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New halide glasses of the CdX_2–PbX_2–KI (X=Cl, Br) systems

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The glass forming regions and some properties of the $CdBr_2$–$PbBr_2$–KI (10 to 50 mol% $CdBr_2$, 10 to 70 mol% $PbBr_2$, 20 to 40 mol% KI), $CdCl_2$–$PbBr_2$–KI (10 to 50 mol% $CdCl_2$, 10 to 80 mol% $PbBr_2$, 10 to 70 mol% KI) and $CdCl_2$–$PbCl_2$–KI (20 to 50 mol% $CdCl_2$, 10 to 70 mol% $PbCl_2$, 5 to 60 mol% KI) ternary systems were studied. Glasses exhibit remarkably high transmittance (up to 80%) in the visible and IR region (down to 250 cm^{-1} for $CdBr_2$–$PbBr_2$–KI, 300 cm^{-1} for $CdCl_2$–$PbBr_2$–KI and 400 cm^{-1} for $CdCl_2$–$PbCl_2$–KI for 1 mm thick plates). The values of glass transition temperature lie between 343 to 353 K and crystallization temperature between 343 to 403 K.

1. Introduction

Recently great attention has been paid to the study of halogenide glasses which are promising materials for infrared optics and communication. Most papers have been devoted to the study of fluoride glasses [1–4] but other halogenides such as chlorides and bromides have been also investigated [3–5].

In this paper the attention has been paid to the systems $CdBr_2$–$PbBr_2$–KI, $CdCl_2$–$PbBr_2$–KI and $CdCl_2$–$PbCl_2$–KI.

2. Experimental details

Anhydrous $CdCl_2$ and $CdBr_2$ were prepared by dehydration of $CdCl_2 \cdot 2H_2O$ and $CdBr_2 \cdot 2H_2O$ at 433 K in vacuum. The mixture of anhydrous halides was heated at 433 K in vacuum in a silica or platinum crucible and then the mixture was melted in an inert atmosphere at 623 to 673 K. The melt was then quenched between two aluminium plates and transparent glasses with thickness of about 0.2 to 1 mm were obtained. The glassy state of the samples obtained was confirmed by X-ray diffraction. The homogeneity of the obtained glasses was checked by electron microscopy.

The glass transition temperature T_g, the crystallization temperature T_c and melting temperature T_m of the obtained glasses were measured by DTA (Perkin-Elmer 7/4) in the range of 293 to 773 K with a heating rate 20 K min^{-1}.

Visible spectra were measured by a spectrophotometer Specord M 40 (Zeiss-Jena) and IR spectra were measured by a spectrophotometer 61 NIR (Zeiss-Jena) and by a spectrophotometer Perkin-Elmer 684.

3. Results and discussion

Glass forming regions of the $CdBr_2$–$PbBr_2$–KI, $CdCl_2$–$PbBr_2$–KI and $CdCl_2$–$PbCl_2$–KI ternary systems studied are shown in Fig. 1. The areas inside the full curve correspond to the formation of glasses (thickness ⩽ 1 mm) obtained by splat cooling. It can be seen that the glass forming tendency is increased markedly by substitution of $CdCl_2$ for $CdBr_2$ in the $CdBr_2$–$PbBr_2$–KI system and it is increased only a little by substitution of chlorine atoms for all bromine atoms in the system mentioned above.

In most cases the glass transition temperature-T_g occurs between 343 and 353 K, the crystallization temperature-T_c occurs between 353 and 403 K and the melting temperature of the glass is in the range 503 to 573 K (Table I). The gradual substitution of chloride atoms for bromide atoms increases the values of T_g, T_c and also the interval T_c–T_g.

The prepared glasses are transparent in a broad spectral region from the visible to the far IR region (Fig. 2). The long-wavelength absorption edge is almost independent of the composition of samples, contrary to the short-wavelength absorption edge which is slowly shifted with increasing content of chloride atoms. The transmission of the studied glasses in the regions near 3500 cm and 1600 cm is influenced by atmospheric moisture. An example is given in Fig. 3. New absorption bands appeared in this region when the sample was kept for a long time in the laboratory atmosphere. The new bands can be assigned to the absorbed water because they can be removed in vacuum. When the intensity of these bands increases,

TABLE I Characterisitc temperature of some glasses.

Glass composition (mol %)	T_g (K)	T_c (K)	T_m (K)	T_c–T_g (K)
10 $CdBr_2$–70 $PbBr_2$–20 KI	347	369	526	12
20 $CdBr_2$–60 $PbBr_2$–20 KI	331	357	518	10
10 $CdCl_2$–70 $PbBr_2$–20 KI	353	377	511	24
20 $CdCl_2$–60 $PbBr_2$–20 KI	350	373	513	23
30 $CdCl_2$–50 $PbBr_2$–20 KI	352	379	518	27
40 $CdCl_2$–40 $PbBr_2$–20 KI	352	372	525	20
20 $CdCl_2$–60 $PbCl_2$–20 KI	351	384	567	33
30 $CdCl_2$–50 $PbCl_2$–20 KI	353	399	544	45
40 $CdCl_2$–40 $PbCl_2$–20 KI	353	401	546	48
50 $CdCl_2$–30 $PbCl_2$–20 KI	353	392	543	39

