

Chapter 16

Boolchand intermediate phases: Glass formation ability and average electronegativity

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The Boolchand intermediate phases (BIP) have been characterized from the point of view of chemical bond by two parameters: glass formation ability (GFA) and mean or average electronegativity (AE). The glass formation ability of these phases is situated in a close range of values around 0.36 that corresponds to a not too large glass formation tendency. The electronegativity of the intermediate phases is situated around 2.38 on the scale of average electronegativity. The width of the Boolchand phases is correlated with both parameters GFA and AE.

1. Introduction

The covalent glasses were understood for many years as continuous random networks of atoms. The first network model for covalent glasses was that of Zachariasen (1932) applied to SiO₂ glass [1].

Around 1980, when J. C. Phillips developed a new theory where the network glasses were viewed as space – filling networks subjected to bond stretching and bond bending constraints [2].

Following this turning point a huge amount of experimental data supported this model and showed that glassy networks undergo stiffness transitions from under-constrained to over-constrained system.

2. Boolchand intermediate phase

P. Boolchand [3] extended his own data on the stiffness transition and discovered the so-called intermediate phase defined by two abrupt stiffness transitions [4].

The Boolchand phase is characterized by a nearly vanishing non-reversible enthalpy of the glass transition and a nearly zero internal network stress. The new intermediate phase has been identified and its limits were accurately established in several chalcogenides, oxides, in silver based electrolytes and even in alcohols, sugars and proteins [5, 6].

3. Glass formation ability

The glass formation ability was a top subject for many years in glass science. Many scientists tried to characterize the easiness to form glasses in different materials, based on various crystallo-chemical properties, especially the type of inter-atomic bonding.

It is well known that, in the same conditions of preparation (cooling rate, deposition rate, etc.), some materials can be frozen in the glassy state and others cannot. Why the melts of various alloys behave so differently during cooling?

Myuller [7] firstly pointed out the main role played in the formation of glassy phase and amorphization in general, of the directional covalent bonds that create an intricate network, hard to transform into a crystalline lattice.

The suggestion of Winter-Klein [8] regarding the optimum number of p-electrons on an atom is a consequence of the second condition of the glass formation proposed by Myuller. These two conditions can be quantitatively considered, introducing the criterion of optimal number of bonds per atom, which forms in the vicinity of T_m in the structural unit of the material.

In the materials consisting of several structural units, the average number of bonds must be calculated considering the concentration of elements which form the structural unit.

Fritzsche [9] fundamented the role played by the average coordination number as an important characteristic that determines the ability of the atoms to form a disordered network.

Myuller et al. [10] and Goryunova et al. [11] have shown that the glass formation ability, essentially diminishes when the chemical bonds are metallized

as a consequence of the delocalization of the valence electrons. The lowering of the glass formation ability of the melt at cooling determines the molecular building characteristic of materials consisting of light atoms [10]. These two effects can be quantitatively considered calculating the average principal quantum number \bar{n} .

The consideration of the optimum average of the number of bonds and optimum mean principal quantum number can be done taking the product of these two factors. The first estimation of the glass ability on this basis was tried by Blinov [12]. Later Baidakov and Blinov [13] introduced the mean number of bonds per atom in the structural unit, \bar{k} . Moreover, the authors normalized the product $\bar{n} \cdot \bar{k}$ to \bar{Z} , the average charge of the nuclei that form the structural unit.

Thus $\frac{\bar{n} \cdot \bar{k}}{\bar{Z}}$ represents more correctly the *glass formation ability*. This parameter is higher for higher glass formation ability.

4. The electronegativity

The ability of atoms to attract the electron is defined as electronegativity. Electronegativity increases in every period of the Periodical Table of elements with the increase of atomic number Z and decreases in every group from up to bottom.

