JOURNAL OF MATERIALS SCIENCE 17 (1982) 329–334

Microhardness of chalcogenide glasses of the system Se-Ge-As

B. -D. MICHELS*, G. H. FRISCHAT
Arbeitsgruppe Glas, Lehrstuhl für Glas und Keramik, Technische Universität Clausthal, Clausthal-Zellerfeld, West Germany

The microhardness of chalcogenide glasses of the system Se–Ge–As was investigated for twelve different compositions. An apparatus was constructed which was capable of recording loading and unloading curves, and the results evaluated according to the method of Fröhlich and Grau. The Vickers microhardness values $L_{2(VH)}$ obtained were independent of load and are thought to be material constants. These $L_{2(VH)}$ values varied between 700 and 1400 N mm^{-2} in the Se–Ge–As system and showed a non-linear dependence on composition. This is explained structurally by the existence of varying proportions of different short-range order units in the different glasses. The elastic recovery after unloading varied between 45 and 61% for a maximum load of 1.96 N.

1. Introduction

The indentation hardness, H, is defined as the ratio of the load, L, to the area of impression, A, which is developed by an indenter of known geometry when pressed into the substance to be examined

$$H = \frac{L}{A}. \quad (1)$$

The actual area of impression depends on the shape of the indenter, for example, Vickers Pyramid.

Most microhardness tests on all kinds of materials (including glasses) reported so far used static methods, that is, the indentation diagonals, d, or depths, t, were measured for different loads after unloading [1, 2]. If the microhardness is measured dynamically under load by continuously recording t as a function of L up to a given load [3–5], the elastic recovery can also be obtained after unloading. A dynamic test procedure was used for the microhardness measurements described below [6].

Conventional microhardness values of glasses are normally dependent on load [2, 4, 7]. Moreover, cracks can be formed even at very small loads [7–9], and in these cases the material constants cannot be obtained.

This paper reports on microhardness investigations of glasses in the chalcogenide system Se–Ge–As. The objective was to determine the material constants, namely hardness values, independent both of the influence of load and of cracks. No such data have been obtained so far for chalcogenide glasses. There are only some conventional microhardness data [10]. In the glass system Se–Ge–As other properties have been reported previously, e.g. densities, glass transition temperature values, elastic constants, self diffusion, bending strength and chemical properties [11–14].

2. Experimental procedure

2.1. Glasses

The glass-forming region of the chalcogenide system Se–Ge–As lies in the Se-rich corner of the phase diagram [15, 16], as shown in Fig. 1. Different compositions of this system were prepared using a rotating sealed-off silica glass ampoule and melting temperatures up to 1050° C. Glass samples of about 70 g could be obtained in this way (the raw materials Se, Ge and As were of 99.999% purity). Composition of the glasses was checked by X-ray fluorescence and their homogeneity was ascertained by scanning electron microscopy. Table I details the compositions and physical properties of the glasses on which the measurements were conducted. The annealed glasses were

* Present address: Hermann C. Starck, Berlin, Werk Goslar, West Germany

0022–2461/82/020329–06$2.60/0

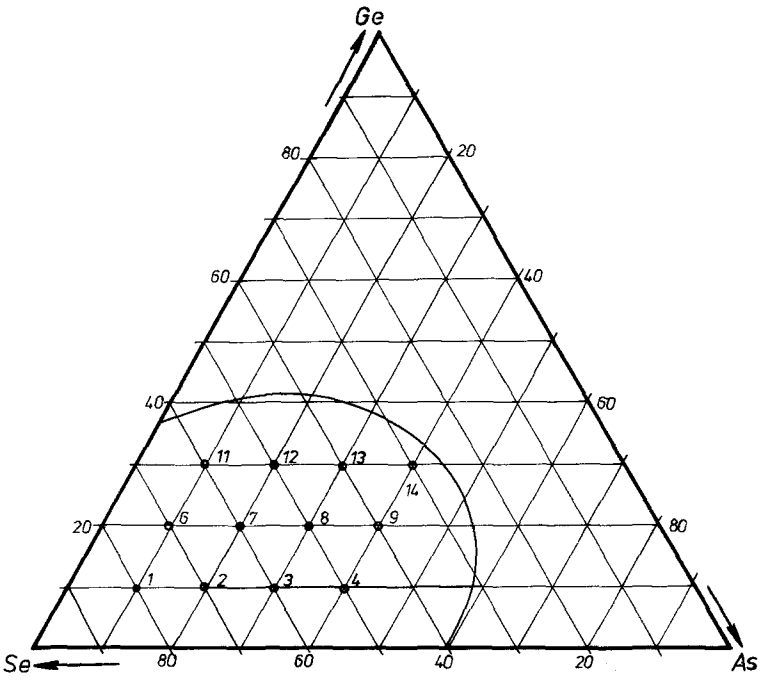

Figure 1 Glass forming region of the ternary chalcogenide Se–Ge–As system showing the positions of the investigated glass compositions.

then prepared as plane-parallel slices. The surfaces were carefully ground and polished. For further details concerning glass preparation and handling see [6].

