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A new family of tellurite glasses

Part 1 *Glass formation*

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Glass formation in three-component tellurite–phosphate and tellurite–borate vitreous systems has been determined, with the latter including metal oxides or metal halides (chloride, fluoride or bromide), respectively. The results obtained have served as a base for the determination of the glass forming tendency in a number of tellurite–metaphosphate and tellurite–metaborate triple combinations. Hence a new family of tellurite glasses has been obtained. It has been established that the glass formation is most observed in alkaline, earth alkaline oxide and halide metaphosphate systems. The three-component tellurite–metaphosphate and metaborate systems investigated have been treated as partial three-component sections of the main four-component tellurite–phosphate and tellurite–borate systems also.

1. Introduction

The synthesis of glasses with high refractive index values is of great importance in the glass science and the optical industries. It is well known that TeO_2 is an appropriate component in a series of optical glass compositions of high refractive indices. Basically it is introduced to increase the refractive index and the transmission ability as well as to improve conditions that favour glass synthesis. Some lead–silicate glasses [1], for example, those modified by 7.2 to 15.7% TeO_2 are known. They show low absorption ability in the visible spectrum region. Other types of glasses, modified by TeO_2 [2] also are known. They are also characterized by a low absorption ability in the visible region and are suitable for contact lenses in photography. In relation to this some binary [3, 4] and ternary [5–11] tellurite systems have been used successfully for glass synthesis with high quantities of heavy metal oxides. A basic system for good glass-forming ability used by many authors is the TeO_2–WO_3 system. Tungsten oxide–tellurite glasses have been obtained showing an extremely high refractive index, low crystallization ability and good chemical resistance [5, 12–17]. This system of glasses also possesses good biological shielding against X-rays and γ-rays [18].

Some optical glass compositions are known which are modified by halides, oxyhalides and/or sulphates as a third component [9–21]. Theoretically and practically these glasses have proved to be successful in investigating these new types of non-crystalline solids. Also in relation to this, tellurite glasses, modified by transition element halides [22, 23] and by halides and oxyhalides of nontransition metal ions [24–26] have been reported.

The present study presents some experimental results of the glass-forming ability of three-component tellurite vitreous systems containing P_2O_5 and B_2O_3 as co-glass formers. Those systems included nontransition metal oxides R_mO_n or stable halides R_mH_n (H = fluorine, chlorine or bromine) from Groups I to V as a third component. On the basis of these results we have investigated the following systems: TeO_2–metaphosphate–metal oxide, TeO_2–metaphosphate–metal halide, TeO_2–metaborate–metal oxide, TeO_2–metaborate–metal halide, TeO_2–metaphosphate–metaborate, TeO_2–metaphos-

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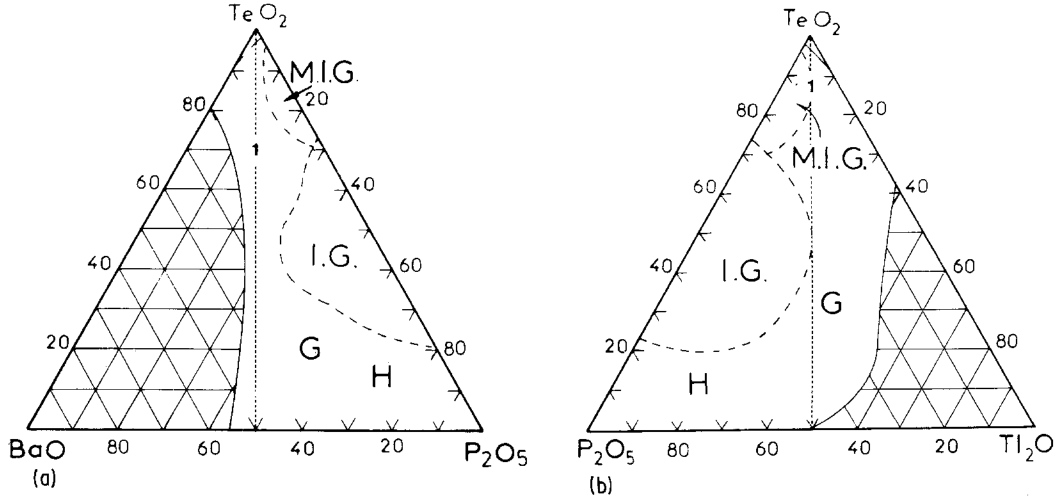