4.1 Pauling electronegativity

In 1932, L. Pauling [14] proposed for the characterization of the electronegativity the parameter:

$$\chi = \sqrt{\Delta E} \quad (1)$$

where

$$\Delta E = E_{AB} - \frac{1}{2}(E_{AA} + E_{BB}) \quad (2)$$

with E_{AA} , E_{BB} and E_{AB} the bonding energy between the atoms A and B in the molecules: AA , BB , and AB . If the energy is not expressed in kilocalories but in electronvolts then:

$$\chi = 0.208\sqrt{\Delta E} \quad (3)$$

Pauling considered that all the values χ exhibit additivity and used these values for estimation of the bond ionicity (covalency) in various compounds.

4.2 Mulliken electronegativity

In 1934, R. S. Mulliken [15] proposed as a measure of electronegativity the half-sum of the first ionization potential I_1 and the electron affinity F .

$$\chi = \frac{1}{2}(I_1 + F) \quad (4)$$

This parameter characterizes the free atom from opposite points of view: the energy necessary to release an electron (I_1) and the energy released when an electron is attracted to atom (F). Later, χ was called orbital electronegativity.

Regarding the characterization of the atoms using electronegativity, the Russian chemist N. S. Ahmetov wrote in 1975: "Simply speaking it is not possible to ascribe to a given element a constant electronegativity (EO). EO depends on many factors in particular valency state and type of compound. Nevertheless, this parameter is useful for quantitative explanation of the properties of the chemical bond in compounds."

4.3 Allred – Rochow electronegativity

Allred and Rochow [16] related the electronegativity to the charge experienced by an electron on the "surface" of an atom: the higher the charge

per unit area of atomic surface, the greater the tendency of that atom to attract electrons.

Taking the surface area of an atom as the square of the covalent radius, r_{cov} , then:

$$\chi = 0.359 \frac{Z^*}{r_{\text{cov}}^2} + 0.744 \quad (5)$$

where Z^* is the effective nuclear charge and the covalent radius, r_{cov} , is in ångströms.

4.4 Sanderson electronegativity

Sanderson [17] observed the relationship between electronegativity and atomic size and used this relation for calculation based on the reciprocal of the atomic size. The basic relation is:

$$\chi = (0.21 \cdot SR + 0.77)^2 \quad (6)$$

where χ is Pauling electronegativity and SR is the so called “stability ratio”, which is the average electron density of the atoms.

4.5 Allen electronegativity

Allen [18] related the electronegativity to the average energy of the valence electrons in a free atom.

$$\chi = \frac{n_s \varepsilon_s + n_p \varepsilon_p}{n_s + n_p} \quad (7)$$

where ε_s , ε_p are the electrons energies of s and p electrons in the free atom and n_s , n_p are the number of s and p electrons in the valence shell. By applying a scaling factor to energies one gets numerical values similar to Pauling electronegativity values.

4.6 Phillips electronegativity

Phillips [19, 20] suggested a natural definition of electronegativity in sp^3 – hybridized valence states. The dielectric definition of electronegativity is superior to ad-hoc chemical definitions including that of Pauling, which omits in calculation the Thomas-Fermi screening factor.

$$\chi_{\alpha} = 3.6 \left(\frac{Z_{\alpha}}{r_{\alpha 0}} \right) f_{\alpha\alpha} + 0.5 \quad (8)$$

where for an atom α , the valence is Z_{α} and, $2r_{\alpha 0}$ is the nearest – neighbour spacing of the diamond-type crystal belonging to the same row as atom α and $f_{\alpha\alpha}$ is a factor depending on the row of the atom in the Mendeleev Table of Elements.

4.7 St. John – Bloch electronegativity

St. John and A. N. Bloch [21] defined a new scale for quantum-defect electronegativity using the Pauling-force model potential which defines a new electronegativity scale consisting of explicit orbital components.

$$\chi = 0.43(X_0 + X_1 + X_2) + 0.50 \quad (9)$$

where X_i is are the orbital components that measure the scattering power of the core for i -th partial wave.