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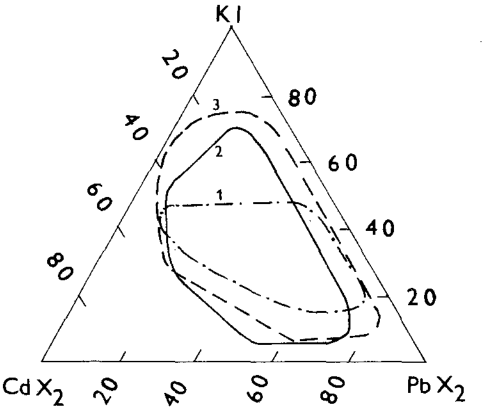

Figure 1 Glass forming regions 1 System $CdBr_2$-$PbBr_2$-KI; 2 System $CdCl_2$-$PbCl_2$-KI; 3 System $CdCl_2$-$PbBr_2$-KI.

the form of these bands is changed and some chemisorption or irreversible hydrolysis probably takes place because the bands cannot be fully removed in vacuum. The sensitivity of individual glasses to water vapour depends on their composition. The glasses with lower KI content are less sensitive.

4. Conclusion

The optical properties of the studied glasses are very attractive and the studied glasses appear promising for application. However, the glass transition temperature is relatively low and the glasses were prepared only by splat cooling. The possibility of preparing more thick massive glasses is being studied.

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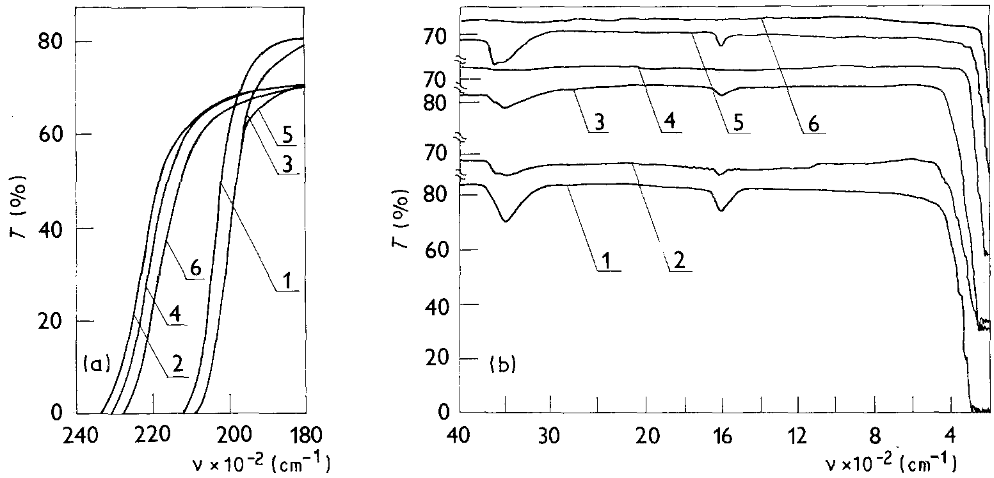

Figure 2 Spectral dependence of the optical transmissivity (a) short-wavelength region; (b) infrared region 1, $(CdCl_2)_{0.3}$ $(PbCl_2)_{0.3}$ $(KI)_{0.4}$, 2, $(CdCl_2)_{0.2}$ $(PbCl_2)_{0.6}(KI)_{0.2}$, 3, $(CdCl_2)_{0.3}(PbBr_2)_{0.3}$ $(KI)_{0.4}$, 4, $(CdCl_2)_{0.2}(PbBr_2)_{0.6}$ $(KI)_{0.2}$, 5, $(CdBr_2)_{0.3}(PbBr_2)_{0.3}$ $(KI)_{0.4}$, 6, $(CdBr_2)_{0.2}$ $(PbBr_2)_{0.6}(KI)_{0.2}$.

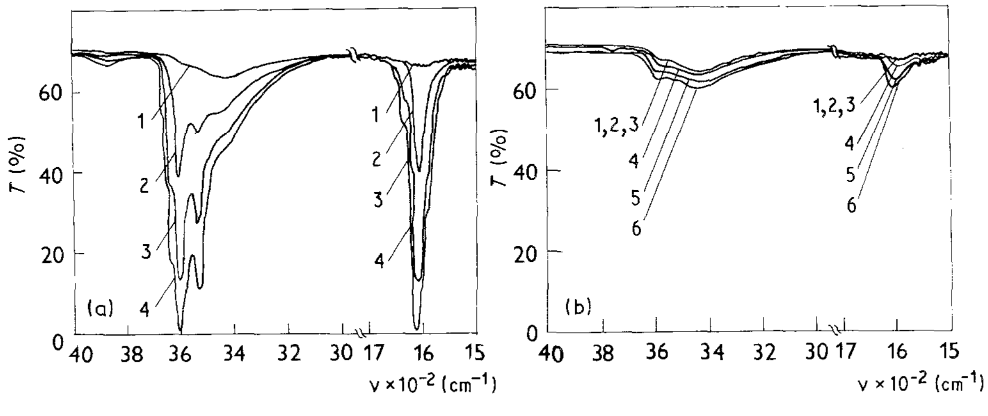

Figure 3 Absorption bands caused by exposition of the glass in water vapour (T = 293 K; (a) 66% relative humidity; (b) 10% relative of humidity). Time of exposition: (1) 0 min, (2) 30 min, (3) 60 min, (4) 90 min, (5) 120 min, (6) 150 min.