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CRYSTALLIZATION BEHAVIOUR OF CADMIUM MIXED-HALIDE GLASSES

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ABSTRACT

Cadmium mixed halide glasses have been recently identified as a potential low-phonon energy host for 1.3 μm Pr^{3+}-doped optical fibre amplifier. We report the crystallization behaviour of the mixed halide glasses while reheated above their glass transition temperature. The effect of impurities in the starting raw materials on the quality of the bulk glass is reported. The OH^- absorption was monitored by FTIR technique, and related to the lifetime of the $^1G_4$ excited state in Pr^{3+}-doped glass. The thermal stability of the glass was studied from heat treatment data using a differential scanning calorimeter.

INTRODUCTION

Cadmium mixed-halide glasses have been proved to be an alternative to ZBLAN glass as a host for praseodymium-doped fibre amplifier [1-3]. Cadmium-based glass has lower phonon energy than ZBLAN, leading to an increase in the non-radiative lifetime of the $^1G_4$ excited state of praseodymium. The prolonged lifetime improves the quantum efficiency and gain at the 1.3 μm wavelength. The lifetime of the $^1G_4$ level of prasoedymium in cadmium-based glass is τ=325 μs [1] compared with τ=100 μs in ZBLAN [4]. Although these glasses possess a good thermal stability, confirmed by their large Hr number (Hr=1.3 compared with 0.9 for ZBLAN glass), their use in the fabrication of optical devices is difficult due to their high sensitivity to moisture and their low glass transition temperature (120°C).

It has been shown [5] that a higher fluorine content in the glass enhances the chemical durability but leads to a decrease in the thermal stability. Moreover, lower devitrification rates are observed in mixed fluoro-halide glasses. The aim of this paper is to determine the effect of impurities such as OH^- and NO_3^- on the devitrification behaviour. The test composition used was 'CD': 50CdF_2, 10$BaCl_2$, 40NaCl, which is a compromise between the two glass features described above. Impurity level must be controlled also in order to avoid luminescence quenching [6]. Indeed, the effect of impurities is to reduce the lifetime, which in turn leads to a decrease in the quantum efficiency of praseodymium-doped fibre amplifier. The $^1G_4$ lifetimes of Pr^{3+}-doped glasses was also compared with the various levels of impurities of these glasses. In particular, the effect of OH^- is reported.

EXPERIMENTAL PROCEDURE

The starting materials were supplied by Tesbourne Ldt (CdF_2), and Aldrich Ldt ($BaCl_2$ and NaCl). The glass samples were prepared and processed under controlled atmosphere of nitogen in order to avoid hydrolysis, and subsequently cast in a 0.5 cm thick brass mould.

A series of 'CD' glasses, undoped and doped with water and nitrates, were prepared. There were indications that the melting schedule influences the final concentration of nitrates and hydroxyl ions dissolved in the glass. Since a rigid schedule coud not be adhered to for all glasses, the OH^- and NO_3^- concentrations were estimated from their absorption coefficients calculated from infra-red spectra (*Figure 1*).

The thermal stability of glasses containing various levels of impurities was investigated using a Differential Scanning Calorimeter (Perkin Elmer DSC-7) set at the heating rate of 10°C/min. During experiments, dry nitrogen was used as a purge gas through the head chamber in order to minimize the adsorption of OH^- on the glass surface while it was heated. Isothermal experiments were also carried out to estimate the time required for the crystallization of the glass. From these results, time temperature transformation (TTT) curves were constructed and the thermal stability of 'CD' glasses was evaluated. The absorption coefficients of the OH^- and NO_3^- impurities and the total integrated area of the OH^- absorption peak were determined using a Nicolet FTIR spectrometer. Fluorescence lifetimes were measured using a Ti:Sapphire laser to excite the Pr^{3+} ions up to the $^1G_4$ level. The $^1G_4 \rightarrow {}^3H_5$ transition was monitored using a solid state detector with a band-pass interference filter centered at 1.3 μm.