4.8 Gordy electronegativity

Gordy [22] calculated the electronegativity of various elements by the relation:

$$\chi = 0.31 \left(\frac{n+1}{r} \right) + 0.50 \quad (10)$$

where n is the number of electrons in valence shells and r the single bond covalent radius, measured in angstroms.

4.9 Jaffe electronegativity

Jaffe [21] used the electronegativity of orbitals to develop group electronegativities for molecular fragments that take into account the charge of a group, the effect of substituents, and the hybridization of the bonding orbital.

5. Average electronegativity and average relative electronegativity

In order to unify different electronegativity scales we have introduced an average scale. The average electronegativity of an element was calculated as:

$$e_{ave} = \frac{\sum e_i}{N} \quad (11)$$

where e_i is the electronegativity of a given element from different scales and N is the number of scales that contain the calculated electronegativity for that element.

Furthermore, we have introduced a scale of relative electronegativities based on the averaging of the values in different scales normalized to the sum of the electronegativities, multiplied by the number of counted values:

$$e_{ave} = \frac{\sum_i \frac{e_i}{\sum_j e_j} \cdot N'}{N} \quad (12)$$

where e_i is the electronegativity of a given element, e_j is the sum of the electronegativities of all elements in one scale, N' is the number of elements contained in one scale and N is the number of scales. The relative electronegativity is no-dimensional parameter.

The new scale is given in Table 1, together with the values of electronegativities in various scales.

Table 1. Electronegativities of elements.

Atomic number	Name	Pauling (revised)	Mulliken	Sanderson	Allred-Rochow	Allen	Jaffe	St. John-Bloch	Phillips	Gordy	Average electronegativity	Average relative electronegativity
1	H	2.2	2.8	2.31	2.2	2.3	2.25			2.17	2.319	1.175
2	He				5.5	4.16	3.49				4.383	2.153
3	Li	0.98	1.282	0.86	0.97	0.912	0.89	0.97	1	0.96	0.980	0.534
4	Be	1.57	1.987	1.61	1.47	1.576	1.81	1.49	1.5	1.38	1.599	0.862
5	B	2.04	1.828	1.88	2.01	2.051	2.28	2	2	1.91	2.000	1.089
6	C	2.55	2.671	2.47	2.5	2.544	2.75	2.5	2.5	2.52	2.556	1.389
7	N	3.04	3.083	2.93	3.07	3.066	3.19	2.99	3	3.01	3.042	1.656
8	O	3.44	3.215	3.46	3.5	3.61	3.65	3.49	3.5	3.47	3.482	1.899
9	F	3.98	4.438	3.92	4.1	4.193	4	3.99	4	3.94	4.062	2.210
10	Ne		4.597		4.5	4.789	4.5				4.597	2.194
11	Na	0.93	1.212	0.85	1.01	0.869	0.56	0.89	0.72	0.9	0.882	0.479
12	Mg	1.31	1.63	1.42	1.23	1.293	1.32	1.45	0.96	1.16	1.308	0.703
13	Al	1.61	1.373	1.54	1.47	1.613	1.71	1.4	1.18	1.48	1.486	0.802
14	Si	1.9	2.033	1.74	1.74	1.916	2.14	1.64	1.41	1.82	1.815	0.975
15	P	2.19	2.394	2.16	2.06	2.253	2.52	1.87	1.64	2.19	2.142	1.148
16	S	2.58	2.651	2.66	2.44	2.589	2.96	2.1	1.87	2.58	2.492	1.335
17	Cl	3.16	3.535	3.28	2.83	2.869	3.48	2.33	2.1	3	2.954	1.575
18	Ar		3.359	3.92	3.31	3.242	3.31				3.428	1.651
19	K	0.82	1.032	0.74	0.91	0.734	0.45	0.77	0.79	0.82	0.785	0.430

