

Research Article

Spectral Investigation of Crystalline (CuHPO_4 , $\text{Cu}_2\text{P}_4\text{O}_{12}$, and $\text{Cu}_2\text{P}_8\text{O}_{22}$) and Glassy Copper Phosphates

Christiane Günther,^{1,2} Dörte Stachel,¹ and Lydia D. Bogomolova³

¹ Otto-Schott-Institute, Friedrich-Schiller-University Jena, Fraunhoferstraße 6, 07745 Jena, Germany

² Fraunhofer IKTS-Institute for Ceramic Technologies and Systems, Michael-Faraday-Straße 1, 07629 Hermsdorf, Germany

³ Skobel'tsyn Research Institute of Nuclear Physics, Moscow State University, Vorob'evy Gory, Moscow 119992, Russia

Correspondence should be addressed to Christiane Günther; christiane.guenther@ikts.fraunhofer.de

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Emerald green crystals of the new composition CuHPO_4 were synthesized and compared to (copper metaphosphate) $\text{Cu}_2\text{P}_4\text{O}_{12}$ and (copper ultraphosphate) $\text{Cu}_2\text{P}_8\text{O}_{22}$. Various copper ultraphosphate and metaphosphate glasses of different compositions between pure P_2O_5 and $\text{Cu}_2\text{P}_4\text{O}_{12}$ were melted in crucibles or in evacuated and sealed silica ampoules at 1473 K or 1373 K for 2 hrs. The UV-VIS-spectra and the IR-spectra of all crystals and glasses were measured and compared. The absorption band of Cu^{2+} was resolved into more component Gaussian bands and differentiated between square-pyramidal and octahedrally coordinated copper. These structural changes are responsible for colour changes from green to turquoise. The infrared spectroscopic properties of the copper phosphate glasses differ between metaphosphate and ultraphosphate structures but show similarities between the crystals and the glasses of the same structure type. EPR studies of some of the glasses show different kinds of spectra, with increasing copper content.

1. Introduction

Orthophosphoric acid condenses to diphosphoric acid under heat treatment. The related salts are called diphosphates (pyrophosphates), which contain P_2O_7 groups, for example, copper hydroxydiphosphate $\text{Cu}_3[\text{P}_2\text{O}_6\text{OH}]_2$ [1] and copper pyrophosphate $\alpha\text{-Cu}_2\text{P}_2\text{O}_7$ [2]. Further condensation in the presence of cations leads to polyphosphates (short chains) or metaphosphates. Two kinds of metaphosphates, the catena phosphates with 2-corner-linked PO_4 tetrahedra (infinite chains of Q^2 units) and the cyclophosphates (rings of Q^2 units), have to be distinguished. In comparison to that, ultraphosphates show linked together Q^2 and Q^3 (2- and 3-corner-linked PO_4 tetrahedra) and build layer or chain structures.

Basically, it is differentiated between nonbonded (Q^0) monophosphates, primary bonded (Q^1) diphosphates, secondary bonded (Q^2) meta- and cyclophosphates, and tertiary bonded (Q^3) framework phosphates (pure P_2O_5). Polyphosphates and ultraphosphates are mixed structures (Q^1 and Q^2 , resp., Q^2 and Q^3) of different bonded structural (PO_4) units [3–5].

The copper ion in the copper phosphates is regularly coordinated with four, five, or six oxygen atoms, but most structures consist of tetrahedral or octahedral CuO groups. About twenty different structures of copper phosphates have been discovered to date. The larger family is that of copper monophosphates, which shows a molar ratio of $\text{Cu}/\text{P} = 1$. The new structure of CuHPO_4 does belong to this group [3]. The copper polyphosphates with a molar ratio of $\text{Cu}/\text{P} < 1$ are much less numerous, for example, the metaphosphate $\text{Cu}_2\text{P}_4\text{O}_{12}$ and the ultraphosphate $\text{Cu}_2\text{P}_8\text{O}_{22}$ [4, 6–9].

Phosphate glasses are hygroscopic, but highly resistant against hydrofluoric acid. They can accommodate high concentrations of transition metal ions and remain amorphous. Therefore, invert glasses with more than 50 mol% CuO are possible [10].