2.2. Apparatus

A schematic representation of the apparatus is given in Fig. 2. It was constructed according to [3–5]. It consists of both an inductive path sensor and a force sensor with digital registration. The indenter (Vickers pyramid) and the inductive path sensor are connected to a microscope cylinder and can be raised and lowered in a defined way by spindle and motor. The speed of the indenter in the load-free state was 10^{-2} mm min^{-1}. The load is measured by a force detector with a maximum load of 20 N. Zero-point shifts can be compensated before indentation of the diamond into the sample. Maximum load and depth resolutions were 0.002 N and 0.01 μm digit^{-1}, respectively.

TABLE I Glass compositions and some physical data of the Se–Ge–As system. ρ and T_g values were taken from [17].

Sample number	Composition (at%)	ρ (g cm^{-3})	T_g* (°C)
1	$Se_{80}Ge_{10}As_{10}$	4.370	116
2	$Se_{70}Ge_{10}As_{20}$	4.479	160
3	$Se_{60}Ge_{10}As_{30}$	4.497	218
4	$Se_{50}Ge_{10}As_{40}$	4.486	228
6	$Se_{70}Ge_{20}As_{10}$	4.412	209
7	$Se_{60}Ge_{20}As_{20}$	4.398	277
8	$Se_{50}Ge_{20}As_{30}$	4.441	284
9	$Se_{40}Ge_{20}As_{40}$	4.511	326
11	$Se_{60}Ge_{30}As_{10}$	4.348	340
12	$Se_{50}Ge_{30}As_{20}$	4.432	363
13	$Se_{40}Ge_{30}As_{30}$	4.521	374
14	$Se_{30}Ge_{30}As_{40}$	4.666	381

*Measured by differential thermal analysis.

Fig. 3 shows a recorded L–t curve, obtained with the apparatus given in Fig. 2. Both loading and unloading curves were recorded ($0 \leqslant L \leqslant 1.96$ N). Usually a relation of the form

$$L = at^n, \tag{2}$$

where a is a constant and n is the Meyer exponent, is assumed [18]. However, as has been shown for different materials [7, 19, 20] this analysis is inappropriate since, over a wide range of loads, for example 0.02 N to 2 N, n is not constant. According to Frölich and Grau [3, 19], L can be developed in a general power series

$$L = \sum_i a_i t^i, \tag{3}$$

where i is a series of integers. By limiting the number of terms one gets

$$L = a_1 t + a_2 t^2. \tag{4}$$

(The term in a_0 is zero since $t = 0$ for $L = 0$).

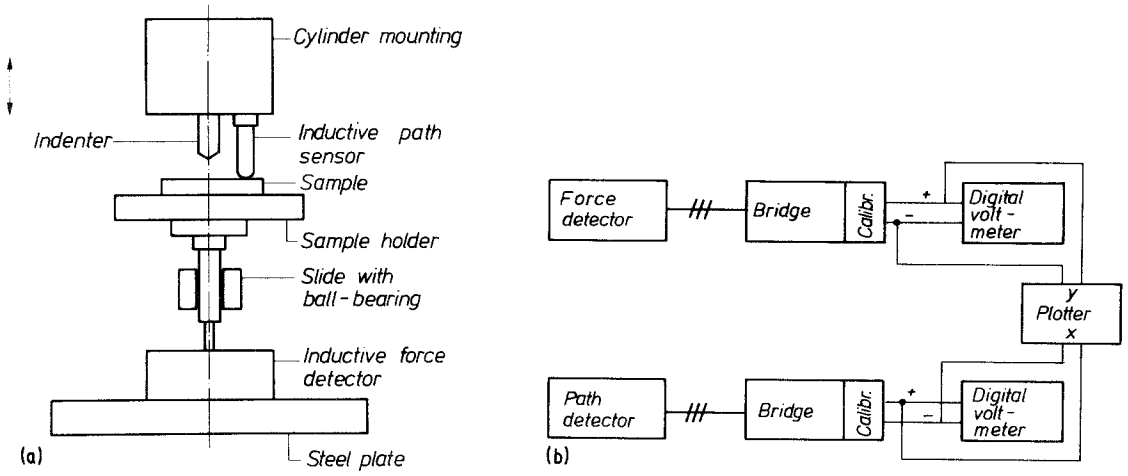

Figure 2 Schematic representation of the microhardness apparatus showing (a) the arrangement of the sample in the apparatus and (b) the general experimental set-up.