Atomic number	Name	Pauling (revised)	Mulliken	Sanderson	Allred-Rochow	Allen	Jaffe	St. John-Bloch	Phillips	Gordy	Average electronegativity	Average relative electronegativity
20	Ca	1	1.303	1.06	1.04	1.034	0.95	1.07	0.91	1.03	1.044	0.565
21	Sc	1.36		1.09	1.2	1.19				1.27	1.222	0.663
22	Ti	1.54				1.38				1.57	1.497	0.849
23	V	1.63				1.53				1.93	1.697	0.963
24	Cr	1.66				1.65				2.24	1.850	1.050
25	Mn	1.55				1.75				2.6	1.967	1.115
26	Fe	1.83				1.8					1.815	1.020
27	Co	1.88				1.84				1.76	1.827	1.035
28	Ni	1.91				1.88					1.895	1.065
29	Cu	1.9				1.85		1.53	0.79	0.96	1.406	0.834
30	Zn	1.65		1.86	1.66	1.59		1.36	0.91	1.21	1.463	0.825
31	Ga	1.81	1.343	2.1	1.82	1.765	2.42	1.46	1.13	1.48	1.703	0.906
32	Ge	2.01	1.949	2.31	2.02	1.994	2.62	1.59	1.35	1.77	1.957	1.040
33	As	2.18	2.256	2.53	2.2	2.211	2.82	1.71	1.57	2.04	2.169	1.155
34	Se	2.55	2.509	2.76	2.48	2.434	3.01	1.84	1.79	2.35	2.414	1.288
35	Br	2.96	3.236	2.96	2.74	2.685	3.22	2.33	2.1	2.68	2.768	1.481
36	Kr	2.9	2.984	3.17	2.91	2.966	2.91				2.973	1.482
37	Rb	0.82	0.994	0.7	0.89	0.706	0.31	0.74	0.66		0.728	0.395

Atomic number	Name	Pauling (revised)	Mulliken	Sanderson	Allred-Rochow	Allen	Jaffe	St. John-Bloch	Phillips	Gordy	Average electronegativity	Average relative electronegativity
38	Sr	0.95	1.214	0.96	0.99	0.963	0.72	0.98	0.83	0.98	0.954	0.518
39	Y	1.22	1.4	0.98	1.11	1.12				1.21	1.173	0.614
40	Zr	1.33				1.32				1.48	1.377	0.780
41	Nb	1.6				1.41					1.505	0.848
42	Mo	2.16				1.47				2.09	1.907	1.086
43	Tc	1.9				1.51					1.705	0.963
44	Ru	2.2				1.54					1.870	1.059
45	Rh	2.28				1.56					1.920	1.087
46	Pd	2.2				1.59					1.895	1.072
47	Ag	1.93				1.87		1.48	0.57	0.91	1.352	0.796
48	Cd	1.69		1.73	1.46	1.52		1.27	0.83	1.13	1.376	0.776
49	In	1.78	1.298	1.88	1.49	1.656	2.14	1.32	0.99	1.36	1.546	0.823
50	Sn	1.96	1.833	2.02	1.72	1.824	2.3	1.4	1.15	1.61	1.757	0.934
51	Sb	2.05	2.061	2.19	1.82	1.984	2.46	1.52	1.31	1.82	1.913	1.018
52	Te	2.1	2.341	2.34	2.01	2.158	2.62	1.62	1.47	2.08	2.082	1.108
53	I	2.66	2.88	2.5	2.21	2.359	2.78	1.67	1.63	2.36	2.339	1.245
54	Xe		2.586	2.63	2.34	2.582	2.34				2.496	1.203
55	Cs	0.79	1	0.69	0.86	0.659		0.72	0.64	0.78	0.767	0.424