Copper phosphate glasses show very interesting electrical and optical properties. So, they can be used as superionic conductors, heat absorbers, solid-state lasers, colour filters, nonlinear optics, or copper releasing degradable phosphate glass fibres, which have potential uses in wound healing or as plant fertilizers [11–14].

With additional water content, the glasses exhibit changes in structure and properties, like density and colour [15–17]. These changes are important for possible applications and need further investigations. According to Bae and Weinberg [10], it is known that by melting, in crucibles a part of the P_2O_5 evaporates during the melting and in spite of that, P_2O_5 can absorb a lot of water. Only pure metaphosphate glasses are relatively stable. So, in this work the metaphosphate glass used for the IR-spectroscopy and the ultraphosphate glasses were melted in silica ampoules, which were sealed under vacuum. Partially, definite amounts of water were added for the investigations. The metaphosphate glasses studied with UV-VIS-spectroscopy were melted in a crucible and cooled under different conditions.

2. Experimental

Phosphoric acid (85%) and copper oxide were mixed in a mortar. This first reaction took several hours. Afterwards, the mixture was tempered at 373 K for a week and further at 503 K for another two days. $Cu_2P_4O_{12}$ with minor rests of $Cu_2P_2O_7$ was obtained in the form of a light green to turquoise coloured solid. After one week tempering at 373 K, emerald-green needles of the composition $CuHPO_4$ grow, if phosphoric acid (65%) is used. By further tempering with residues of H_3PO_4 , these needles decompose to $Cu_2P_4O_{12}$. If the green crystals are kept in the air for several hours, they absorb water, become blue, and decompose to the powder of $CuHPO_4 \cdot H_2O$. The storage in nonaqueous solvents or under vacuum also leads to decomposition, but this time into turquoise powder. So, the crystals are kept in ethanol. The single crystal X-ray analysis of the new $CuHPO_4$ crystals was published in Günther et al. [3]. The X-ray diffraction of these crystals was performed on a D5000 of Siemens and is given in Figure 1.

The copper phosphate glasses were prepared of the synthesized $Cu_2P_4O_{12}$, P_2O_5 , and partially definite amounts of water. The metaphosphate glasses 1 and 2 were melted in a crucible at 1473 K for 2 hrs and cooled under different conditions. The glasses 3 and 4 were melted in silica ampoules (sealed under vacuum) with slowly cooling. The metaphosphate glass was also melted at 1473 K and the ultraphosphate glasses at 1373 K for 2 h. All those glasses were broken into pieces; the pieces were embedded, cut to plates, and polished for the spectroscopic investigations.

The contents of Cu^{2+} and Cu^{1+} of some glasses were determined via complexometric titration [18].

The microcrystal spectrometer (Fa. Genuine Jackman Parts, Research School of Chemistry, Australian National University) of the University Bonn (working group of Professor, Dr. R. Glaum) provided the UV-VIS-spectrum of $CuHPO_4$. A Shimadzu type UV-3101PC was utilized for the other UV-VIS-spectra.

The infrared spectra of the crystals were measured of powdered samples using the KBr pellet technique, with the help of an IFS 66 Spectrometer of Bruker. The spectra of the glasses were calculated from their reflectance spectra by Kramers-Kronig transformation.

TABLE 1: List of investigated samples.

Powders		
1	$CuHPO_4$	Copper(II) hydrogen phosphate
2	$Cu_2P_4O_{12}$	Copper(II) metaphosphate
3	$Cu_2P_8O_{22}$	Copper(II) ultraphosphate
Glasses		
1	50 mol% CuO	Meta, rapidly cooled, melted in open crucible
2	50 mol% CuO	Meta, slowly cooled, melted in open crucible
3	17 mol% CuO + 1 mol% H_2O	Ultra, slowly cooled, melted in ampoule
4	50 mol% CuO	Meta, slowly cooled, melted in ampoule

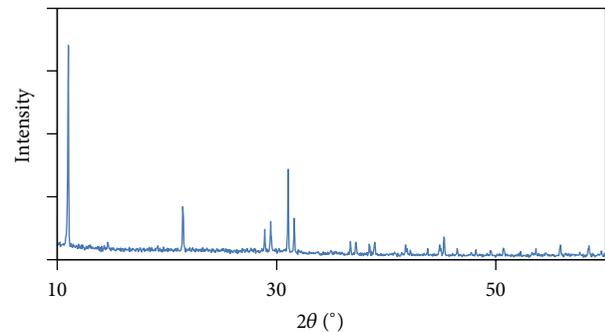


FIGURE 1: XRD pattern of $CuHPO_4$.