Thus, the total load L can be separated into two parts:

$$L_1 = a_1 t \tag{5}$$

and

$$L_2 = a_2 t^2. \tag{6}$$

$L_1 = a_1 t$ can be seen to be proportional to the work, S_0, which is necessary to increase the indentation area, A. Increase of area can be achieved by:

(a) the indentation of the Vickers pyramid itself; and

(b) the formation and propagation of cracks, especially for brittle materials (formation of inner surfaces).

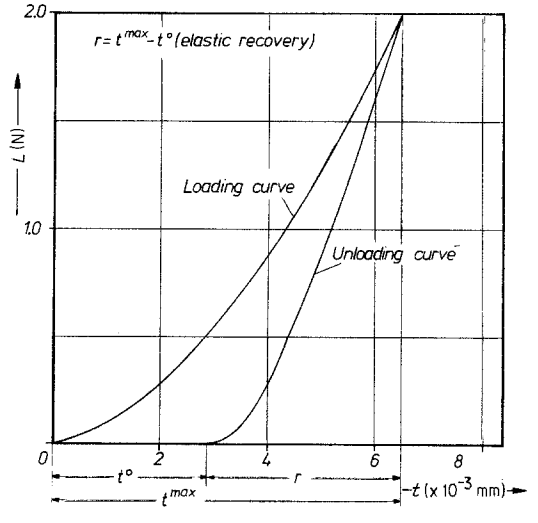

Figure 3 Loading and unloading curves, $L(t)$, as obtained by the apparatus shown in Fig. 2, for a dynamic microhardness measurement.

Equation 6 corresponds to the principle of Kick [21], with a Meyer exponent of $n = 2$, that means the work S_v to deform the bulk material is proportional to t^3. L_2 consists both of the work for elastic and permanent deformation during indentation. L_2 was used to define a new hardness number [3, 19], $L_{2(\mathrm{VH})}$

$$L_{2(\mathrm{VH})} = \frac{L_2}{A} = \frac{a_2 t^2}{t^2} K^* = a_2 K^*, \tag{7}$$

where $K^* = 3.784 \times 10^{-2}$ for the Vickers pyramid. This hardness value is "crack-free", since the influence of the cracks is eliminated by L_1. As may be seen from Equation 7, the hardness value $L_{2(\mathrm{VH})}$ is also independent of load. Transforming Equation 4 into the form

$$\frac{L}{t} = a_1 + a_2 t, \tag{8}$$

the coefficients a_1 and a_2 can be calculated by linear regression.

Equation 8 has been shown to hold [7, 22] for several oxide glass compositions with two straight sections of differing slopes. These slopes are representative of different hardnesses of the material near the surface, $L^{\mathrm{sur}}_{2(\mathrm{VH})}$, and in the bulk, $L^{\mathrm{vol}}_{2(\mathrm{VH})}$.

The elastic recovery, r, can be obtained from Fig. 3 according to

$$r = t^{\max} - t^0, \tag{9}$$

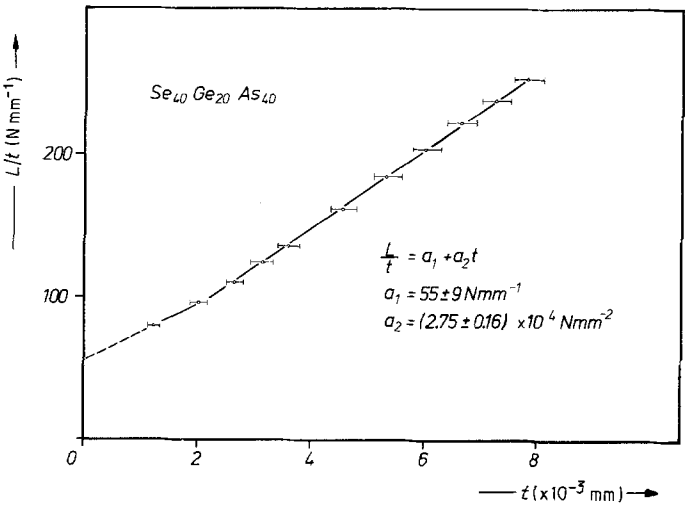

Figure 4 Evaluation of a dynamic microhardness measurement for $Se_{30}Ge_{30}As_{40}$ glass, according to Equation 8: $0 \leqslant L \leqslant 1.96$ N.

where t^{max} is the penetration depth for maximum load and t^0 is the penetration depth after complete unloading ($L = 0$). This elastic recovery depends on maximum load applied during indentation.