Atomic number	Name	Pauling (revised)	Mulliken	Sanderson	Allred-Rochow	Allen	Jaffe	St. John-Bloch	Phillips	Gordy	Average electronegativity	Average relative electronegativity
56	Ba	0.89		0.93	0.97	0.881		0.92	0.79	0.93	0.902	0.517
57	La	1.1		0.92	1.08					1.17	1.068	0.580
58	Ce	1.12									1.120	0.656
59	Pr	1.13									1.130	0.662
60	Nd	1.14									1.140	0.668
61	Pm	1.13									1.130	0.662
62	Sm	1.17									1.170	0.685
63	Eu	1.2									1.200	0.703
64	Gd	1.2									1.200	0.703
65	Tr	1.2									1.200	0.703
66	Dy	1.22									1.220	0.715
67	Ho	1.23									1.230	0.720
68	Er	1.24									1.240	0.726
69	Tm	1.25									1.250	0.732
70	Yb	1.1									1.100	0.644
71	Lu	1.27				1.09					1.180	0.665
72	Hf	1.3				0.06					0.680	0.397
73	Ta	1.5				1.34					1.420	0.800

Atomic number	Name	Pauling (revised)	Mulliken	Sanderson	Allred-Rochow	Allen	Jaffe	St. John-Bloch	Phillips	Gordy	Average electronegativity	Average relative electronegativity
74	W	2.36				1.47					1.915	1.087
75	Re	1.9				1.6					1.750	0.987
76	Os	2.2				1.65					1.925	1.088
77	Ir	2.2				1.68					1.940	1.096
78	Pt	2.28				1.72					2.000	1.131
79	Au	2.54				1.92		2.22	0.64	0.92	1.648	0.974
80	Hg	2		1.92	1.44	1.76		1.39	0.79	1.12	1.489	0.838
81	Tl	2.04		1.96	1.44	1.789		1.37	0.94	1.34	1.554	0.879
82	Pb	2.33		2.01	1.55	1.854		1.41	1.09	1.56	1.686	0.957
83	Bi	2.02		2.06	1.67	2.01		1.46	1.24	1.83	1.756	0.893
84	Po	2				2.19		1.5		1.98	1.918	1.101
85	At	2.2				2.39		1.56			2.050	1.175
86	Rn					2.6					2.600	1.399
87	Fr	0.7				0.67					0.685	0.385
88	Ra	0.9				0.89					0.895	0.503
89	Ac	1.1									1.100	0.644
90	Th	1.3									1.300	0.761
91	Pa	1.5									1.500	0.879

Atomic number	Name	Pauling (revised)	Mulliken	Sanderson	Allred-Rochow	Allen	Jaffe	St. John-Bloch	Phillips	Gordy	Average electronegativity	Average relative electronegativity
92	U	1.38									1.380	0.808
93	Np	1.36									1.360	0.797
94	Pu	1.28									1.280	0.750
95	Am	1.3									1.300	0.761
96	Cm	1.3									1.300	0.761
97	Bk	1.3									1.300	0.761
98	Cf	1.3									1.300	0.761
99	Es	1.3									1.300	0.761
100	Fm	1.3									1.300	0.761
101	Md	1.3									1.300	0.761
102	No	1.3									1.300	0.761

6. The glass formation ability and electronegativity

Various compositions either in glassy or crystalline form can be characterized using two parameters: $\frac{\bar{n} \cdot \bar{k}}{\bar{Z}}$ (Glass Formation Ability, GFA) and Average Electronegativity (AE). Fig 1 a, b shows the result in the case of the systems where Boolchand phase was identified and accurately measured. The values of the intermediate phase boundaries are given in Table 2.

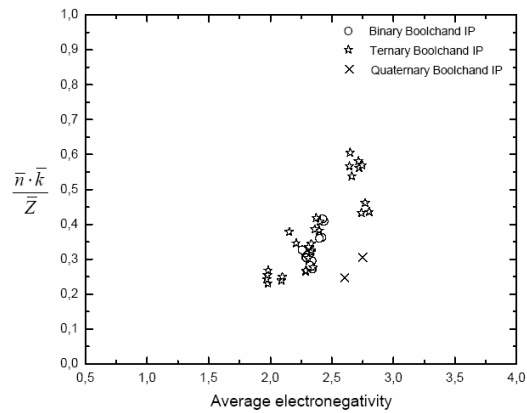


Fig. 1a. The position of BIP when glass formation ability is plotted versus average electronegativity