The EPR spectra of some glasses were measured using a spectrometer RE-1306 (Russian model) of X band frequency at 298 K. A list of the investigated samples is given in Table 1.

3. Results and Discussion

3.1. UV-VIS Spectroscopy. The absorption spectra of the regular octahedrally coordinated Cu^{2+} ion show one broad-band at 12500 cm^{-1} due to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition. The Jahn-Teller effect causes a tetragonal distortion of the structure, which leads to the splitting of the d orbital energy levels. So, three energy transitions are possible $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{xy}, d_{yz} \rightarrow d_{x^2-y^2}$ [18].

The absorption band of the octahedrally coordinated Cu^{2+} of the turquoise crystals of copper metaphosphate ($Cu_2P_4O_{12}$) is found in the range between 8000 cm^{-1} and 13000 cm^{-1} (Figure 2). In the same range lies the broad Cu^{2+} band of the octahedrally bonded copper ultraphosphate ($Cu_2P_8O_{22}$) [19]. This broad band can be resolved into three-component Gaussian absorption bands at 8900 cm^{-1} , 10200 cm^{-1} , and 12600 cm^{-1} , due to the three energy transitions. One strong band at 10200 cm^{-1} and weaker ones at lower and higher wavenumbers are refined [15–17].

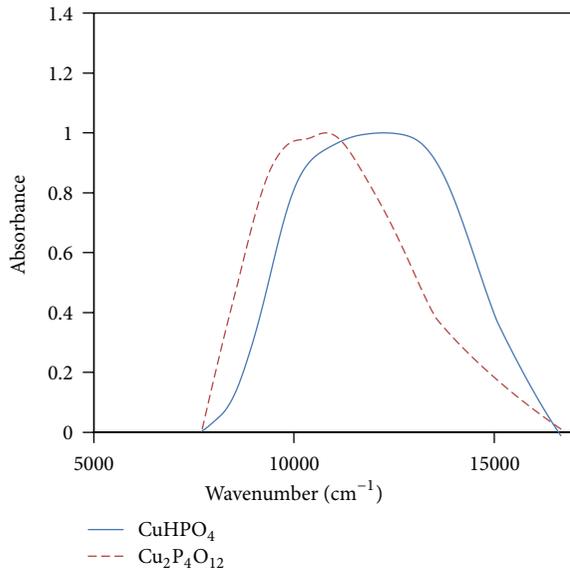


FIGURE 2: Absorbance spectra of CuHPO_4 and $\text{Cu}_2\text{P}_4\text{O}_{12}$.

The copper of the emerald green crystals of copper hydrogen phosphate (CuHPO_4) is square-pyramidal coordinated, and the absorption band is shifted to higher wavenumbers in the range between 9000 cm^{-1} and 15000 cm^{-1} (Figure 2).

In this coordination, two energy transitions are possible $d_{x^2-y^2}, d_{xy} \rightarrow d_{z^2}$ and $d_{xz}, d_{yz} \rightarrow d_{z^2}$ [20]. So, this band was resolved into two-component Gaussian bands centred at 10528 cm^{-1} and 13233 cm^{-1} , while the second one is slightly stronger (Figure 3).

The metaphosphate glasses 1 and 2 show shifted maxima and a different form of the Cu^{2+} band in the range between 7000 cm^{-1} and 16000 cm^{-1} (Figure 4). Glass 1 was rapidly cooled to the temperature of cold water, and glass 2 was slowly cooled to room temperature (approx. 5 K/min). Thus different kinds of structures were generated. The absorption band of glass 1 is shifted to higher wavenumbers than the band of glass 2, and that of glass 3 is shifted to even lower wavenumbers. So, glass 1 contains the highest part of square-pyramidal coordinated Cu^{2+} .

