

A STUDY OF THE STRUCTURE OF BINARY MAGNESIUM ULTRAPHOSPHATE GLASSES BY VIBRATIONAL SPECTROSCOPY

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The infrared spectra of a series of binary magnesium ultraphosphate glasses $x \text{ MgO} \cdot (1-x) \text{ P}_2\text{O}_5$ with $0.0 \leq x \leq 0.5$ were measured and evaluated by means of principal component analysis. The structure of the magnesium ultraphosphate glasses is analyzed in comparison to the binary calcium and zinc ultraphosphate glasses, respectively. As in the case of the $\text{ZnO-P}_2\text{O}_5$ glasses the structure of these $\text{MgO-P}_2\text{O}_5$ glasses is dominated by three structural elements, vitreous P_2O_5 , $\text{MgP}_4\text{O}_{11}$, and $\text{Mg}(\text{PO}_3)_2$, which separate the ultraphosphate region into two regions with a binary distribution of the limiting structural elements. In the region with low MgO content (less than $x = 0.3$) the infrared spectra show certain similarities with the spectra of the $\text{CaO-P}_2\text{O}_5$ glasses.

INTRODUCTION

In our last work [1] the binary metaphosphate glasses of divalent cations were divided in groups, which differ in the structure of the glasses. Each group of glasses with unique structure is always formed by the metaphosphate glasses of those cations whose crystalline metaphosphates are isomorphous. It was shown, that zinc and magnesium metaphosphate glasses belong to the same structural group, whereas the calcium metaphosphate glass is a member of another structural group. Differences in the ionic radii of the cations were recognized as main reason for the separation into groups according to the structure of the crystalline metaphosphates and their glasses. Now our interest is directed to the structural classification of the binary magnesium ultraphosphate glasses.

The glassy systems $x \text{ MeO} \cdot (1-x) \text{ P}_2\text{O}_5$ with $0.0 \leq x \leq 0.5$ and $\text{Me} = \text{Zn}, \text{Ca}$ were already investigated by IR and Raman spectroscopy [2-4]. In 1995 some IR reflectance spectra of magnesium ultraphosphate glasses were published [5], but they do not allow a detailed analysis of the structure of the glasses. It is well known that the crystalline ultraphosphates $\text{ZnP}_4\text{O}_{11}$ [6] and $\text{MgP}_4\text{O}_{11}$ (LT) [7] are isomorphous. But at 850 °C a further modification of $\text{MgP}_4\text{O}_{11}$ (HT) [8] with a complicated structure is formed being unknown for $\text{ZnP}_4\text{O}_{11}$. Zinc and magnesium metaphosphates occur with the same structure in the case of the α_1 [9, 1] and the β [9, 1] modifications. The α_2 form is only known for $\text{Zn}(\text{PO}_3)_2$ [10]. It is unsolved, whether the compounds $\text{ZnP}_4\text{O}_{11}$ (HT) and $\alpha_2\text{-Mg}(\text{PO}_3)_2$ could not be isolated up to now or whether these modifications do not exist because of certain differences between the cations.

In the present work the IR spectra of binary magnesium ultraphosphate glasses $x \text{ MgO} \cdot (1-x) \text{ P}_2\text{O}_5$ with

$0.0 \leq x \leq 0.5$ are evaluated by methods of multivariate statistics to detect the number of structural components which dominates the glass structure in this composition range. Furthermore the structure of the magnesium ultraphosphate glasses is classified by the comparison of the spectra with the spectra of crystalline compounds and zinc and calcium ultraphosphate glasses of corresponding composition.

EXPERIMENTAL PROCEDURES

The glasses were melted in evacuated and sealed silica glass tubes packed in locked steel sockets from mixtures of P_4O_{10} (p.a., Merck, at least 98 % P_4O_{10}) and dried $\text{Mg}(\text{PO}_3)_2$ (Piesteritz). Melting temperature and time depend on the composition of the glasses (1050 °C and 1 h for $0.0 \leq x \leq 0.33$, 1100 °C and 1 h for $x = 0.4$ and 0.45). Only the magnesium metaphosphate glass was melted in a closed silica crucible for 30 min because of its high melting temperature of 1400 °C. At the end of the melting time the sockets were set into an oven with a temperature of 580 °C and cooled down to room temperature by switching off the oven. The raw materials and the melting conditions guarantee, that the glass samples are nearly anhydrous [11] and free of silicon [12] which may be introduced by the crucible at higher melting temperatures or longer melting times. The real composition of the samples deviates not more than 2 mol% from the synthesis composition. The glasses were cut and polished in an anhydrous environment to prepare polished plates for the spectroscopic measurements.