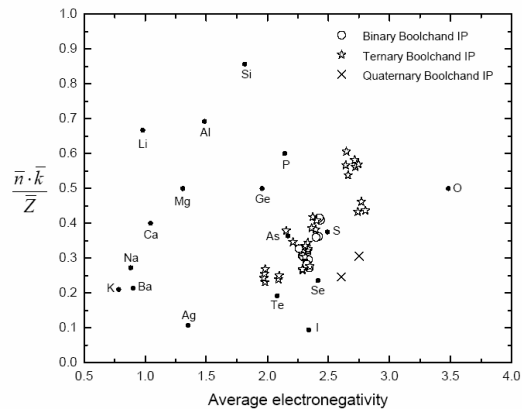


Fig. 1b. The same graph as in Fig. 1a with the points representing the composition limits for the systems.

Table 2. Boolchand intermediate phases used in the plot: Glass Formation Ability-Electronegativity.

Boolchand Phase	$x_c(1)$	$x_c(2)$	$\frac{\bar{n} \cdot \bar{k}}{\bar{Z}}$ (1)	$\frac{\bar{n} \cdot \bar{k}}{\bar{Z}}$ (2)	ϵ_{ave} (1)	ϵ_{ave} (2)	ϵ_{are} (1)	ϵ_{are} (2)
As_xS_{100-x}	22	29	0.362	0.360	2.421	2.398	1.295	1.283
P_xS_{100-x}	16	19	0.409	0.416	2.436	2.426	1.305	1.299
As_xSe_{100-x}	29	37	0.272	0.282	2.343	2.323	1.249	1.239
P_xSe_{100-x}	28	40	0.296	0.327	2.338	2.305	1.249	1.232
Si_xSe_{100-x}	20	26	0.304	0.327	2.294	2.258	1.225	1.207
Ge_xSe_{100-x}	20	28	0.286	0.306	2.323	2.286	1.238	1.219
$Ge_xAs_xS_{100-2x}$	11	15	0.382	0.386	2.398	2.363	1.283	1.264
$Ge_xAs_xSe_{100-2x}$	29	37	0.347	0.378	2.210	2.154	1.178	1.147
$Ge_{7.5}As_xTe_{92.5-x}$	21	28	0.239	0.250	2.091	2.097	1.113	1.116
$Ge_xP_xS_{100-2x}$	10	13.5	0.407	0.418	2.404	2.373	1.287	1.270
$Ge_xP_xSe_{1-2x}$	9	14.5	0.276	0.303	2.348	2.308	1.253	1.231
$Ge_xP_xTe_{100-2x}$	9	14.5	0.276	0.303	2.348	2.308	1.253	1.232
$Ge_{2.5}I_xS_{75-x}$	16.5	15.3	0.320	0.325	2.333	2.335	1.246	1.247
$Ge_{2.5}I_xSe_{75-x}$	16.5	15.4	0.265	0.268	2.287	2.288	1.219	1.219
$Al_{15}Si_xTe_{85-x}$	4	8	0.231	0.243	1.982	1.971	1.057	1.051
$Al_{20}As_xTe_{80-x}$	16	24	0.255	0.268	1.977	1.984	1.054	1.058
$(Li_2O)_x(SiO_2)_{100-x}$	25		0.606		2.647		1.440	
$(Na_2O)_x(SiO_2)_{100-x}$	24	17.9	0.567	0.581	2.643	2.716	1.437	1.477
$(CaO)_x(SiO_2)_{100-x}$	50		0.538		2.661		1.447	
$(BaO)_x(SiO_2)_{100-x}$	29		0.461		2.771		1.510	
$(K_2O)_x(SiO_2)_{100-x}$	16.4	14.5	0.562	0.569	2.723	2.746	1.481	1.494
$(Na_2O)_x(GeO_2)_{100-x}$	14	19	0.436	0.433	2.803	2.740	1.520	1.487
$(Ag_2S)_x(As_2S_3)_{1-x}$	8	13	0.344	0.336	2.332	2.311	1.249	1.239
$(AgI)_x(AgPO_3)_{100-x}$	9.5	37.8	0.306	0.247	2.750	2.604	1.508	1.429