Figure 1 Glass forming regions (G) in the systems (a) TeO_2–P_2O_5–BaO and (b) TeO_2–P_2O_5–Tl_2O; region (H) is the region of a high hygroscopic ability; MIG is the metastable immiscibility gap; IG is the stable immiscibility gap and tie line 1-TeO_2-metaphosphate.

phate–metaphosphate and TeO_2–metaborate–metaborate. Taking into account the large amount of experimental data in [27, 28], we intend to generalize the experiments and discussion in this study.

2. Experimental details

In order to define the glass formation in our systems we prepared glasses according to the technology described by Kozhukharov *et al.* [29]. In order to reduce the volatility of halide-modified compositions during the melting process we used the synthesis method given by Urosovskaya *et al.* [30]. Glasses of 2 to 3 g were poured onto a copper plate at about $100\,K\,sec^{-1}$ and their states (transparent glass, opaque or opalescent glass, glass plus bulk or surface crystallization, full crystallization process) were studied visually or with the help of an optical microscope (Peraval, C. Zeiss Jena). In order to confirm the presence or absence of a liquation process in the glasses, some compositions were investigated using a Phillips EM-301 electron microscope.

3. Results and discussion

The first step in achieving our purpose was to determine the glass-forming regions in the three-component systems of the TeO_2–P_2O_5–R_mO_n, TeO_2–P_2O_5–R_mH_n, TeO_2–B_2O_3–R_mO_n and TeO_2–B_2O_3–R_mH_n types. Figs. 1 and 2 show

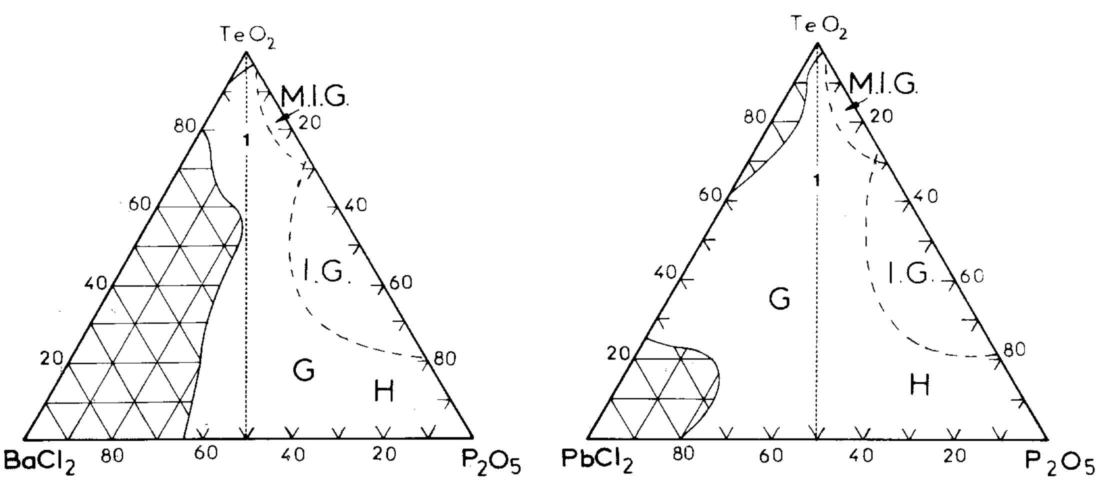
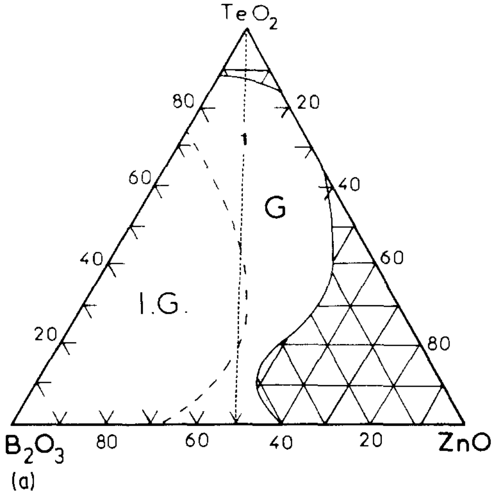