3. Results and discussion

3.1. Microhardness under load

Fig. 4 shows an example of an (L/t)–t-curve according to Equation 8, for a glass of $Se_{30}Ge_{30}As_{40}$ composition. $L_{2(VH)} = 1390 \pm 70$ N mm^{-2}, and is constant for all loads; no change in hardness near the surface could be found. Similar results were obtained for glass Samples 1, 3, 6, 7 12 and 13 (see Table II). For some other compositions deviations near the surface were found, for example, see Fig. 5, for a glass composition of $Se_{40}Ge_{20}As_{40}$. In this case $L^{vol}_{2(VH)}$ was found to be 1040 ± 60 N mm^{-2}; $L^{sur}_{2(VH)}$ had a lower value of 800 ± 200 N mm^{-2}. Similar surface effects were obtained for glass Samples 2, 4, 8 and 11. The origin of these different surface hardnesses may be attributed to the influence of polishing [6, 22].

As has been demonstrated earlier for oxide glasses [7–9, 23], Vickers indentations cause microcracks at the corners and the sides of the indentation pits. Fig. 6 shows that the same is true for these chalcogenide glasses. However, since $L_{2(VH)}$ eliminates the influence of this crack formation, these hardness values fulfil the condition for "crack-free" constants.

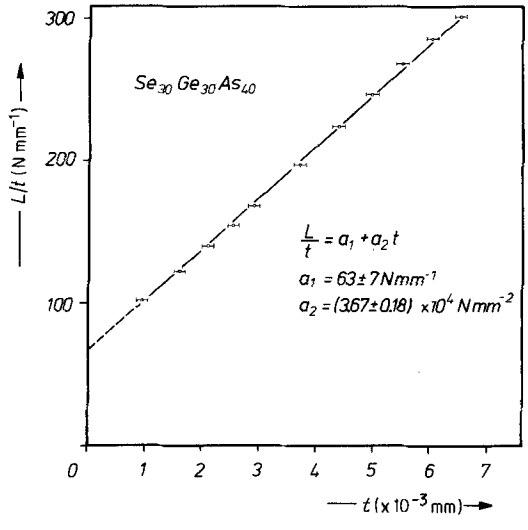

Figure 5 Evaluation of a dynamic microhardness measurement for $Se_{40}Ge_{20}As_{40}$ glass, according to Equation 8: $0 \leqslant L \leqslant 1.96$ N, showing the influence of surface effect.

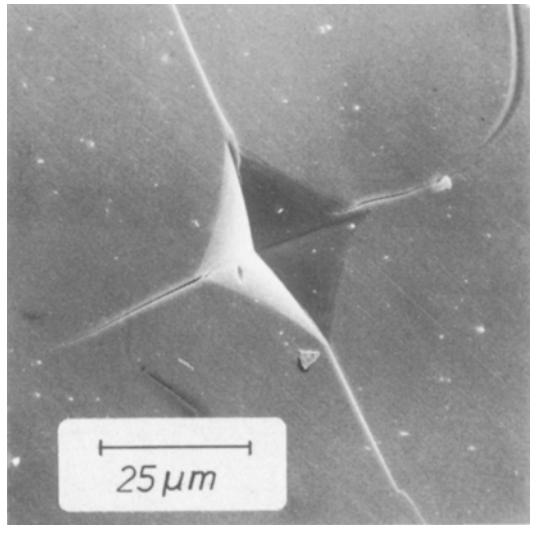

Figure 6 Scanning electron micrograph of a Vickers indentation in $Se_{60}Ge_{20}As_{20}$ glass: $L = 1.96$ N.

