NEWS FROM THE OLD GLASS SYSTEM $\text{Ca}(\text{PO}_3)_2$ - $\text{Mg}(\text{PO}_3)_2$

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Abstract Both single glasses are characterised by a relatively good chemical durability against water and water solutions. In this system, some compounds between calcium metaphosphate and magnesium metaphosphate are known, mostly as corrosion inhibitor materials. Cobalt-calcium metaphosphates are used as anticorrosive pink coloured pigments. Our interest was to investigate the crystallisation behaviour with change of composition between 100% $\text{Ca}(\text{PO}_3)_2$ and 100% $\text{Mg}(\text{PO}_3)_2$. The glasses crystallised into phases, which could not be identified clearly by X-ray diffractometry. By this reason, an exchange of Mg by Co was applied. The optical microscopy showed some different coloured crystalline phases in the resulting vitroceramics. Additional investigations by Scanning Electron Microscopy and EDX analyses were obtained to identify the different crystals.

INTRODUCTION

Calcium metaphosphate based glasses are already in use to substitute bone material in the human body, as well as glass-ceramics, derived from compositions near the calcium diphosphate [1]. One of the advantages of the magnesium metaphosphate glass should be its good compatibility to living things. Combining these characteristics of the glasses, one could expect a new applicable glass resp. glass-ceramic material for bone reconstructive purposes. Moreover, after crystallisation, the obtained glass-ceramics with variable contents of Ca and Mg should cover most of the thinkable applications by tailored properties. Structure design would be possible. Former investigations after tempering process showed the appearance of more than one crystalline phase [2]. These phases could not be identified satisfactorily.

At the beginning of the 1990 years, some new mixed crystals of the calcium magnesium metaphosphate system as well as the calcium cobalt metaphosphate were published [4-7]. Table 1 shows these species.

Investigations concerning structure designed glass ceramics [3] showed no success to obtain mixed structures between the needle-like (catena-)calcium metaphosphate and the more plate-like (tetracyclo-)magnesium metaphosphate.

Thinkable also is a mixed-layer structure between both structure types [8].

Formula	mol% Ca(PO ₃) ₂	mol% Mg(PO ₃) ₂	mol% Co(PO ₃) ₂	Authors
CaO . 9 MgO . 10 P ₂ O ₅	10	90	0	Trojan, M.; Benes, L. Materials Research Bulletin (1991), 26(7), 693-700
2 CaO . 8 MgO . 10 P ₂ O ₅	20	80	0	Trojan, M.; Benes, L. Materials Research Bulletin (1991), 26(7), 693-700
CaO . 3 MgO . 4 P ₂ O ₅	25	75	0	Trojan, Miroslav, PATENT NO. CS 266784
3 CaO . 7 MgO . 10 P ₂ O ₅	30	70	0	Trojan, M.; Benes, L., Materials Research Bulletin (1991), 26(7), 693-700
4 CaO . 6 MgO . 10 P ₂ O ₅	40	60	0	Trojan, M.; Benes, L., Materials Research Bulletin (1991), 26(7), 693-700
CaO . MgO . 2 P ₂ O ₅	50	50	0	Trojan, M.; Benes, L. Materials Research Bulletin (1991), 26(7), 693-700
2 CaO . MgO . 3 P ₂ O ₅	67	33	0	Prokupkova, P.; Mosner, P.; Koudelka, L.; Vlcek, M., Journal of Materials Science (1998), 33(3), 743-748
CaO . 7 CoO . 8 P ₂ O ₅	12.5	0	87.5	Trojan, M., Journal of Materials Science (1990), 25(4), 2159-64
CaO . 3 CoO . 4 P ₂ O ₅	25	0	75	Trojan, M. Journal of Materials Science (1990), 25(4), 2159-64
3 CaO . 5 CoO . 8 P ₂ O ₅	37.5	0	62.5	Trojan, Miroslav, PATENT CS 257546
CaO . CoO . 2 P ₂ O ₅	50	0	50	Trojan, M.; Brandova, D.; Paulik, F.; Arnold, M. Journal of Thermal Analysis (1990), 36(3), 929-38

Table 1: published mixed phases between Ca(PO₃)₂ and Mg(PO₃)₂
resp. Ca(PO₃)₂ and Co(PO₃)₂

EXPERIMENTAL

All glasses were melted from self-prepared Ca(PO₃)₂, Mg(PO₃)₂ and Co(PO₃)₂, which were done by chemical reaction between the analytical grade substances CaCO₃, basic MgCO₃ resp. Co₃O₄ with 85% analytical grade H₃PO₄ at normal temperature. This

reaction leads to the dihydrogen monophosphate hydrates, which have to be temperature treated in several steps, first at about 120°C, then until about 400°C for some hours until finally to 48 hrs. in the case of $\text{Co}(\text{PO}_3)_2$. As crucible material fused silica was used. The glasses were melted at temperatures from 1150°C to at least 1350°C in the case of the pure $\text{Mg}(\text{PO}_3)_2$ glass for in maximum 1 hour. After melting, the glasses were casted into graphite moulds and annealed from about 500°C, depending on glass composition, to room temperature with a rate of about 7.5 K h^{-1} . Thermal analyses (DTA, TGA) were applied to get information about the purity of the raw materials, the Tg temperatures of the glasses as well as the crystallisation regions and the liquidus temperatures. After that, the glasses were ceramised at the crystallisation temperatures and characterised by optical microscopy and X-ray diffraction. Some of the glasses were polished at the surface and investigated with Scanning Electron Microscopy and EDX analyses to get more information about the mostly not understandable diffractograms.