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The infrared reflectance spectra (angle of incidence of 20°, perpendicular polarized radiation) of the just polished glass samples were measured in the region between 4000 and 100 cm⁻¹ using a FT-IR spectrometer BRUKER IFS 66. In order to compare the spectra of the glasses with the measured absorbance spectra of powdered crystalline compounds the absorbance spectra of the glasses were calculated from the measured reflectance spectra via Kramers-Kronig analysis as described in [11]. Furthermore the calculation of the absorbance spectra is a prerequisite for the application of multivariate statistics, because the additivity of component spectra according to Lambert-Beer's law can not be assumed for the reflectance spectra.

Principal component analysis (PCA) as a method of multivariate statistics based on the eigen analysis of the set of spectra (data matrix **D**) was performed with the absorbance spectra of the glasses to detect the number of components by the number of eigenvalues (diagonal of the square matrix λ) which are larger than the experimental error.

$$\mathbf{Q}^T \times \{\mathbf{D}^T \times \mathbf{D}\} \times \mathbf{Q} = \lambda \quad (1)$$

The eigen spectra (matrix **R**) were calculated from the eigen vectors (matrix **Q**) and the original absorbance spectra of the glasses.

$$\mathbf{D} \times \mathbf{Q} = \mathbf{R} \quad (2)$$

The eigen spectra, whose variance is larger than the experimental error, are linear combinations of the same number of component spectra corresponding to the spectra of the dominating structures of the system. The percentage of each component in the spectrum of a glass is determined by the so-called target transformation. More details of the procedure are given in [13]. The spectra were evaluated with self-written PASCAL programs developed on the basis of this work [13].

RESULTS

The infrared absorbance spectra of the glasses $x \text{ MgO} \cdot (1-x) \text{ P}_2\text{O}_5$ with $0.0 \leq x \leq 0.5$ are presented in figure 1. In principle the spectra show the same changes with the composition of the glasses which are known from the other ultraphosphate systems [2 - 4]. The maximum position of band complex I ($\nu(\text{P}=\text{O})$ and $\nu_{\text{as}}(\text{PO}_2)$ vibrations, 1400 - 1250 cm⁻¹) is shifted to smaller wavenumbers with increasing content of MgO. Simultaneously the $\nu_s(\text{PO}_2)$ band at 1180 cm⁻¹ (part of band complex II) is increased in intensity and shifted to smaller wavenumbers for $x > 0.33$. The maximum position of band complex II ($\nu_{\text{as}}(\text{P}-\text{O})$ vibrations, 1100 - 850 cm⁻¹) is moved slightly to smaller wavenumbers for $x < 0.33$, but in a larger extent for $x > 0.33$. The height at the maximum position of band complex II is decreased compared with that of band complex I because the number of non-bridging oxygens is increased with the MgO content. The maximum position of band complex III ($\nu_s(\text{P}-\text{O})$ vibrations, 850 -