Figure 2 Glass forming regions (G) of tellurite phosphate systems with halides. (a) System TeO_2–P_2O_5–$BaCl_2$ and (b) system TeO_2–P_2O_5–$PbCl_2$. For regions (H), MIG and IG and tie line 1 see Fig. 1.



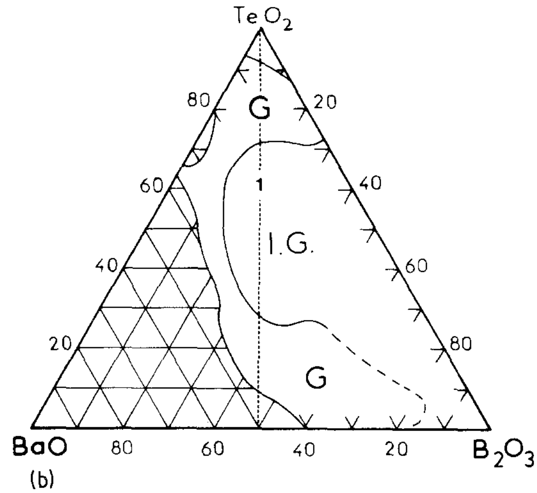
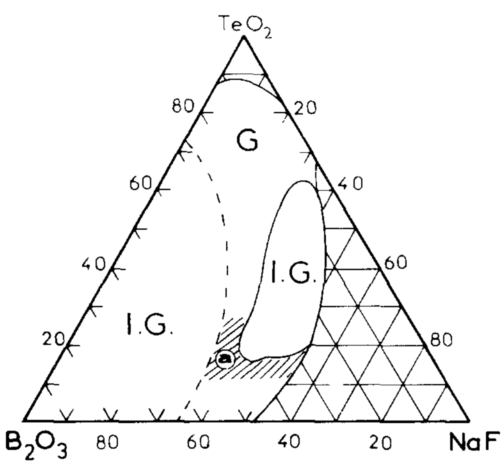


Figure 3 Glass forming regions (G) in the systems (a) $TeO_2-B_2O_3-ZnO$ and (b) $TeO_2-B_2O_3-BaO$. For IG and tie lines 1 see Fig. 1.

glass forming regions of tellurite systems containing P_2O_5 as a co-glass former. As seen from the figures, there are large metastable (MIG) and stable (IG) immiscibility gap regions. Compositions in these regions or near them are not suitable for the synthesis of high optical quality glasses. Glasses in the H-region (the P_2O_5 corner region) posses high hygroscopic ability and are chemically unstable. Therefore they can not be used for practical purposes. On the other hand, glass formation limits in the binary systems $TeO_2-R_mO_n$ and $TeO_2-R_mH_n$ [21, 31], which in our case are R_mO_n = BaO, Tl_2O and R_mH_n = $BaCl_2$, $PbCl_2$ (see Figs. 1 and 2), are relatively narrow. It is mainly this peculiar fact that reduces the probability of glass synthesis; the latter being of high crystallization ability. In order to avoid these disadvantages we drew a tie line from TeO_2 to the respective metaphosphate. As seen from Figs. 1 and 2 the glasses on that line give the optimum compositions, which lack the above mentioned disadvantages, and show good technological characteristics [32].

