Some properties of glass-forming systems containing sodium metaphosphate

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The temperature of glass transition, temperature of crystallization, and temperature of melting of binary glass systems containing sodium metaphosphate was studied by DTA method. The influence of content of magnesium fluoride, calcium fluoride, strontium fluoride, barium fluoride, and lead fluoride on these parameters and on the solubility of prepared glass was investigated in the whole composition range of glass formation in these systems.

Температура остеклененния, температура кристаллизации и температура плавления бинарных стекловидных систем, содержащих метафосфат натрия, были изучены с помощью метода ДТА. Влияние содержания фторида магния, фторида кальция, фторида стронция, фторида бария и фторида свинца на эти параметры, а также на растворимость полученного стекла было исследовано во всем интервале состава стеклообразования этих систем.

Sodium metaphosphate has attached attention as material for preparation of glass systems in the middle of sixties. Many types of glass on its basis have been patented by researchers of the establishment Carl Zeiss, Jena [1—4].

Important are the optical properties of this material, *viz.* low dispersity and refraction index. The lowest achieveable theoretical value of damping of light signal is 0.1 dB km^{-1}. In contradistinction to fluoride and chalcogenide glass the metaphosphate glass is not very suitable for using in far infrared region. The limit of their application is at $\lambda = 3$ μm, which is comparable with silicate glass.

Metaphosphate alone shows a good glass-forming ability and it retains this property also in combination with a series of other substances. The greatest disadvantage of glass on the basis of alkaline metaphosphates is its remarkable hygroscopicity. This holds also for glass developed in Jena which uses as basic material barium metaphosphate. From the point of view of solubility and leaching glass based on aluminium metaphosphate gives partly better results.

Investigations of French researchers [5, 6] made in the last decade show that the solubility of metaphosphate glass can be lowered by several orders when it is modified by fluorides of Ba and 3*d* transition metals.

In despite of some disadvantages mentioned above the metaphosphate glass is a very promising material for preparation of windows of Nd high-power lasers.

For these reasons we decided to investigate the influence of the addition of fluorides of magnesium, calcium, strontium, barium, and lead to sodium metaphosphate on the solubility, temperature of glass transition, temperature of crystallization, and melting temperature of these binary systems. Thermal stability of the prepared glass was investigated by thermogravimetric method.

Experimental

Sodium metaphosphate was prepared by mixing equimolar amounts of sodium hydrogenphosphate and ammonium chloride of anal. grade (Lachema, Brno) and dissolving this mixture in water. After purification by repeated crystallization sodium ammonium hydrogenphosphate was prepared. By heating this product slowly in an electrical furnace up to 850 °C sodium metaphosphate was obtained. Its melt was poured into platinum dish. Because of its hygroscopicity it was cooled and stored in a desiccator. Chemical analysis proved that the product contained 99.66 mass % of sodium metaphosphate.

Used fluorides were anal. grade and Suprapur (Lachema, Merck, Fluka).

Preparation of glass plates requires solution of several technical problems. A suitable temperature of melting and temperature and time necessary for homogenization (clarifying) of the melt are to be found. Also the temperature of casting and preheating of pads at the preparation of plates is important. This results from the tendency of metaphosphate glass to stick strongly to the pad. Finally the thermal treatment of plates for diminishing stress in the material (and thus also its brittleness) is to be carried out. It is influenced by the temperature and time of the thermal treatment.

It was found that the following procedure gives optimum results: Weighted amount of substance is melted in a platinum crucible at the temperature of 700 °C. The molten mixture is kept for 6 h at 850 °C (homogenization). Glass is casted on polished brass or platinum plate heated to the temperature about 20 °C lower than is the temperature of glass transition. Suitable shape of glass plates is obtained by pressing with a preheated tool. Thermal treatment of glass plate is made for at least 2 h at the temperature about 5—10 °C higher than is the temperature of glass transition. The sample is cooled at the rate 1—3 °C min^{-1}.

Glass prepared in this way is stable. Some samples proved their stability for the period longer than one year.

