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Glass formation in oxide–halide systems

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Recently the halide and oxidechalide glasses have been the object of great interest because they are promising materials for optics. Up to now many unsolved problems exist in relation to their glass formation, chemical resistance and the thermal stability of these glasses. An object of our investigation is the study of the glass formation in halide systems with the participation of $PbCl_2$, NaCl, KCl, $BaCl_2$ and oxide–halide systems with the participation of the TeO_2. The ranges of glass formation in the systems: TeO_2–$PbCl_2$–NaCl–KCl and TeO_2–$BaCl_2$–$CdCl_2$–NaCl are determined at different cooling rates. Stable glasses possessing low melting temperature, good chemical resistance were prepared.

1. Introduction

The oxide–halide glasses are a comparatively new group of inorganic glasses which have been the object of intensive investigations recently. They are divided in several groups depending on the concentration of dominant anion in the lattice [1–4]: (a) fluoride glasses: based on the examination of BaF_2 glasses distinguished in relation to its structure as an analogue of SiO_2 and recently, the optical glasses based on ZrF_4; (b) chloride glasses based mainly on the $ZnCI_2$. There are existing data for the glass formation in the systems with the participation of $BiCI_3$, $PbCI_2$, $CdCI_2$; (c) glasses with the participation of bromides AgBr, CsBr, CdBr and iodides AgI, CsI, CdI, KI.

One of the main characteristics of the glasses are their optical properties; a broad range of optical transmittance covering the ultraviolet, visible, and infrared range of the spectrum, comparatively low values of refraction index (1.2–1.6), low values of optical losses in comparison with the oxide silicate glasses (10^{-2}–10^{-3} dM km^{-1}). These characteristics make them challenging materials for the infrared optics, as optical fibres with super low losses, and high powerful lasers, etc.

The high toxicity of these glasses is an apparent defect as well as their chemical instability, high trend to crystallization and the difficulties involved in their synthesis, because of the volatility of some of the components.

From the fundamental and application points of view the mixed oxide–halide systems are of great interest because they combine the good optical properties of halide glasses with the improved thermal and chemical resistance of oxide glasses. There are data in the literature about the glass formation and some more important properties in mixed oxide–halide binary and ternary systems. They are combinations in which a basic glass-former is used B_2O_3 [5–7], Pb [8], Sb [9], Te [10–16] and chalogenides of the metals. In order to draw some conclusions about the practical application of these glasses it is very important to prepare different model glasses and to study their properties.

The aim of the present investigation is to study the glass formation in the TeO_2–$PbCI_2$–NaCI–KCI and TeO_2–$BaCI_2$–$CdCI_2$–NaCI systems, and the examination of the properties of glasses prepared.

2. Experimental details

TeO_2, 95% (Fluka), $PbCI_2$ (Merck, DBR), $BaCI_2 \cdot 2H_2O$ (Merck, DBR), $CdCI_2$ H_2O (May and Baker, England), KCI (reagent grade, Polland), NaCI (reagent grade) were used as the initial raw materials.

The batches were determined for 5 g glass. After homogenization in an agar mortar they were put in dryer, after which they were melted in a porcelain covered crucible in a Kantal furnace at 500–800° C depending on the composition of the mixture. The quenching was performed on a copper plate at cooling rates of 1000° C min^{-1}.

For the examination of glass properties samples were prepared by pouring them into specific graphite moulds heated in advance at 200° C, after which they were tempered for 1 h at 200° C and cooled to room temperature. Polishing to a mirror surface was the last stage of the procedure.

3. Results and discussion

3.1. TeO_2–$PbCl_2$–NaCl–KCl system

The glass formation ranges in binary and ternary systems building up the four-component systems were studied. The sections investigated by us are presented in Fig. 1; the glass formation ranges are presented in Fig. 2. It is apparent that with increase of TeO_2 content the range of glass formation broadens and it is drawn to the higher $PbCI_2$ concentrations. The glasses are transparent to pale green. They are thermally resistant up to the melting temperature. In accordance with the data from the DTA curve they are characterized by T_g 250–320° C, T_{cryst} 350–380° C, T_{melt} 610–690° C. At the section corresponding to the 80 mol % TeO_2 only milk glasses were produced.