Figs. 3 and 4 represent glass forming regions of three-component tellurite–borate systems with oxides and halides, respectively. Because of the presence of a wide area of stable immiscibility in the binary $TeO_2-B_2O_3$ system [33–35], the triple combinations exhibit a wide field of phase separation processes. The processes, being analogous to those in the binary $TeO_2-P_2O_5$ –[36] system, greatly restrict the applicable section of the



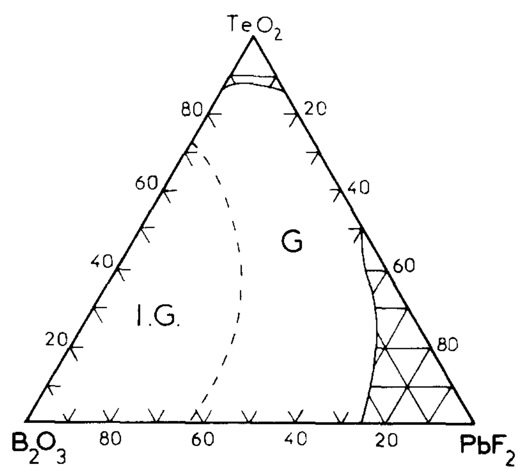


Figure 4 Glass forming regions (G) of ternary tellurite borate systems with halides (a) system $TeO_2-B_2O_3-NaF$ and (b) $TeO_2-B_2O_3-PbF_2$; IG is the immiscibility gap and area *a* represents glasses with the Tindal effect.

TABLE I Glass formation regions in the tellurite systems

Sample number	System	Surface (*S*) (%)	IG surface (*S*) (%)
1	TeO_2–P_2O_5–BaO	42.8	14.8
2	TeO_2–P_2O_5–Tl_2O	52.0	23.0
3	TeO_2–P_2O_5–$BaCl_2$	50.9	13.7
4	TeO_2–P_2O_5–$PbCl_2$	74.0	13.0
5	TeO_2–B_2O_2–ZnO	31.5	42.7
6	TeO_2–B_2O_3–BaO	27.0	36.0
7	TeO_2–B_2O_3–NaF	63.0	11.5
8	TeO_2–B_2O_3–PbF_2	50.6	38.8
9	TeO_2–$Cd(PO_3)_2$–ZnO	38.0	–
10	TeO_2–$NaPO_3$–$BaCl_2$	53.0	–
11	TeO_2–$Zn(PO_3)_2$–$Ba(PO_3)_2$	99.7	–
12	TeO_2–$TlPO_3$–$Zn(PO_3)_2$	99.8	–
13	TeO_2–$TlPO_3$–$Ba(PO_3)_2$	99.8	–
14	TeO_2–$Ba(PO_3)_2$–$BaCl_2 \cdot P_2O_5$	99.8	–
15	TeO_2–$Cd(BO_2)_2$–ZnO	27.6	–
16	TeO_2–$Pb(BO_2)_2BiCl_3$	50.5	–
17	TeO_2–$Zn(PO_3)_2$–$BiBO_3$	47.2	–
18	TeO_2–$Ba(PO_3)_2$–$Zn(BO_2)_2$	75.0	–
19	TeO_2–$BiBO_3$–$Pb(BO_2)_2$	98.2	–
20	TeO_2–$NaF \cdot B_2O_3$–$PbF_2 \cdot B_2O_3$	44.0	53.6

region, where glasses without the liquation process are formed.

Comparing the glass forming regions of oxide tellurite–phosphate and tellurite–borate three-component systems we established that the halides increase the glass forming ability. Introducing them, however, does not inhibit stable phase separation, which is characteristic for binary TeO_2–P_2O_5 and TeO_2–B_2O_3 systems [34, 36]. In analogy to tellurite–phosphate systems, tellurite–borate triple combinations along TeO_2–metaborate sections (tie line 1), can easily give rise to the synthesis of phase-separation free glasses.

Following the idea of using the TeO_2–metaphosphate and TeO_2–metaborate sections (i.e. tie line 1), we have prepared glasses of a "second generation", whose compositions are included in systems of the type: TeO_2–metaphosphate–metal oxide, TeO_2–metaphosphate–metal halide, TeO_2–metaborate–metal oxide, TeO_2–metaborate–metal halide, TeO_2–metaphosphate–metaphosphate, TeO_2–metaborate–metaborate and TeO_2–metaphosphate–metaborate.