The parameters \bar{n} , \bar{k} and \bar{Z} for A_xB_y , where $x+y=1$, are calculated in the following way:

$$\begin{cases} \bar{n} = xn_A + yn_B \\ \bar{k} = xk_A + yk_B \\ \bar{Z} = xZ_A + yZ_B \end{cases} \quad (13)$$

As seen in Fig. 1a the intermediate phases from various systems are all concentrated in a narrow region of the graph corresponding to $\frac{\bar{n} \cdot \bar{k}}{\bar{Z}}$ in the range 0.2 – 0.6 while the average electronegativity of the Boolchand intermediate phase (BIP) extends from 1.9 to 2.8.

Fig. 1b shows the values ascribed to the boundary elements of the systems that contain the BIP phases.

In Fig. 2 we can see that in case glass formation ability is plotted versus the average relative electronegativity, the BIP is situated in a narrow region, between 1.0 and 1.5 on the scale of average relative electronegativity.

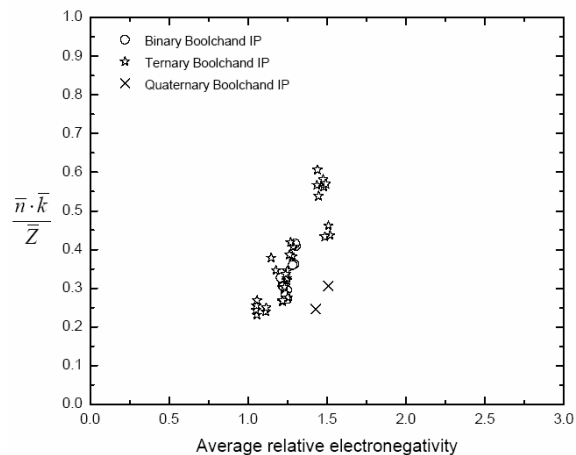


Fig. 2. The position of BIP when glass formation ability is plotted versus average relative electronegativity

7. Boolchand windows of the intermediary phases

As shown by Boolchand [23] in a given range of compositions glass transitions become almost completely reversible and for that reason the composition interval is often referred as the reversibility window (we shall call it Boolchand window (BW)). These windows correspond to the domain of existence of the intermediate phase. BP translates into a network conductivity that spans a well

defined range of r . Boolchand observed that BW in ternary alloys comprising of both group IV and group V elements with the chalcogenides possess rather large widths. BP in ternary $\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$ glasses is one of the widest reported to date. BW in the Ge-As-Se ternary is approximately the sum of windows in the As-Se and Ge-Se binaries. These data are suggestive that widths of BWs are determined by the stoichiometry of specific local structures that contribute to the BWs. The centroid of the BWs, appears to be tied to the degree of network polymerization. In ternary sulfides containing equal proportion of group IV and group V elements the intermediary phases possess smaller widths than their selenide counterparts, although their centroids appear to be nearly the same. To explain this feature Boolchand suggested that there are two characteristics of the sulfides that come into play here, one (a) the tendency of pure sulfur to crystallize as a molecular crystal composed of S8 rings rather than form polymeric chains as in the case of the selenides and second (b) binary arsenic sulfides as As_4S_3 and As_4S_4 , which form molecular cages rather than polymeric structures demixing, demixing from backbones of the As and Ge concentration approaches approximately 13 % [24]. Demixing of these molecular species at the low end and at the high end of the intermediary phase limits the range of r across which a backbone structure can prevail. The natural consequence is a shift of the low end of the intermediary phase up and of the high end of the intermediary phase down resulting in a narrowing of the width of the intermediary phase on the sulfides in relation to the selenides. These phases seem to be in fact partially polymerized network glasses.