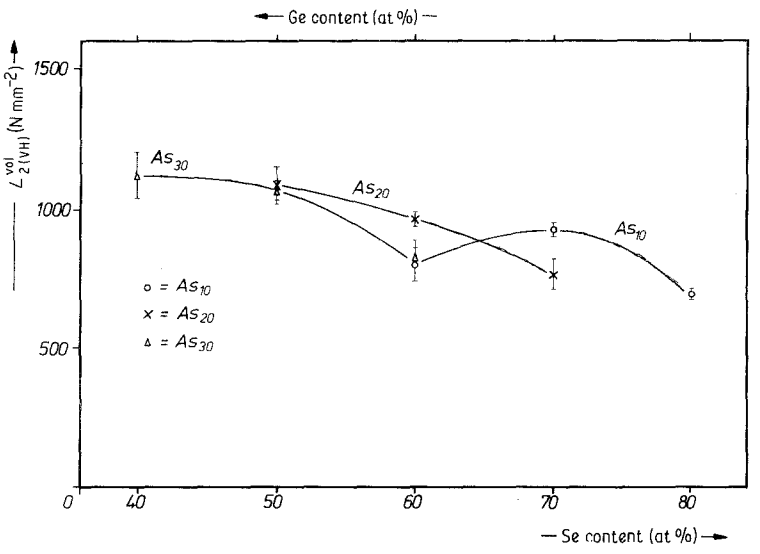

Figure 7 Microhardness values, $L^{vol}_{2(VH)}$, as a function of composition for glasses with constant As-contents: As_{30}, As_{20} and As_{10}.

3.2. Influence of glass composition

Fig. 7 shows the dependence of $L^{vol}_{2(VH)}$ as a function of glass composition. The hardness value changes in a non-linear way as a function of composition. Similar non-linearities hold for most other compositions and have also been found for other properties, for example, the glass transition temperatures, densities, elastic constants [11, 17]. Glasses of the system Se–Ge–As may contain different short-range order groupings [24], as indicated in Fig. 8. Depending on the actual overall composition, the relative proportions of these different units may vary. Pernot [25] gave relations for their approximate calculations. For the glasses with As_{30} (Fig. 7) the approximate structural compositions are:

25% $GeSe_{4/2}$, 50% $AsSe_{3/2}$, 25% $As_2Se_{4/2}$ (Glass 3);

50% $GeSe_{4/2}$, 25% $As_2Se_{4/2}$, 25% $AsAs_{3/3}$ (Glass 8);

and

50% $GeSe_{4/2}$, 36% $AsAs_{3/3}$, 13% $GeGe_{4/4}$ (Glass 13).

Since these different structure units have different properties the effect of non-linearity may be understood at least qualitatively.

The microhardness value in the ternary glass system Se–Ge–As is sensitively dependent on changes in chemical and structural compositions. However, when compared with hardness values of silicate glasses ($L^{vol}_{2(VH)} = 2660$ N mm^{-2} for plate glass) these glasses are relatively weak materials. This may be explained in terms of the differences in chemical bonding: chalcogenide glasses are largely covalent, while silicate glasses are ionic and covalent.

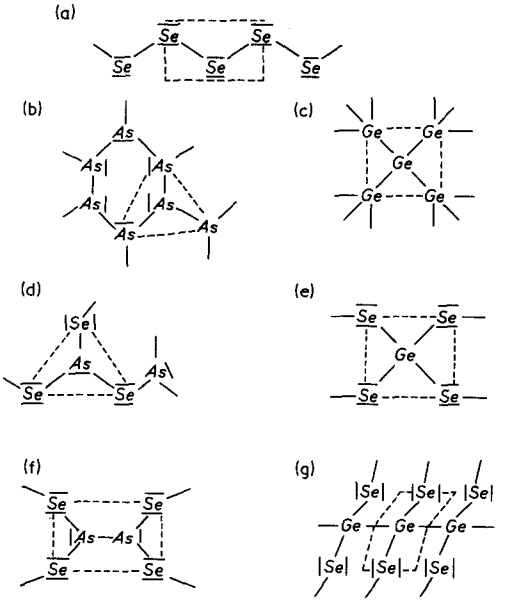

Figure 8 Possible structural units in glasses of the system Se–Ge–As. (a) $SeSe_{2/2}$; (b) $AsAs_{3/3}$, (c) $GeGe_{4/4}$, (d) $AsSe_{3/2}$, (e) $GeSe_{4/2}$, (f) $As_2Se_{4/2}$, and (g) $GeSe_{2/2}$.

3.3. Elastic recovery

The relative elastic recovery values, calculated according to Equation 9, are given in Table II. Dependent on glass composition, these values range between 0.45 and 0.61. They show that the geometry of the indentation is markedly changed after unloading. This supports the argument for using hardness values under load as material constants.