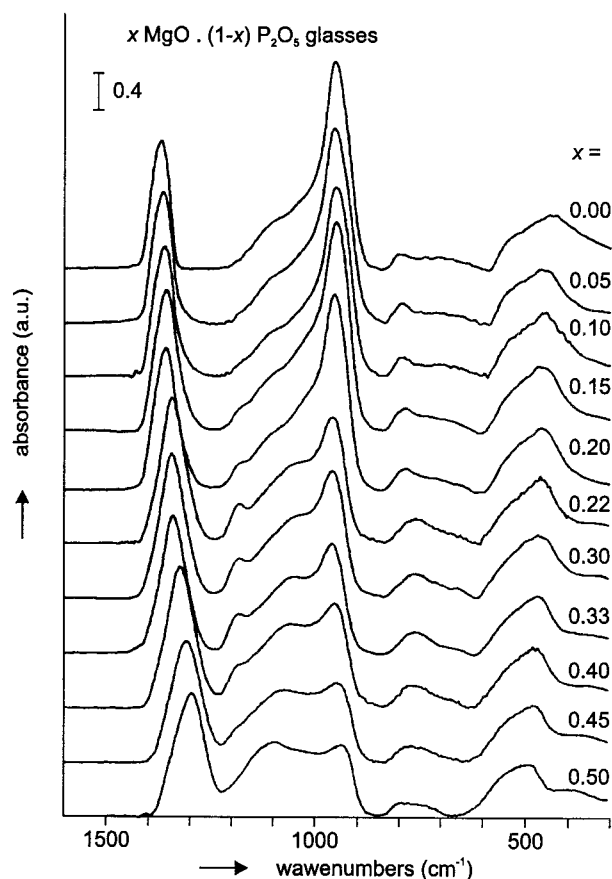


Figure 1. Infrared absorbance spectra of MgO-P₂O₅ glasses.

-650 cm⁻¹) is shifted with increasing MgO content at first to smaller wavenumbers for $x < 0.33$ and then to larger wavenumbers for $x > 0.33$. The maximum position of band complex IV (deformation vibrations of PO₄ tetrahedra, 650 - 400 cm⁻¹) shows a continuous shift to larger wavenumbers. The shapes of all four band complexes are changed with the composition of the glasses because all band complexes are formed by bands of threefold connected (Q³) and double connected (Q²) tetrahedra whose percentage in the structure vary with the composition of the glass.

The application of PCA to the set of spectra in figure 1 results in the following series of eigenvalues: 11.8504; 0.9286; 0.1845; 0.0151; 0.0075; 0.0066; ... Only the first three eigenvalues are larger than the experimental error (usually 1 %). The calculated eigen spectra are given in figure 2 (on the left). The first one is the average spectrum of the normalized absorbance spectra that means a linear combination of the component spectra with positive coefficients only. The minima and maxima of the second and the third eigen spectrum make clear that each band complex can be separated in several parts which belong to different component spectra. The linear combination of the component spectra can be resolved with the condition, that all intensities in the real component spectra are larger than zero and the

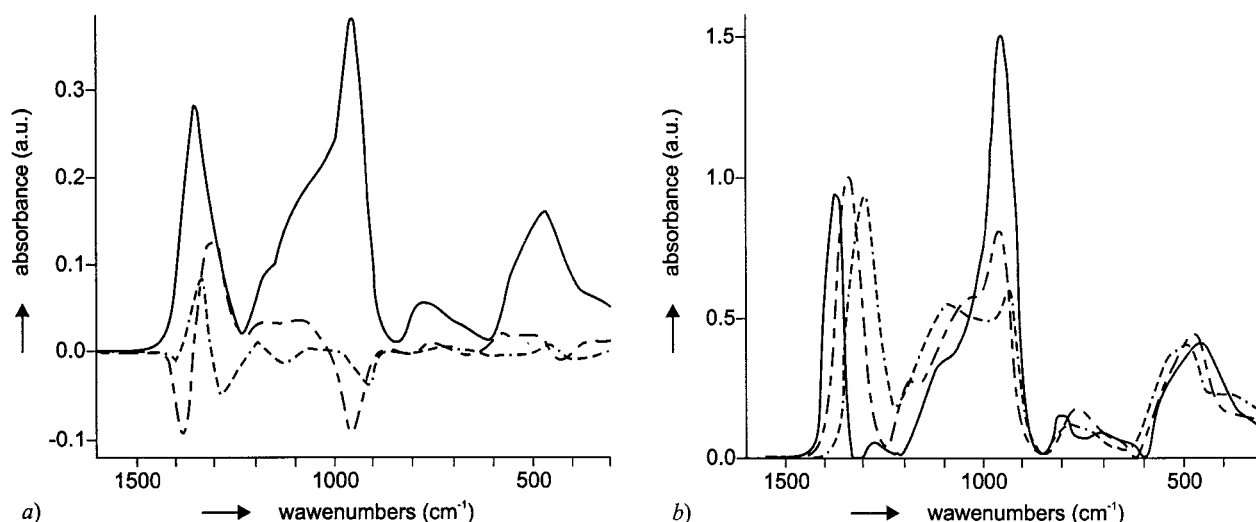


Figure 2. Eigen spectra and component spectra of the system $x \text{ MgO} \cdot (1-x) \text{ P}_2\text{O}_5$ with $0.0 \leq x \leq 0.5$.