The temperature of glass transition T_g and temperature of crystallization T_c were determined in the differential scanning microcalorimeter DSM-2M. The rate of scanning was 16 K min^{-1}. The samples of the mass 30—50 mg were sealed in aluminium pans (mass 48 mg).

Calibration of the apparatus was carried out in a usual way [7]. Melting temperatures T_m, some temperatures of crystallization, and thermogravimetric characteristics were

measured using the DTA apparatus STA 409 NETZSCH. Sintered alumina or platinum crucibles were used. Mass of samples was about 160 mg, rate of heating was 10 °C min^{-1}. The experimental data were treated using software supplied with the apparatus. T_g was evaluated as an extrapolated onset of signoid and T_c and T_m as the temperatures of peak maximum. Sensitivity of the apparatus was 0.35 μV/mW.

Solubility and the tendency to extraction of prepared glass was tested using glass plates of 30 mm diameter and 2 mm thickness. The samples were placed in a beaker containing 800 cm^3 of water 20 °C warm stirred with constant rate. The plate was taken out in regular time intervals, dried and weighted for determination of the loss of mass.

Results and discussion

The system sodium metaphosphate—magnesium fluoride

According to [5] this system is glass-forming in the composition range $x(NaPO_3) = 0.45$—1. In this work mole fraction of metaphosphate was changed from 1 to 0.5. The obtained results are summarized in Table 1. DTA curves are presented in Fig. 1. It follows that in the composition range $x = 0.9$ and $x = 0.8$

Table 1

The data on T_g, T_c, T_m and on solubility of the systems containing sodium metaphosphate

System	$x(NaPO_3)$	T_g °C	T_c °C	T_m °C	Solubility 10^{-3} g cm^{-2} h^{-1}
$NaPO_3$	1.0	257.2	441.2	527.4	420.00
$NaPO_3$—MgF_2	0.9	323.1	(521.8)	(591.0)	4.71
	0.8	300.9	—	(664.7)	0.16
	0.7	399.5	581.1	741.3	0.15
	0.6	382.5	552.4	780.0	0.11
	0.5	424.5	542.2	796.2	0.12
$NaPO_3$—CaF_2	0.9	287.4	(553.7)	(620.1)	24.60
	0.8	325.1	—	(652.8)	6.78
$NaPO_3$—SrF_2	0.9	298.5	(494.2)	(585.1)	15.80
	0.85	286.6	474.2	543.8	4.72
$NaPO_3$—BaF_2	0.9	264.7	(453.1)	(499.1)	14.50
	0.8	306.9	(423.1)	(548.4)	2.25
$NaPO_3$—PbF_2	0.9	253.0	446.0	520.3	159.00
	0.8	259.0	449.5	523.1	30.90
	0.7	283.5	371.7	619.4	0.79

The data in brackets are only approximate.

crystallization in the course of heating is not conclusive. (For better comparison the same scale on the axis of temperature differences was used.) Loss of mass in the whole investigated temperature interval did not exceed 0.55 %.

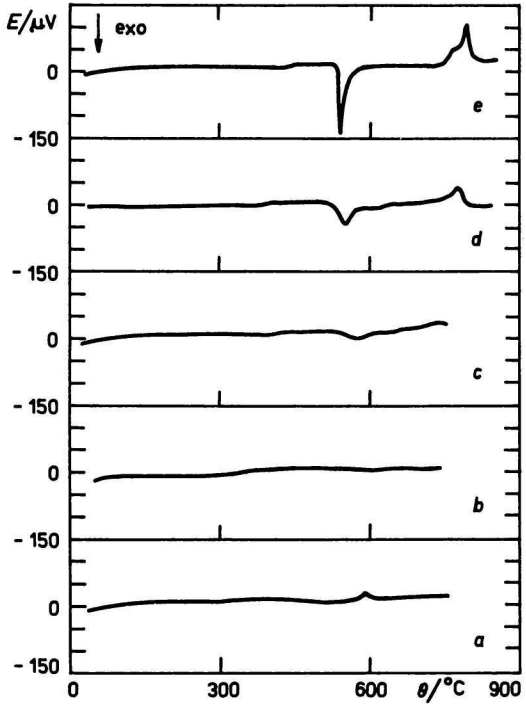

Fig. 1. DTA curves for glass of the composition (in mole fractions) $x(NaPO_3)$ and $(1 - x)MgF_2$. x: *a*) 0.9, *b*) 0.8, *c*) 0.7, *d*) 0.6, *e*) 0.5.