TABLE II Microhardness values for volume ($L^{vol}_{2(VH)}$) and surface ($L^{sur}_{2(VH)}$) and relative elastic recovery values r/t (for a maximum load of 1.96 N) as a function of glass composition

Sample number	$L^{sur}_{2(VH)}$ (N mm^{-2})	$L^{vol}_{2(VH)}$ (N mm^{-2})	$\frac{r}{t}$
1	–	700 ± 19	0.53 ± 0.02
2	550 ± 104	770 ± 53	0.45 ± 0.02
3	–	820 ± 76	0.49 ± 0.01
4	650 ± 108	870 ± 56	0.51 ± 0.03
6	–	930 ± 23	0.48 ± 0.02
7	–	970 ± 23	0.61 ± 0.03
8	800 ± 98	1070 ± 40	0.49 ± 0.01
9	800 ± 200	1040 ± 60	0.51 ± 0.03
11	615 ± 86	810 ± 60	0.54 ± 0.02
12	–	1090 ± 60	0.58 ± 0.01
13	–	1120 ± 80	0.59 ± 0.03
14	–	1390 ± 70	0.58 ± 0.02

Acknowledgements

The authors gratefully acknowledge the financial support of this work given by the Deutsche-Forschungsgemeinschaft (DFG), Bonne-Bad Godesberg.

References

1. R. SCHULZE, *Feinwerktechn.* **55** (1951) 190.
2. H. VAUPEL, Dissertation, Technische Universität Clausthal, 1971.
3. F. FRÖHLICH and P. GRAU, Proceedings of the XIth International Congress on Glass, Prague, July 1977, Vol. II, edited by J. Götz, (North Holland Publishing Co. Amsterdam, 1977) p. 567.
4. D. DENGEL and E. KROESKE, *VDI-Ber.* **308** (1978) 63.
5. *Idem, Materialprüfg.* **18** (1976) 161.
6. B. -D. MICHELS, Dissertation, Technische Universität Clausthal, 1980.
7. W. GRELLMANN, Dissertation, Martin–Luther Universität, Halle–Wittenberg, 1978.
8. W. KLEMM, *Glastechn. Ber* **19** (1941) 386.
9. V. SCHMIDT and J. HOPPE, *Wiss. Z. Friedrich–Schiller Universität Jena, Math. -Nat. R.* **28** (1979) 465.
10. Y. HASEGAWA and H. TAGAI, Proceedings of the XIth International Congress on Glass, Prague, July 1977, Vol. II, edited by J. Götz (North Holland Publishing Co. Amsterdam, 1977) p. 579.
11. U. TILLE, G. H. FRISCHAT and K. -J. LEERS, in "Non-Crystalline Solids", edited by G. H. Frischat (Trans Tech Publications, Aedermannsdorf, Switzerland, 1977) pp. 631–638.
12. U. EICHHORN and G. H. FRISCHAT, *J. Non-Cryst. Solids* **30** (1978) 211.
13. B. -D. MICHELS and G. H. FRISCHAT, *Glastechn. Ber.* **54** (1981), to be published.
14. G. H. FRISCHAT and M. BRAEDT, *ibid.* **52** (1979) 92.
15. L. A. BAIDAKOV, in "Solid State Chemistry", edited by R. L. Myuller (New York Consultants Bureau, New York, 1966) pp. 194–201.
16. J. A. SAVAGE and S. NIELSEN, *Phys. Chem. Glasses* **5** (1964) 82.
17. U. EICHHORN, Dissertation, Technische Universität Clausthal, 1977.
18. F. SCHULZE and H. HANEMANN, *Z. Metallkde.* **33** (1941) 124.
19. F. FRÖHLICH and P. GRAU, *Phys. Stat. Sol. (a)* **42** (1977) 79.
20. H. BÜCKLE, "Mikrohärteprüfung und ihre Anwendung" (Verlag Berliner Union, Stuttgart, 1965).
21. F. KICK, "Das Gesetz der proportionalen Widerstände und seine Anwendungen" (Verlag A. Felix, Leipzig, 1885).
22. P. GRAU, Private communication, 1977
23. K. PETER, *Glastechn. Ber.* **37** (1964) 333.
24. R. L. MYULLER, (ED), in "Solid State Chemistry" (New York Consultants Bureau, New York, 1966) p. 1–36.
25. F. PERNOT, *Verres Réfract.* **27** (1973) 45.

Received 12 March
and accepted 20 May 1981