In accordance with the data from DTA, the lowest crystallization ability was assigned to the glasses in 40 mol % TeO_2 section. For this reason the compositions from this section were modified by exchange of

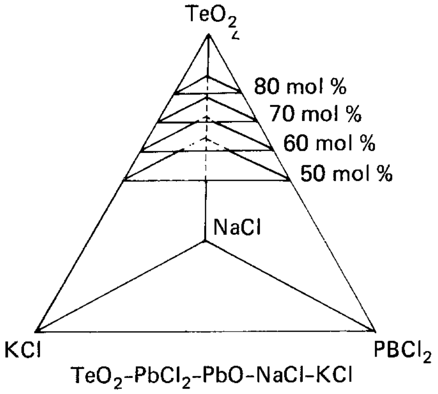

Figure 1 The investigated sections in the TeO_2-$PbCl_2$-KCI-NaCI system.

part of $PbCI_2$ with PbO (10–35 mol %). Stable transparent glasses with T_g 250–280° C, T_{cryst} 350–380° C, T_{melt} 450–500° C were prepared. The values of the coefficient of linear thermal expansion are high (20–200° C = 249 × 10^{-7} K^{-1}) near the coefficient of thermal expansion of the aluminium (235 × 10^{-7} K^{-1}).

The spectral properties of glasses in a 0.2–25 μm range were studied (Fig. 3). They do not transmit in the ultraviolet range, but their transmissivity in the visible range of the light is apparent and it attains up to 6.5 μm in the infrared range of the spectrum. The transmittance of these glasses coincides with the values of similar ones.

3.2. TeO_2-$BaCl_2$-$CdCl_2$-NaCl system

Based on the results obtained for glass formation in ternary and binary systems we have examined compositions from the sections at 10, 30, 40, 50 and 80 mol % TeO_2 (Table I) by keeping constant the $BaCI_2$ + $CdCI_2$: NaCI (9 : 1) ratio. The stable transmittant glasses are prepared at a concentration of TeO_2 of 40 to 80 mol %.

An attempt was made to modify the compositions from these sections by partial exchange of $BaCI_2$ with BaO (2–12 mol %), NaCI with KCI (5–7 mol %). At all combinations of the compositions, it was found that glass formation is possible, as the lowest crystallization ability possess glasses at the section at 50 mol % TeO_2. They were an object of further investigation of their properties. They are characterized by: T_g 250–270°C, T_{cryst} 350–400° C, T_{melt} 500–550° C, coefficient of linear thermal expansion (20–200° C) = 195 × 10^{-7} K^{-1} near the coefficient of thermal expansion of the copper. These glasses are of interest for the preparation of seals. The spectral properties of glasses from this system (Fig. 4) show similarity with the investigated ones. In the ultraviolet range they are not transmissible, and they become transparent in the visible range of the spectrum and their highest transmittance is at 0.58 μm. They are transmissible in whole near infrared range. Their transmittance attains 6.6–7 μm.

It was of interest to follow up the losses of chlorine during the synthesis of glasses. For this reason the methods of thermogravimetry (TG) [17] and ion-selectivity [18] were used. The results of both the methods are close and show the difference between the batch and analogous composition in relation to the halogen content from 2 to 4 mol %.