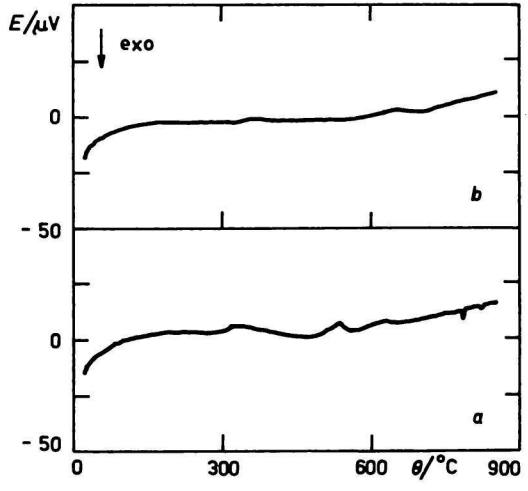

Fig. 2. DTA curves for glass of the composition $x(NaPO_3)$ and $(1 - x)CaF_2$. x: *a*) 0.9, *b*) 0.8.

The system sodium metaphosphate—calcium fluoride

Literature data on the glass forming in this system are not available. We found that our samples were glass-forming in the composition range from $x = 1$ to $x = 0.8$. The experimental results are summarized in Table 1 and in Fig. 2. Similarly as in the case of magnesium glass also in this system it is very difficult to observe crystallization at given rate of heating. Loss of mass was lower than 0.39 %.

The system sodium metaphosphate—strontium fluoride

Also for this system no literature data on glass forming are available. We found glass-forming ability in the range from $x = 1$ to $x = 0.85$, which is the narrowest interval of composition from all the systems investigated in this work. Experimental results are given in Table 1 and in Fig. 3. It follows that crystallization can be neglected in the whole glass-forming region. At heating this glass shows the lowest loss of mass, *viz.* lower than 0.05 %.

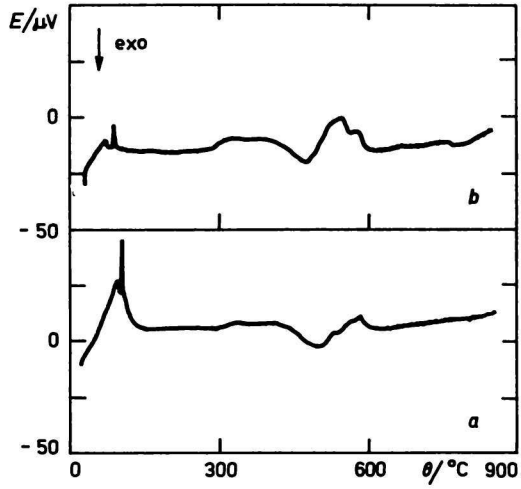

Fig. 3. DTA curves for glass of the composition $x(NaPO_3)$ and $(1 - x)SrF_2$. x: *a*) 0.9, *b*) 0.85.

The system sodium metaphosphate—barium fluoride

In contradistinction to the former system this one has a broader range of glass-forming ability [5], *viz.* from $x = 1$ to $x = 0.7$. We succeeded in preparation of glass in the composition range from $x = 0.8$ to $x = 1$. The experimental

results are presented in Table 1 and in Fig. 4. The tendency to crystallization is in the whole composition range low and the prepared glass is stable. Mass loss does not exceed 0.09 %.