The resolved bands for the octahedral and square-pyramidal coordinated Cu^{2+} of the crystals were used to create five-component Gaussian absorption bands for the broad Cu^{2+} band in the glasses. The extinction coefficients of the Cu^{2+} in the crystals were used to estimate the parts of the different coordinations in the glasses. So, it was discovered that in the metaphosphate glass 1 nearly the half of the copper is square-pyramidal coordinated, in glass 2 nearly one-third, and in the ultraphosphate glass at least a quarter. Therefore, the increase of the copper content leads to more square-pyramidal coordinated copper.

Also the colour in the glasses changed slightly. Glass 1 is green, and glasses 2 and 3 are more turquoise. It is assumed that if the glasses are greener, more copper is square-pyramidal connected. One point in this favour is the structure of the emerald green CuHPO_4 crystals. Also rapid cooling leads to more square-pyramidal coordinated Cu^{2+} than slowly cooling.

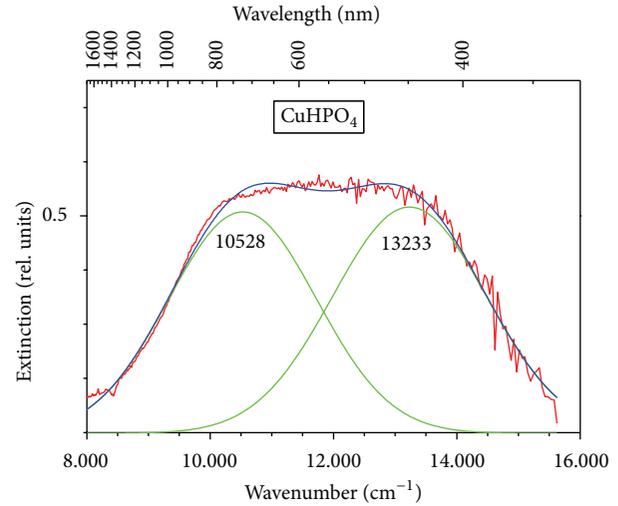


FIGURE 3: Peak fitting of the absorbance spectrum of CuHPO_4 (Origin).

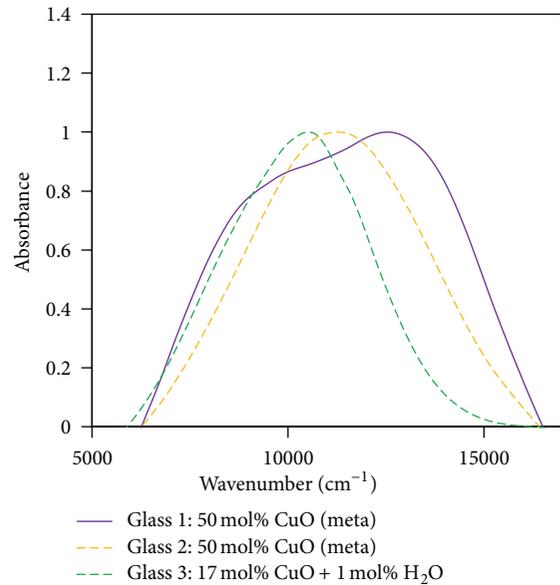


FIGURE 4: Absorbance spectra of the metaphosphate glasses 1 and 2 and the ultraphosphate glass 3.

Furthermore, it can be assumed that the green glasses contain more Cu^{1+} (up to $4\text{ mol}\%$) than the turquoise ones, because of the stronger tail of the UV absorption edge which extends into the visible spectrum region [21]. Thus, the amount of the square-pyramidal coordinated Cu^{2+} seems to be connected to the amount of Cu^{1+} . Also in all glasses with green colour, certain amounts of water (about $1\text{ mol}\%$) were identified, but the glasses with purposefully added water showed a turquoise colour. Hence, the green colour is connected to water, Cu^{1+} , and a change in the coordination to square-pyramidal coordinated Cu^{2+} .