We have investigated the relation between the BW in various compositions as a function of the Glass Formation Ability and Average Electronegativity. Figures 3 and 4 show the results.

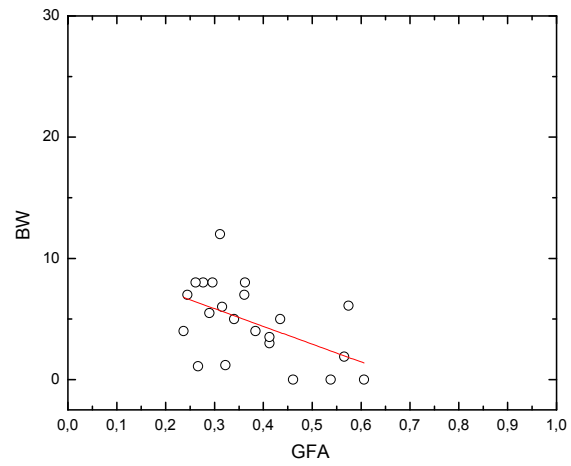


Fig. 3. The plot of the Boolchand windows versus the Glass Formation Ability for all the investigated chalcogenide glasses.

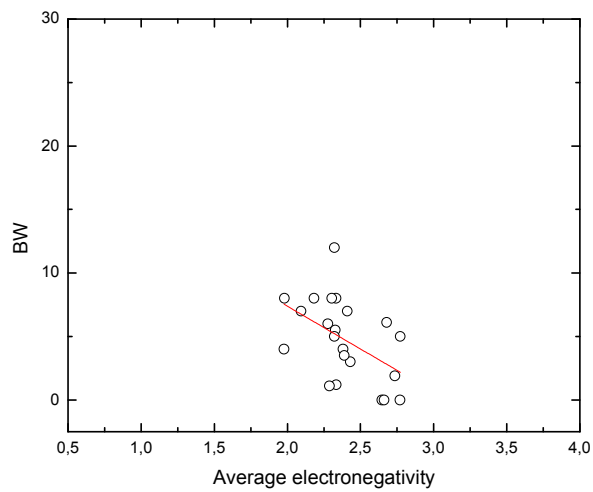


Fig. 4. The BW width versus the Average Electronegativity for all the investigated chalcogenide glasses.

When GFA is considered it is easy to observe a significant correlation between BW and GFA. For larger GFA the BW is lower. A linear fit of the observed plot gives the following results: -14.65 for the slope of the linear fit and 5.48 for the standard deviation of the points on the graph. In this fit the system with silver $\text{AgI}_x(\text{AgPO}_3)_{100-x}$ was excluded. The BP in this system exhibits an abnormal BW width. The observed linear dependence suggests that demixing of the molecular species (low BW width) is correlated with high glass formation ability. As concerning the relation between the width of the BW and the electronegativity a similar linear dependence demonstrates that for high average electronegativity of the glass the BW width becomes lower. The parameters of the linear fit in this case are: -6.74 and standard deviation 2.66. This interesting feature can be explained by the role played by the electronegativity in the glassy systems. Low electronegativities facilitate the crystallization of the glass and therefore the BW becomes narrower.

8. Conclusions

Boolchand intermediate phases are special phases in close relation with the electronegativity of the alloys and to their glass formation ability. The average electronegativity of the intermediate phases is situated around 2.38 or 1.28 on the scale of average electronegativity (AE) and average relative electronegativity (ARE).

The glass formation ability (GFA) for BIP is situated in the range 0.20 – 0.60 corresponding to a not too large glass formation ability.

From the point of view of the crystallo-chemical parameters, the Boolchand phases are concentrated in a strictly limited region situated in the middle part of the GFA and AE parameters.

The width of the Boolchand phase is significantly correlated with the Glass Formation Ability parameter. In the same time the BW width decreases with the increase of the electronegativity of the chalcogenide material in its intermediary phase.

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