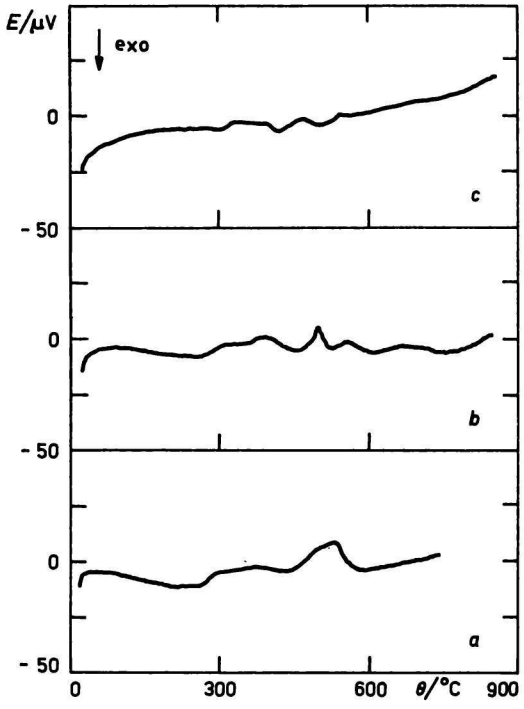

Fig. 4. DTA curves for glass of the composition $x(NaPO_3)$ and $(1 - x)\,BaF_2$. x: *a*) 1.0, *b*) 0.9, *c*) 0.8.

The system sodium metaphosphate—lead fluoride

Glass-forming ability of this system is good as well. We succeeded in preparation of glass samples in the composition range $x = 1$ to $x = 0.7$. The obtained data are given in Table 1 and in Fig. 5. From all the studied systems the glass containing lead fluoride has the lowest resistance against crystallization and the narrowest temperature region for its preparation, *i.e.* the temperature difference T_c and T_g. Mass loss does not exceed 0.18 %.

Conclusion

As follows from presented data the broadest range of glass formation is observed in the system sodium metaphosphate—magnesium fluoride. Simul-

taneously this system has the best resistance against crystallization and the glass with higher content of magnesium fluoride is at the room temperature only very little soluble. Similar low solubility was observed only for metaphosphate glass containing lead fluoride. However, disadvantage in the latter case is the narrow temperature interval for manufacturing the glass which usually does not exceed 100 °C.

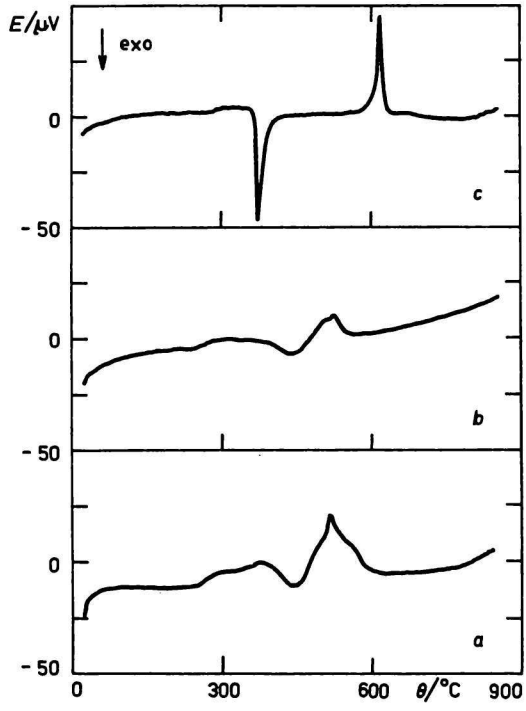

Fig. 5. DTA curves for glass of the composition $x(NaPO_3)$ and $(1 - x)PbF_2$. x: *a*) 0.9, *b*) 0.8, *c*) 0.7.

Generally it can be stated that the addition of fluorides to metaphosphate glass significantly lowers its solubility, in some cases more than by three orders. With the exception of lead fluoride this addition does not diminish remarkably stability of the glass. From the thermogravimetric measurement it follows that this glass, in contradistinction to that containing metaphosphates of alkali earths [8—10], does not liberate in the studied temperature range, *i.e.* up to 900 °C, POF_3.

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