RESULTS AND DISCUSSION

Figure 1 gives an overview to the obtained X-ray diffractograms in the crystallised glasses within the system $\text{Ca}(\text{PO}_3)_2$ - $\text{Mg}(\text{PO}_3)_2$ from 100 to 0mol% $\text{Ca}(\text{PO}_3)_2$.

Figure 1: Situation of crystallised samples in the system $\text{Ca}(\text{PO}_3)_2$ - $\text{Mg}(\text{PO}_3)_2$

The upper diffractogram fits with the pure β - $\text{Ca}(\text{PO}_3)_2$ and this at the bottom represents the tetracyclo- $\text{Mg}(\text{PO}_3)_2$. The mixed compositions show some new peaks, which are marked with arrows. Trojan et.al. described these, specifically in the Mg-rich region, as tetracyclophosphates. We investigated the region between the pure $\text{Ca}(\text{PO}_3)_2$ and the 50-50-composition with $\text{Mg}(\text{PO}_3)_2$ resp. $\text{Co}(\text{PO}_3)_2$ to get more optical information. Figure 1 shows a crystallised sample. The glass crystallised inhomogeniously, where more bright and more dark (pink) crystal regions resulted.

Figure 1: Inhomogeniously crystallised glass with 80 mol% $\text{Ca}(\text{PO}_3)_2$ + 20 mol% $\text{Co}(\text{PO}_3)_2$, M: 10x

Figure 2: Scanning Electron Microscopy image of the crystallised glass with 66 mol% $\text{Ca}(\text{PO}_3)_2$ + 33 mol% $\text{Mg}(\text{PO}_3)_2$. The darker regions represent the Mg rich parts

By the very small areas of the crystals, chemical analyses with EDX are difficult and give only approximate concentrations. The comparison with the crystallised glasses in the Ca-Co-metaphosphate system proves this, see figures 3 and 4. By this reason, we used crystalline $\text{Ca}(\text{PO}_3)_2$ as analytical standard to get better results.

Figure 3: Crystallised glass with
50 mol% $\text{Co}(\text{PO}_3)_2$

Figure 4: Crystallised glass with
25 mol% $\text{Co}(\text{PO}_3)_2$

The brighter phase is possibly 50 $\text{Co}(\text{PO}_3)_2$ -50 $\text{Ca}(\text{PO}_3)_2$, the darker parts contain more $\text{Ca}(\text{PO}_3)_2$. The chemical analyses by EDX supply some compositions with little bit different contents of MgO resp. CoO. This is given in table 2.

visual grade in sample	mol% P_2O_5	mol% CaO	mol% MgO	mol% CoO	ratio CaO:MgO resp. CaO:CoO (ca.)
figure 2: dark	51.25	36.3	12.45	0	3:1
figure 2: dark	51.19	37.5	11.31	0	3:1
figure 2: grey	56.50	34.97	8.54	0	4:1
figure 2: grey	50.21	40.41	9.38	0	4:1
figure 2: bright	51.26	46.38	2.36	0	impurity?
figure 2: bright	48.99	49.40	1.61	0	impurity?
figure 4: bright	48.68	27.01	0	24.09	1:1
figure 4: bright	48.35	23.41	0	27.99	1:1
figure 4: grey	54.14	35.69	0	8.78	4:1
figure 4: grey	53.22	35.50	0	9.80	4:1
figure 4: dark	48,85	50.1	0	1.05	impurity?
figure 4: dark	48.42	47.74	0	3.84	impurity

Table 2: EDX analyses of mixed crystallised glasses $\text{Ca}(\text{PO}_3)_2$ - $\text{Mg}(\text{PO}_3)_2$
resp. $\text{Ca}(\text{PO}_3)_2$ - $\text{Co}(\text{PO}_3)_2$

CONCLUSIONS

Some of the found crystalline phases are not referred in literature, until now. We propose 3 new substances, possibly $\text{Ca}_4\text{Mg}(\text{PO}_3)_{10}$, $\text{Ca}_3\text{Mg}(\text{PO}_3)_8$, and $\text{Ca}_4\text{Co}(\text{PO}_3)_{10}$. The 1:1 Ca-Mg metaphosphate and the 1:1 Ca-Co metaphosphate are described already by Trojan et.al. Structure design of new glass-ceramics is very difficult to realise, since the crystallisation of the phases leads to holes in the structure, which diminish the demand on mechanical stability. Our present work is focussed on single crystal growth and their structure solution to support this given paper.

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