a) — first eigen spectrum, ---- second eigen spectrum, -.- third eigen spectrum;
b) — first component, ---- second component, -.- third component.

spectra should differ as much as possible. The calculated component spectra are shown in figure 2 (on the right). The comparison of the calculated component spectra with the original absorbance spectra of the $\text{MgO-P}_2\text{O}_5$ glasses allows the following assignment: The first component corresponds to vitreous P_2O_5 ($\nu\text{-P}_2\text{O}_5$), the second to magnesium ultraphosphate glass with $x = 0.33$ ($\nu\text{-MgP}_4\text{O}_{11}$), and the third to magnesium metaphosphate glass ($\nu\text{-Mg(PO}_3)_2$).

This result could be confirmed by repeating the principal component analysis with different parts of the original set of absorbance spectra. Restricting the set of spectra to the composition range $0.0 \leq x \leq 0.33$ or $0.33 \leq x \leq 0.5$ two components were identified in every case. As soon as the limit $x = 0.33$ is exceeded the third

component is detected by the PCA algorithm. The calculated component spectra in figure 2 show slight deviations from the original absorbance spectra with $x = 0.0$, 0.33 , and 0.5 . The deviation of the first component spectrum in the region between 1200 and 1300 cm^{-1} is especially conspicuous. Usually such deviations are caused by a strong overlapping of the bands of the component spectra and the disturbance of the additivity of the component spectra by interactions between the corresponding structures. Nevertheless the original absorbance spectra were fitted by a weighted sum of these component spectra. The calculated percentages of the component spectra are given in table 1 together with the expected percentages, which were calculated from the composition of synthesis.

Table 1. Sample composition of synthesis and percentages of the component spectra calculated by PCA

x	Composition of synthesis			Percentages calculated by principal component analysis (%)		
	Expected percentages (%)					
	$\nu\text{-P}_2\text{O}_5$	$\nu\text{-MgP}_4\text{O}_{11}$	$\nu\text{-Mg(PO}_3)_2$	$\nu\text{-P}_2\text{O}_5$	$\nu\text{-MgP}_4\text{O}_{11}$	$\nu\text{-Mg(PO}_3)_2$
0.0	100	0	0	100.0	0.0	0.0
0.05	85	15	0	77.1	22.9	0.0
0.10	70	30	0	67.8	32.2	0.0
0.15	55	45	0	53.2	46.8	0.0
0.20	40	60	0	47.0	53.0	0.0
0.22	34	66	0	44.3	55.6	0.0
0.30	10	90	0	8.1	91.9	0.0
0.33	0	100	0	0.0	100.0	0.0
0.40	0	60	40	0.0	60.3	39.7
0.45	0	30	70	0.0	24.1	75.9
0.50	0	0	100	0.0	0.0	100.0