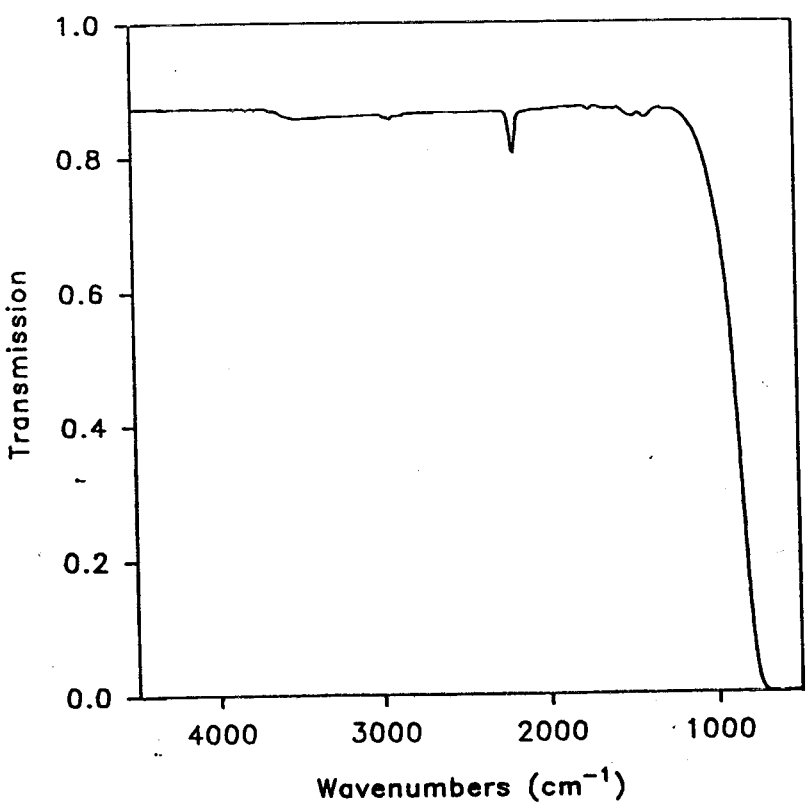

Figure 1: Absorption spectrum of cadmium-based glass (CD1)

RESULTS AND DISCUSSION

Incorporating $Ca(NO_3^-)_2$ into the glass structure at a very low concentration has a very strong effect on the thermal stability. Two different parameters can be used to judge glass stability against devitrification. The difference T_x-T_g (the onset of crystallization and the glass transition temperatures respectively) is an indication of the nucleation rate, large values corresponding to increased stability. The parameter $S=(T_x-T_g)(T_p-T_x)/T_g$ [7] (T_p being the peak crystallization temperature) emphasizes the crystallization behaviour upon reheating the glass. Indeed, assuming the crystalline fraction is always the same when an exothermic peak reaches its maximun value, a narrow crystallization peak implies a higher rate of devitrification at a given heating rate. When the $Ca(NO_3^-)_2$ concentration is increased (CD1-CD4), the two stability parameters decrease. The S parameter drops more sharply indicating reduced stability of these glasses (see *Table 1 and 2*). However, if KNO_3^- replaces $Ca(NO_3^-)_2$ in the glass structure at comparable concentrations as in CD5, the characteristic temperatures are less affected, implying that the presence of Ca^{2+} cations adversely influences thermal stability to a greater extent than the anion NO_3^- does. This was further confirmed by adding CaF_2 to the glass (CD8). Despite large differences in the OH^- absorption coefficient (*Table 2*, CD1,6,7), the characteristic temperatures remain unchanged.