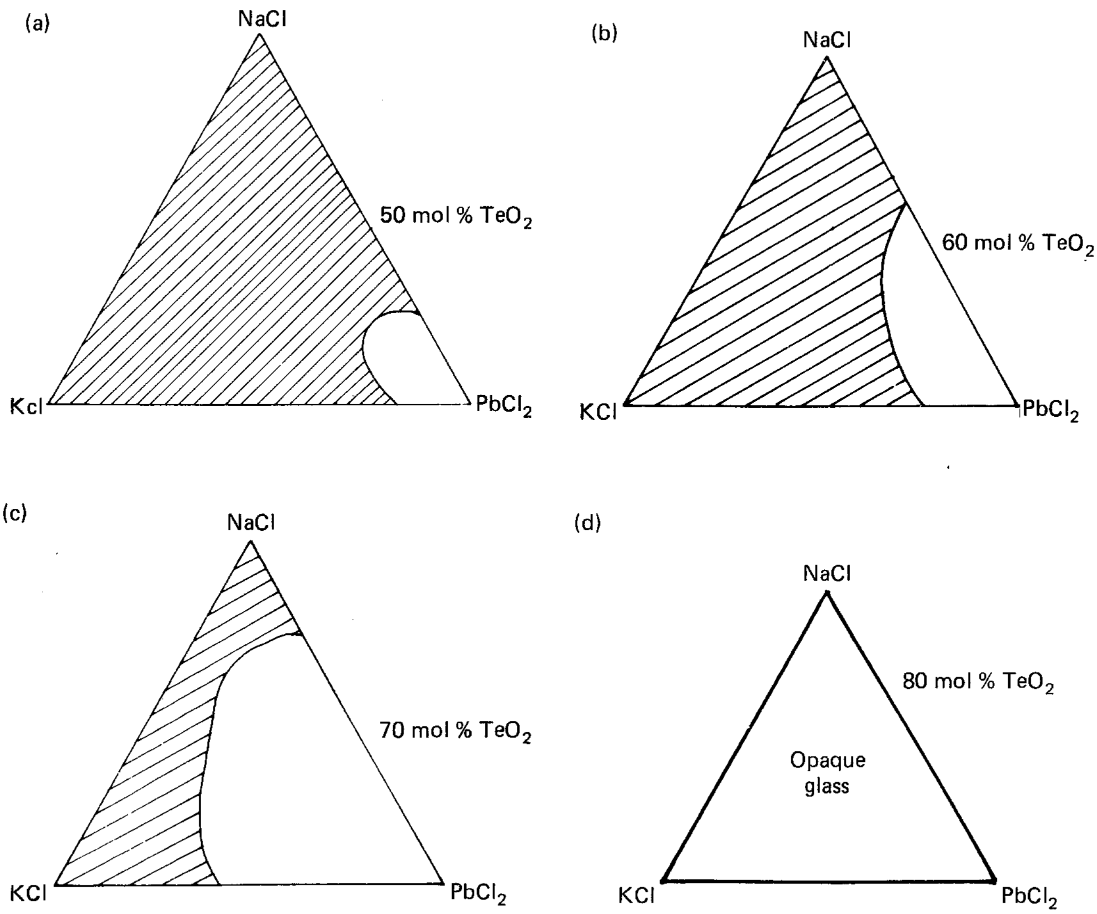

Figure 2 Glass formation ranges in the sections with (a) 50, (b) 60, (c) 70 and (d) 80 mol % TeO_2.

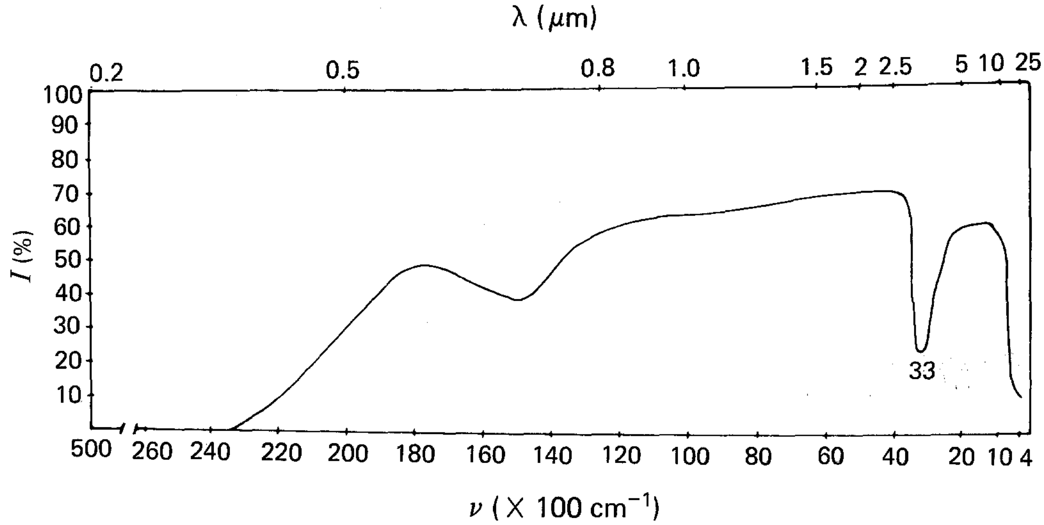

Figure 3 Spectral transmission of clear glass in the system TeO_2–$PbCl_2$–PbO–KCl–NaCl.