Figs. 5 and 6 represent the glass forming regions of three-component systems in some of the above combinations. In comparing them, we have established that metaphosphate systems show better glass forming ability. This conclusion corresponds logically to the measured area in the glass forming regions given in Table I. The glass forming ability of metaborates is the worst, but in this case we can introduce into the tellurite–borate matrix higher concentrations of heavier metal oxides such as: Bi_2O_3, PbO, Tl_2O, CdO, WO_3, BaO, i.e. oxides of higher polarizational ability.

From another point of view, the systems we have investigated may be treated as partial triple combinations of their respective four-component combinations. In general this fact is illustrated in Fig. 7 where two typical cases are shown. In fact, the glass forming regions of the systems above represent partial triple combinations lying on elementary ternary diagrams of four-component systems.

It then follows that using compositions lying on the TeO_2–metaphosphate and TeO_2–metaborate tie line in the triple tellurite–phosphate and tellurite–borate systems we have realized successfully the synthesis of a new family tellurite glasses. We have proved too, that by these means, glasses with extremely high glass forming regions are obtained.

4. Conclusions

The glass forming ability of some three-component tellurite–phosphate and tellurite–borate systems have been investigated. As a third component, acting as a modifier, oxides and stable halides

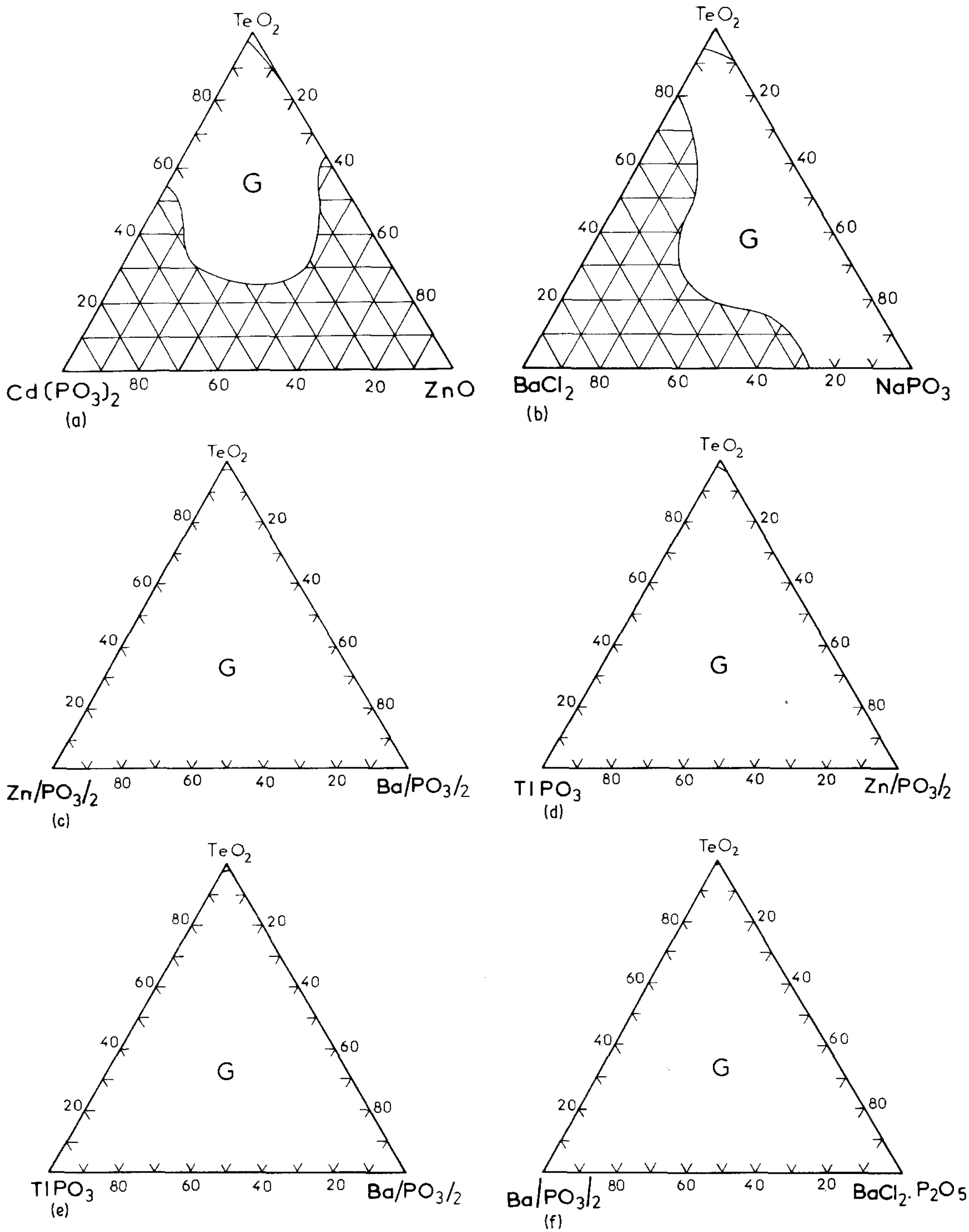


Figure 5 Some examples of glass forming regions in three-component tellurite–metaphosphate systems; (a) system with a metal oxide as a third component, (b) system with metal halide, (c) to (e) systems with two metaphosphates and (f) system with a metaphosphate and halide metaphosphate.

(fluorides, chlorides and/or bromides) have been used successfully. On the bases of these preliminary results, glasses of a "second generation" with good technological, physicochemical and optical characteristics have been obtained. This has been realized by using TeO_2–metaphosphate and TeO_2–metaborate systems. It has been established that this property is expressed best for metaphosphate and halide containing systems when compared to these which include metal