Table 1: Characteristic temperatures for cadmium mixed-halide glasses

Glass	T_g	T_x	T_{p1}	T_{p2}	T_{p3}	T_m	T_x-T_g	S
CD1	119	205	208	226	265	315	86	2.46
CD2	129	203	206	227	265	313	74	1.66
CD3	133	196	198	228	266	313	62	1.17
CD4	136	190	192	228	264	315	55	0.89
CD5	134	209	212	229	264	316	75	1.85
CD6	116	205	208	227	266	316	92	2.74
CD7	116	204	207	226	264	315	90	2.41
CD8	118	188	190	226	263	315	70	1.19
CD0	136	229	237	248	285	314	95	5.59

Table 2: Absorption coefficients and impurity concentrations in cadmium halide glasses

Glass	absorption coefficient $\alpha(cm^{-1})$			concentration (in ppm)		
	OH^-	NO_3^-	SO_4^{2-}	$Ca(NO_3^-)2,4H_2O$	KNO_3^-	CaF_2 (ppm)
CD1	0.042	0.040	-	-	-	-
CD2	0.087	0.063	0.394	460	-	-
CD3	0.104	0.148	0.325	1970	-	-
CD4	1.005	0.250	0.297	3170	-	-
CD5	0.441	0.590	0.782	-	4350	
CD6	0.534	0.052	-	-	-	-
CD7	0.645	0.052	-	-	-	-
CD8	0.015	0.017	-	-	-	2080
CD0	2.18	0.80	large	-	-	-

Isothermal analysis was carried out on the glasses CD1, CD6, CD7, CD8. *Figure 2* represents their isothermal curves at the onset of crystallization temperature. CD1, CD6, CD7 isothermal curves have two well-defined devitrification peaks, corresponding to the first two primary crystalline phases, also observed in non-isothermal measurements, *i.e.* T_{p1}, T_{p2} in *Table 1*. The third peak is not observed on an isothermal curve because its crystallization energy is 20 times lower than that of the first two peaks, and the crystallization occurs at higher temperatures. The isothermal curve for CD8 glass shows one peak only, which is explained by the fact that the first two peaks of crystallization in CaF_2-doped glass are much farther apart. The OH^- concentration has a smaller effect on the time temperature transformation (TTT) curves, as shown in *Figure 3* and *Table 3*, compared with the presence of the dopant CaF_2. The effect of the latter on glass devitrification was confirmed by non-isothermal experiments. Nevertheless, it is evident from *Figure 3* that the glass stability against devitrification is marginally improved when OH^- concentration decreases.

The CD0 glass was prepared using CdF_2 supplied by Alfa Product, and $BaCl_2,2H_2O$ supplied by BDH (Merck). The characteristic temperatures, as shown in *Table 1*, indicate that the glass is more stable, with larger values of T_x-T_g and S, and its devitrification rate is slower (see *Figure 3*), despite the fact that this glass was prepared using chemicals of lower purity than the other 'CD' glasses, and therefore contains high concentrations of OH^-, nitrates and also sulphates. The glass appeared translucent due to the presence of microscopic crystals. This suggest that the presence of large concentrations of impurities induces extensive bulk crystallization during glass preparation. The composition of the remaining matrix is therefore expected to change. It is possible that a compositional change could have improved the thermal stability of the glass, explaining the delay of crystallization in the CD0 glass.