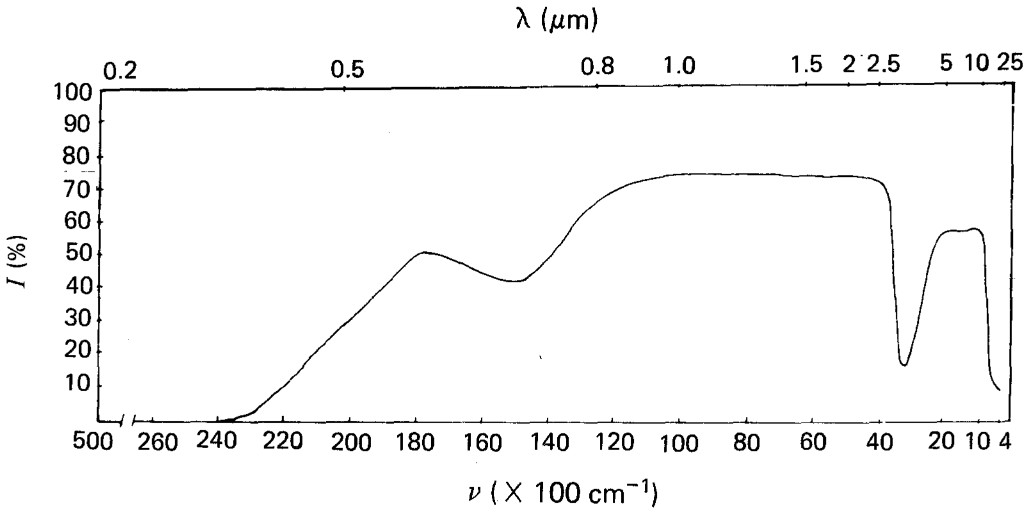

Figure 4 Spectral transmission of clear glass in the system TeO_2–$BaCl_2$–BaO–KCl–NaCl.

4. Conclusion

As a result of the investigations carried out the following conclusions could be drawn:

1. At the cooling rates used, low melting stable transparent glasses in the TeO_2–$PbCI_2$–NaCI–KCI system, characterized by T_g 250–280° C, T_{cryst} 290–320° C, T_{melt} 450–500° C, a coefficient of linear thermal expansion (20–200° C) = 249 × 10^{-7} K^{-1} were successfully synthesized.

2. Low melting, stable transparent glasses in TeO_2–$BaCI_2$–$CdCI_2$–NaCI (BaO, KCI) with T_g 250–270° C, T_{cryst} 350–400° C, T_{melt} 500–550° C, coefficient of linear thermal expansion (20–200° C) = 195 × 10^{-7} K^{-1}.

3. The addition of the TeO_2 improves the thermal stability and the stability of glasses against the influence of air.

4. The glasses synthesized have spectral transmittance up to 7 μm in the infrared range of the spectrum.

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TABLE I

Composition								Visual characteristics
TeO_2 (mol %)	$CdCI_2$ (mol %)	$BaCI_2$ (mol %)	NaCI (mol %)	TeO_2 (wt %)	$CdCI_2$ (wt %)	$BaCI_2$ (wt %)	NaCI (wt %)	
80	9	9	2	77.8	10.05	11.42	0.71	Transparent glass
50	22.5	22.5	5	46.7	24.1	27.49	1.71	Transparent glass
40	27.0	27.0	6.0	36.89	28.6	32.49	2.03	Dark brown glass
30	31.5	31.5	7.0	27.31	32.94	37.42	2.33	Liquation
10	40.5	40.5	9.0	9.74	45.3	51.48	3.2	Grey crystals

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