3.2. IR-Spectroscopy. The IR-spectrum of CuHPO_4 exhibits a broad OH band at 3130 cm^{-1} (Figure 5, Table 2). In

TABLE 2: Data of the infrared spectra of CuHPO_4 , $\text{Cu}_2\text{P}_4\text{O}_{12}$, $\text{Cu}_2\text{P}_8\text{O}_{22}$, glass 3 (17 mol% CuO + 1 mol% H_2O (ultra)), and glass 4 (50 mol% CuO (meta)); data in cm^{-1} ; s: strong; m: middle; w: weak; b: broad.

	CuHPO_4	$\text{Cu}_2\text{P}_4\text{O}_{12}$	$\text{Cu}_2\text{P}_8\text{O}_{22}$	Glass 3	Glass 4
$\nu(\text{OH})$	3130 m, b	3410 w, b	—	—	—
$\nu(\text{P=O})$,		1325 m	1360 w	1396 w	1375 w
$\nu_{\text{as}}(\text{PO}_2)$	1214 w	1295 m	1330 m	1364 s	1326 w
		1279 m	1300 m	1310 m	1295 m
				1274 w	1251 s
					1211 w
$\nu_{\text{s}}(\text{PO}_2)$	1113 m	1130 w	1150 m	1167 w	1166 w
	1065 m	1100 w	1140 w	1109 m	1116 m
			1190 w		
$\nu_{\text{as}}(\text{P-O})$	1043 s	1042 s	1030 w	1046 m	1062 s
	1005 s	1013 m	995 m	1003 m	992 m
	914 m		960 s	955 s	944 m
			930 s	939 w	919 w
$\nu_{\text{s}}(\text{P-O})$	—	725 m, b	760 m	760 m, b	750 m, b
			750 w	670 m, b	
			710 m		
			690 m		
			640 m		
Deformation	611 w	578 w	570 w		
vibration	578 m	562 m	550 m		
	544 w	521 m	500 s	470 m, b	510 m, b
	571 m	498 m	470 s		
		461 w	440 m		
			410 w		

the spectrum of $\text{Cu}_2\text{P}_4\text{O}_{12}$, a weak OH band is also present. This can be due to adsorbed water at the surface or little amounts of additional water in the structure. The IR-spectrum of $\text{Cu}_2\text{P}_8\text{O}_{22}$ does not show an OH band. The OH bands of the glasses cannot be investigated because the glasses are very hygroscopic and adsorb different amounts of water depending on the humidity and the temperature of the environment. The metaphosphate glasses are more resistant than the ultraphosphate glasses, but nonetheless sensitive. Only a very small band in the range between 1400 cm^{-1} and 1200 cm^{-1} is registered and no band in the range between 800 cm^{-1} and 700 cm^{-1} in the spectrum of CuHPO_4 . Thus, no $\nu(\text{P=O})$ -, asymmetric $\nu(\text{PO}_2)$ -, and symmetric $\nu(\text{P-O})$ -vibrations can be found (Table 2). The structure of this molecule does not allow them, because no pure P=O -groups are present, and to each PO_4 tetrahedron, one hydrogen and one copper ions are bound. Only two bridging oxygens are left for each tetrahedron, from which one is connected to the phosphor atom and one is connected to the copper ion of a neighbouring tetrahedron. The short P-O distance between P1-O4 is related to the P-O-Cu bond (O4-Cu : 2.36 \AA) and no real double bond [3, 15–17].