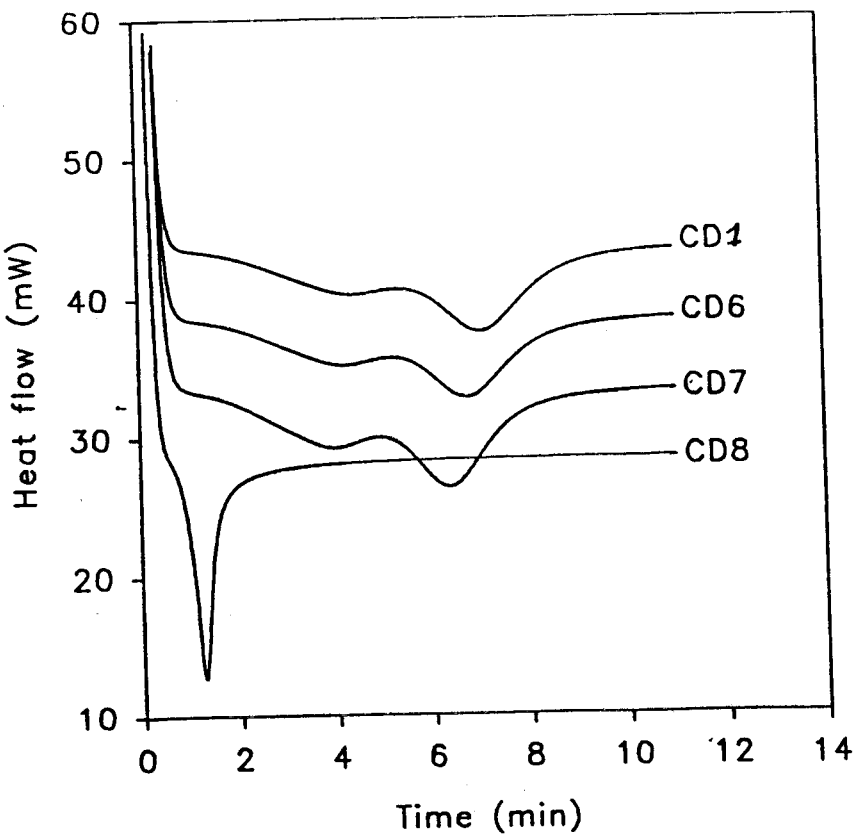

Figure 2: Isothermal curves at the onset of crystallization

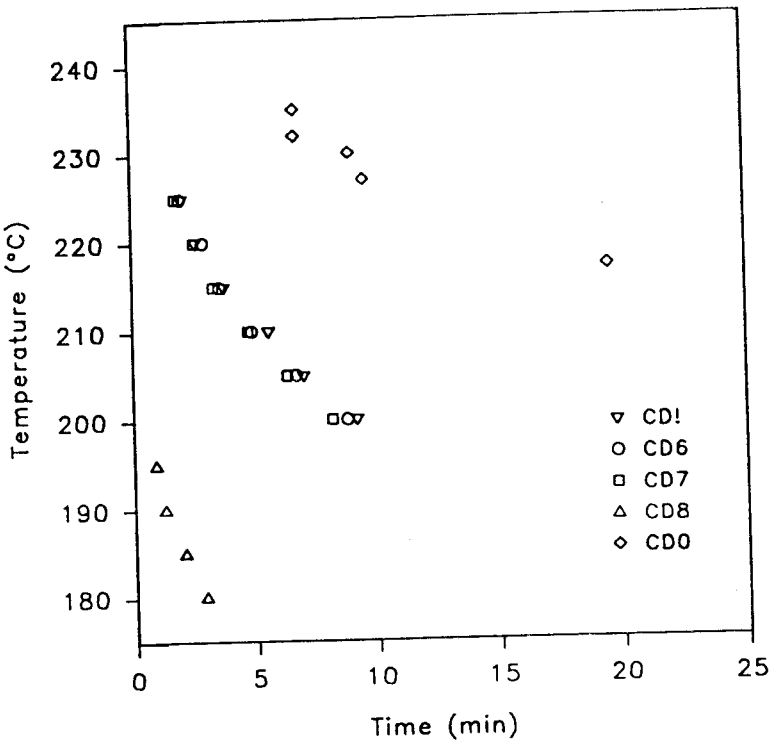

Figure 3: Time Temperature Transformation curves for the CD1, CD6, CD7, CD8, and CD0

Table 3: Time of the peak of crystallization for an isothermal transformation at the onset crystallization temperature