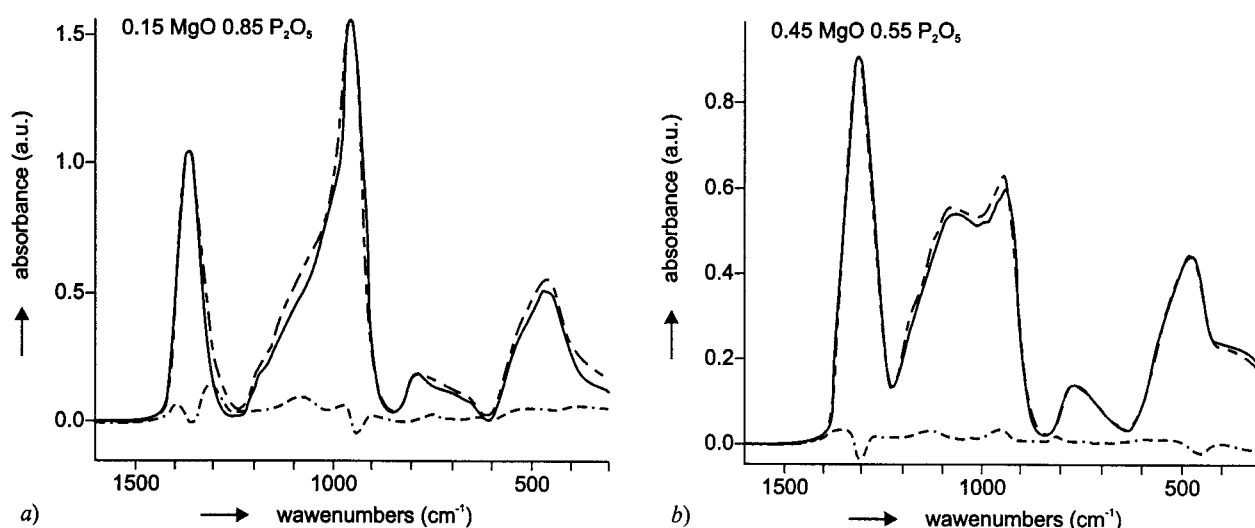


Figure 3. Comparison of the measured spectra of the glasses with the spectra fitted with the component spectra.

a) — measured spectrum, ---- calculated spectrum, -.- difference (calc.-meas.)

b) — measured component, ---- calculated component, -.- difference (calc.-meas.).

The largest differences between the expected and the calculated percentages of the component spectra occur at $x = 0.20$ and 0.22 with maximum 10 %. But it is remarkable, that the spectra of the glasses with $0.0 < x < 0.33$ are fitted only by the spectra of $\nu\text{-P}_2\text{O}_5$ and $\nu\text{-MgP}_4\text{O}_{11}$, and the spectra of $\nu\text{-MgP}_4\text{O}_{11}$ and $\nu\text{-Mg}(\text{PO}_3)_2$ only contribute to the spectra of the glasses with $0.33 < x < 0.5$. The quality of the fit is shown on example in figure 3. There are only small deviations between the measured and the calculated spectra of the glasses. The largest deviations between the measured and the calculated spectra are observed for the compositions around $x = 0.2$ in the region of the $\nu_{\text{as}}(\text{PO}_2)$ and $\nu_{\text{s}}(\text{PO}_2)$ bands between 1300 and 1000 cm^{-1} . Even the fit for the glass with $x = 0.15$ in figure 3 (on the left) shows this deviation from the measured spectrum. Against a very good correspondence is reached for the sample with $x = 0.45$ (figure 3, on the right), although the deviation from the expected percentage is about 6 %.

DISCUSSION

The great advantage of PCA is that not any additional information is necessary to detect the number of component spectra and to assign the various bands to the components. Assumptions on the number and the shape of the bands of the components as needed for band separation procedures are not required. The application of PCA shows, that three independent factors (that means, three component spectra corresponding to three basic structural elements in the middle-range order) determine the infrared spectra (and structure) of the binary magnesium ultraphosphate glasses. All three component spectra could be assigned to glasses with the composition of crystalline compounds. Figure 4 shows, that the spectra of the glasses with $x = 0.33$ and 0.5 may

be regarded as the envelopes of the spectra of the crystalline high temperature modifications, $\text{MgP}_4\text{O}_{11}$ (HT) and $\beta\text{-Mg}(\text{PO}_3)_2$, respectively. That means, that the main middle-range order structural elements of the corresponding glasses $\nu\text{-MgP}_4\text{O}_{11}$ and $\nu\text{-Mg}(\text{PO}_3)_2$ should be the substructures of the crystalline compounds $\text{MgP}_4\text{O}_{11}$ (HT) and $\beta\text{-Mg}(\text{PO}_3)_2$. Consequently all binary magnesium ultraphosphate glasses are formed by the substructures of $\nu\text{-P}_2\text{O}_5$, $\nu\text{-MgP}_4\text{O}_{11}$, and $\nu\text{-Mg}(\text{PO}_3)_2$.