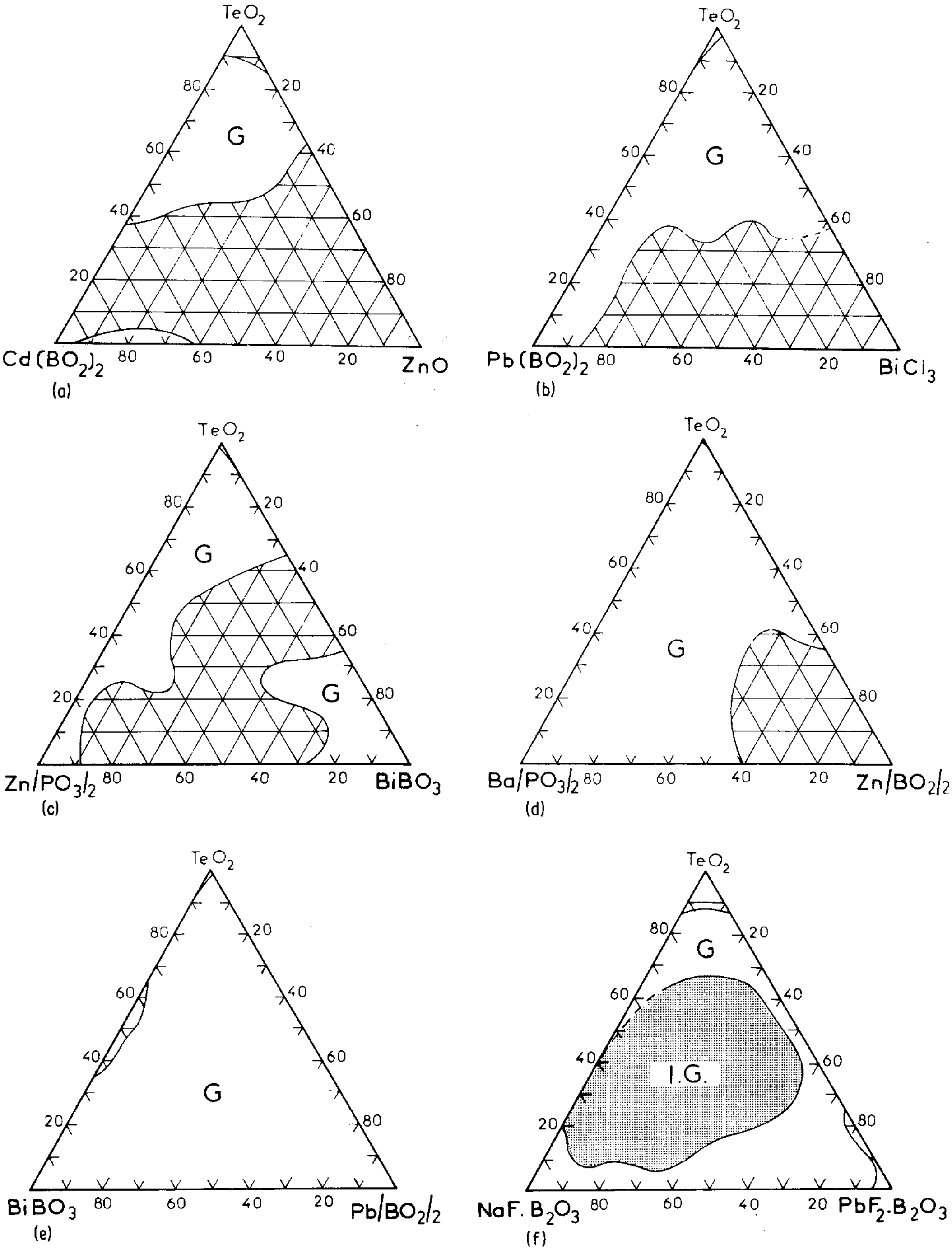


Figure 6 Some examples of glass forming regions in three-component tellurite–metaborate systems; (a) system with a metal oxide as a third component (see Fig. 5a), (b) system with a metal halide, (c) and (d) systems with a metaborate and metaphosphate as a third component and (e) and (f) systems with two metaborates, the second having a metal halide base.

oxides. Three-component tellurite–metaphosphate and tellurite–metaborate systems can be treated as partial three-component sections of the respective four-component tellurite–phosphate and tellurite–borate combinations.