Glass	CD1	CD6	CD7	CD8	CD0
Time (min)	7.07	6.80	6.45	1.63	9.05

The main obstacle in achieving an efficient praseodymium-doped amplifier is the short lifetime of the $^1G_4$ metastable level [1-3]. Pr^{3+}-doped cadmium-based glass, having a lower phonon energy than silica and ZBLAN glasses [4], gives rise to 1.3 μm fluorescence with a lifetime of 325 μs [1]. However, impurities in glass can reduce the lifetime via two different mechanisms: they can act as activators in energy transfer in which the energy migrates from a Pr^{3+} ion to an impurity ion and is lost non-radiatively, or, if they are incorporated in the structure, as origins of high-energy phonons which facilitate non-radiative transitions. In halide glasses, the main impurities are the hydoxyl group, nitrates and sulphates.

The effect of OH^- dopant concentration on the lifetime of the $^1G_4$ excited state of praseodymium in cadmium-based 'CD' glass is shown in *Table 4*. It is clear that the strongest effect on the lifetime is due to the presence of OH^- in the glass. *Figure 4* shows the relationship between the measured $^1G_4$ lifetime and the integrated intensity of the OH^- absorption peak. It is expected that the lifetime could be further improved if the impurity levels are reduced. It is worth noting that the CD0 glass, having the highest content of all three impurities, OH^-, nitrates, sulphates, also demonstrated the shortest lifetime (210μs). The role of NO_3^- and SO_4^{2-} ions on fluorescence lifetime is not very clear at this stage, and further analysis is required to establish their effect on both $^1G_4$ lifetime and stability.

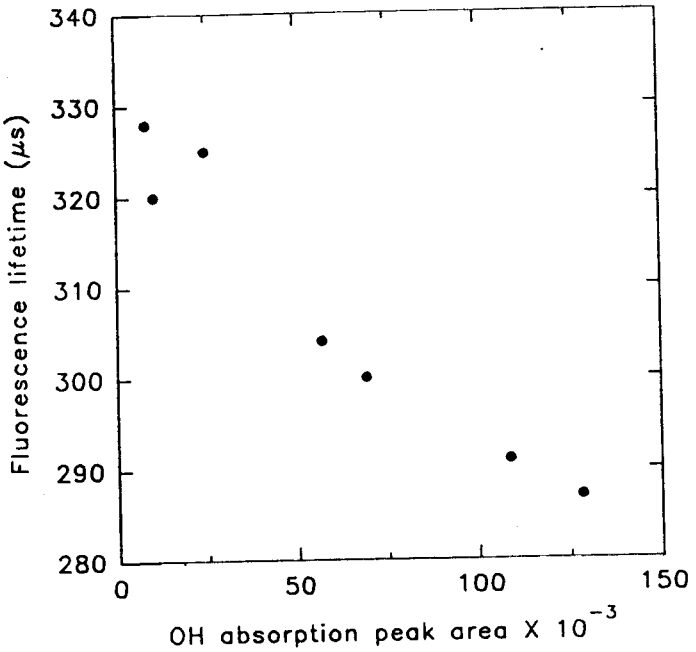

Figure 4: The $^1G_4$ lifetime as a function of the integrated OH^- absorption peak

Table 4: The $^1G_4$ lifetime in Pr^{3+}-doped 'CD' glass as a function of the integrated intensity of the OH^- absorption peak

Glass	CD1	CD5	CD6	CD7	CD8	CD9	CD10	CD11	CD0
OH^- peak area	8.30	-	57.09	69.13	24.79	10.38	108.67	128.41	-
Lifetime (μs)	328	240	304	300	325	320	291	287	210

CONCLUSIONS

It has been shown that the OH^- dopant influences the kinetics of crystallization in cadmium-based glasses, although it does not destabilize the glass to the same extend as the cation Ca^{2+} does. Moreover, it is highly detrimental to the $^1G_4$ excited state lifetime in the praseodymium-doped cadmium halide glass.

The variation in the purity of different starting materials may influence the devitrification rate of the glass and have a destabilizing effect.

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