Therefore the systems $x \text{ MeO} \cdot (1-x) \text{ P}_2\text{O}_5$ (with $0.0 \leq x \leq 0.5$) of zinc and magnesium are similar not only by the composition and the structure of the existing crystalline compounds but also by the number and the molecular structure of the substructures of the glasses in this composition range. Nevertheless there is a difference between the spectra of the binary zinc and magnesium ultraphosphate glasses with $x < 0.33$. In order to discuss the nature of this difference the absorbance spectrum of a magnesium ultraphosphate glass with $x = 0.2$ is compared with the spectra of a zinc ultraphosphate glass [3] and a calcium ultraphosphate glass [4] of equal composition in figure 5. It is very easy to recognize, that the band complex I of the $\nu(\text{P}=\text{O})$ and $\nu_{\text{as}}(\text{PO}_2)$ bands is clearly split into two bands in the case of the zinc ultraphosphate glass, whereas the spectra of the calcium and magnesium ultraphosphate glasses show only one maximum and not any structure in the shape of this band complex. The reason for this effect is the electron configuration of the cations. Magnesium and calcium are members of the second main group of the periodic table of the elements. Their divalent cations have the electron configuration of inert gases. The spheric symmetry of the electron density prevents a directed interaction with the non-bridging oxygen atoms (NBOs) of the Q^2 tetrahedra. The double bonded oxygen atoms (DBOs) of the Q^3 tetrahedra are stronger influenced by the electric field of the cation, the $\text{P}=\text{O}$

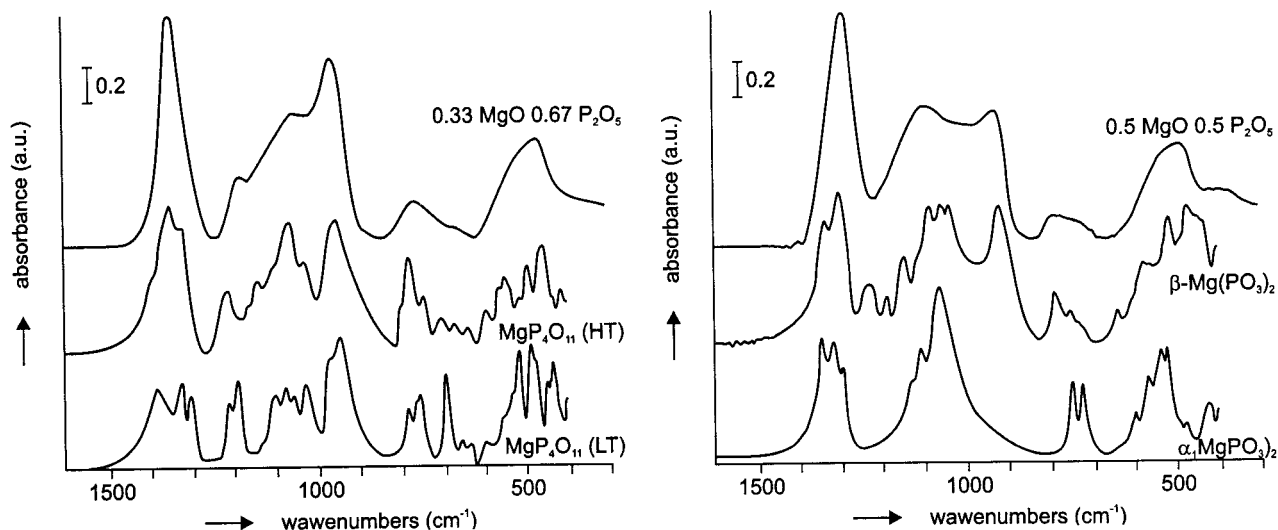


Figure 4. Comparison of the spectra of the modifications of the crystalline compounds $\text{MgP}_4\text{O}_{11}$ and $\text{Mg}(\text{PO}_3)_2$ with the spectra of the glasses of corresponding composition.

bond distance is lengthened, the bond number of the $\text{P}=\text{O}$ bond is decreased, and the wavenumber of the $\nu(\text{P}=\text{O})$ band is also decreased. The interaction of the zinc cations is stronger directed to the NBOs of the phosphate network, the influence on the DBOs is essentially smaller, and therefore the shift of the $\nu(\text{P}=\text{O})$ band to smaller wavenumbers is more slightly. This is the reason for the two maxima of band complex I of the spectra of the zinc ultraphosphate glasses with $x < 0.33$.

