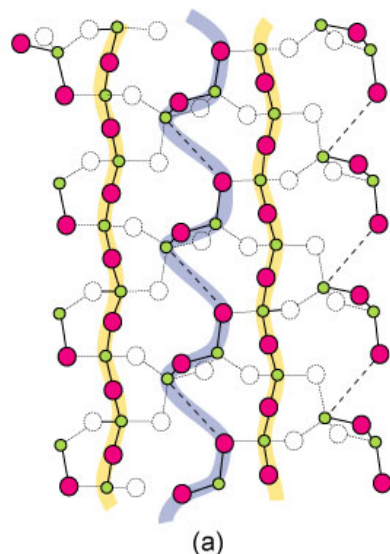
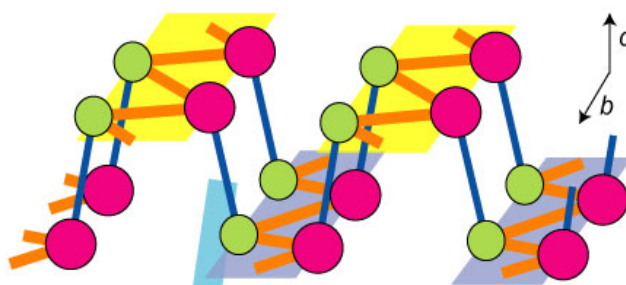


Fig. 3 A model of the structural development in Ge-S glasses from Ge 33 % (a-GeS₂) to Ge-rich region.

after subtracting Se atoms to be Ge 50%



Formation of double layer (b)



Formation of the 3rd bond (c)

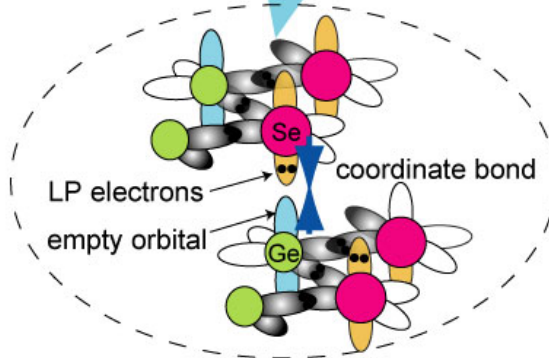


Fig. 4 (a) Atomic arrangement at Ge 50 %. Se atoms are subtracted from the structure of GeSe_2 . (b) Formation of the double layer structure from Ge-Se chains. Color of the chain corresponds to that in (a). (c) Formation of the third bond (indicated by blue in (b)).