Aiming to clarify the nature of this new family of tellurite glasses, investigations referring to the glass forming ability, glass properties and structure are to be the subject of the next collaborative study.

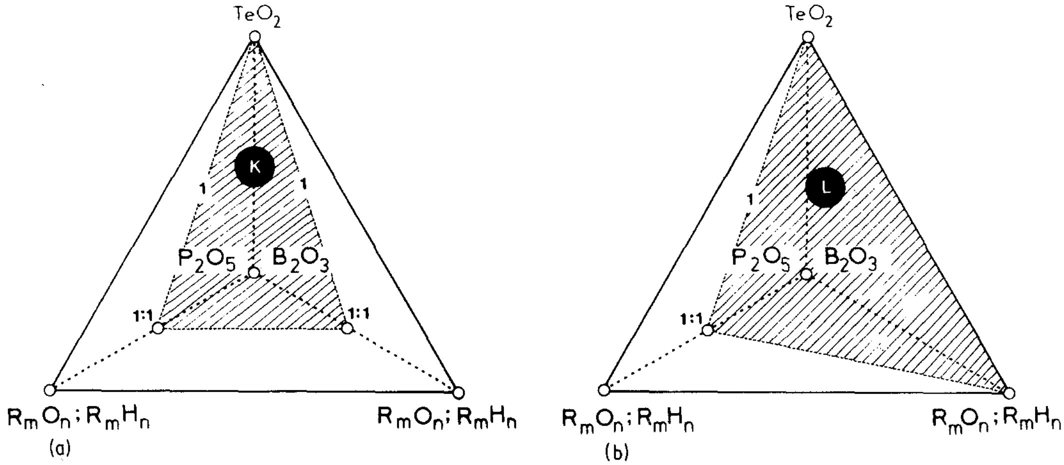


Figure 7 Four-component tellurite–co-glass former system: (a) TeO_2–P_2O_5 or B_2O_3, i.e. a metal oxide or a metal halide (section K, elementary triangular TeO_2–metaphosphate–metaphosphate or TeO_2–metaborate–metaborate) and (b) a combination with section L, elementary triangular TeO_2–metaphosphate or metaborate, i.e. metal oxide or halide.

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