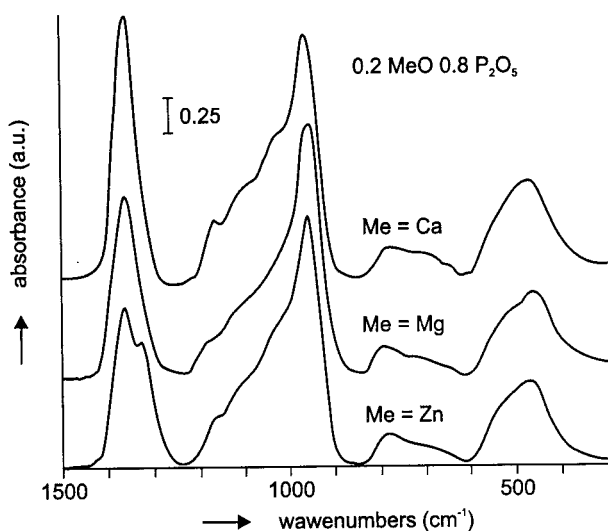


Figure 5. Absorbance spectra of binary ultraphosphate glasses of zinc, magnesium, and calcium with $x = 0.2$.

Nevertheless there is a clear correspondence between the spectra of zinc and magnesium ultraphosphate glasses concerning the shape of band complexes II and III and the ratio of the intensities (height at ma-

ximum position) of band complex I and II. This correspondence of the spectra is caused by a similar arrangement of PO_4 tetrahedra around the Zn^{2+} and Mg^{2+} cations and the interconnection of the PO_4 tetrahedra to the same substructures in the network of zinc and magnesium ultraphosphate glasses. As the shape of the bands and the intensity ratio of band complex I and II in the spectrum of the calcium ultraphosphate glass in figure 5 the structure of the calcium ultraphosphate glasses is essentially different from that of the magnesium ultraphosphate glasses.

CONCLUSIONS

By the evaluation of the infrared spectra of the glasses $x \text{ MgO} \cdot (1-x) \text{ P}_2\text{O}_5$ with $0.0 \leq x \leq 0.5$ the structural similarity with the binary zinc phosphate glasses was shown concerning the number and the molecular structure of the substructures in this composition range. The infrared spectra indicate even differences between the cations in the number of valency electrons in the outer shell by the different influence of the cations on the NBOs and DBOs of the phosphate network. But such differences do not affect the molecular structure of the substructures of the glasses in general. As in the case of the metaphosphate glasses the ionic radii of the cations determine mainly the structure of the ultraphosphate glasses.

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STUDIUM STRUKTURY
BINÁRNÍCH HOŘEČNATOFOSFOREČNÝCH SKEL
INFRAČERVENOU SPEKTROSKOPIÍ

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Infračervená spektra binárních hořečnatofosforečných skel $x \text{ MgO} \cdot (1-x) \text{ P}_2\text{O}_5$ ($0.0 \leq x \leq 0.5$) byla měřena a vyhodnocena komponentní analýzou. Struktura skel byla porovnána se strukturou binárních vápenato a zinečnatofosforečných skel. Stejně jako u $\text{ZnO-P}_2\text{O}_5$ skel jsou pro strukturu $\text{MgO-P}_2\text{O}_5$ skel dominantní tři strukturní elementy P_2O_5 , $\text{MgP}_4\text{O}_{11}$ a $\text{Mg}(\text{PO}_3)_2$, které oddělují oblast spektra na dvě části s binární distribucí limitních strukturních prvků. V oblasti s nízkým obsahem MgO ($x < 0.3$) ukazují infračervená spektra určité podobnosti se spektry $\text{CaO-P}_2\text{O}_5$ skel.