The IR-spectra of the crystals of $\text{Cu}_2\text{P}_4\text{O}_{12}$ and $\text{Cu}_2\text{P}_8\text{O}_{22}$ show a lot of bands in all the ranges between 1400 cm^{-1} and 400 cm^{-1} . Both structures contain (P=O) -groups and a multitude of different structure elements. The metaphosphate

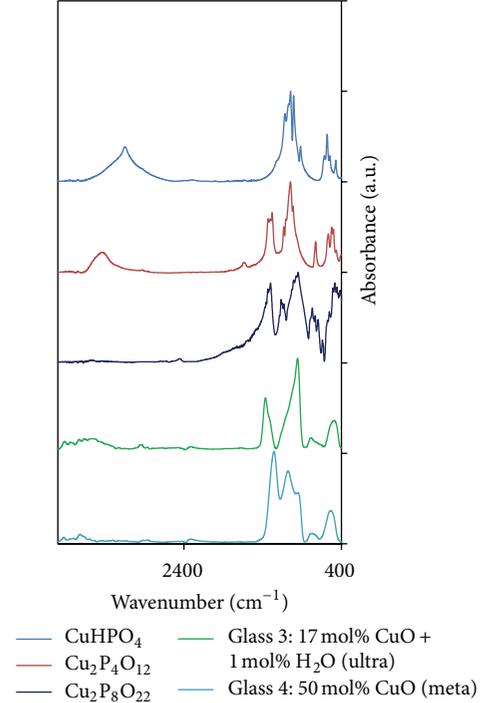


FIGURE 5: IR-spectra of the crystals of CuHPO_4 , $\text{Cu}_2\text{P}_4\text{O}_{12}$, $\text{Cu}_2\text{P}_8\text{O}_{22}$, the ultraphosphate glass 3, and the metaphosphate glass 4.

($\text{Cu}_2\text{P}_4\text{O}_{12}$) crystal structure is built up of Q^2 -bonded rings and the ultraphosphate ($\text{Cu}_2\text{P}_8\text{O}_{22}$) crystal structure of Q^2 - and Q^3 -bonded layers of 10-membered rings. The additional Q^3 bonds lead to even more bands in the spectrum of $\text{Cu}_2\text{P}_8\text{O}_{22}$.

The spectra of the glasses exhibit much broader bands than the crystals. The symmetric $\nu(\text{P-O})$ -vibrations and the deformation vibrations in the range between 850 cm^{-1} and 400 cm^{-1} are very similar in all glasses and can be compared to that ones in $\text{Cu}_2\text{P}_4\text{O}_{12}$ and $\text{Cu}_2\text{P}_8\text{O}_{22}$ crystals. The most differences in the spectra of the glasses appear in the range between 1400 cm^{-1} and 850 cm^{-1} [21]. So, these band complexes were separated with the help of Gaussian fitting (Table 2). In this range, the spectrum of the ultraphosphate glass 3 exhibits a similar trend to the spectrum of the ultraphosphate crystals ($\text{Cu}_2\text{P}_8\text{O}_{22}$), although the metaphosphate glass 4 shows similarities to the metaphosphate crystals ($\text{Cu}_2\text{P}_4\text{O}_{12}$). Accordingly, the structures of the glasses can be compared to those of the crystals.

3.3. EPR. The EPR spectra could be categorized into four types. The metaphosphate glasses 1 and 2 showed type I spectra (Figure 6). The copper content in these two glasses is very high, and so the spectra show a very broad line with $g = 2.207$ and peak-to-peak width $\Delta H_{\text{pp}} = 2000\text{ G}$ for glass 1 (green) and $g = 2.206$ and $\Delta H_{\text{pp}} = 1900\text{ G}$ for glass 2 (turquoise). The number of Cu^{2+} ions contributed to the EPR spectra is about 25% of the total amount of the introduced copper. The rest of the copper might form copper clusters or crystalline units

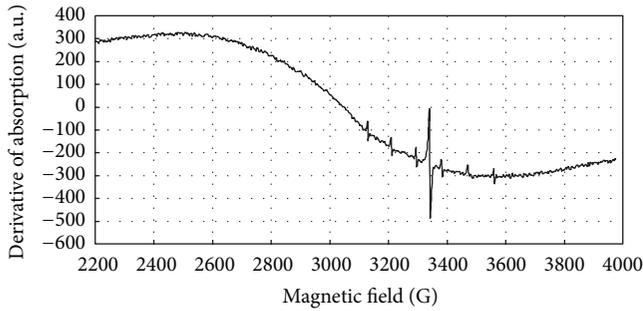


FIGURE 6: EPR spectrum type I (metaphosphate glasses, 50 mol% CuO).

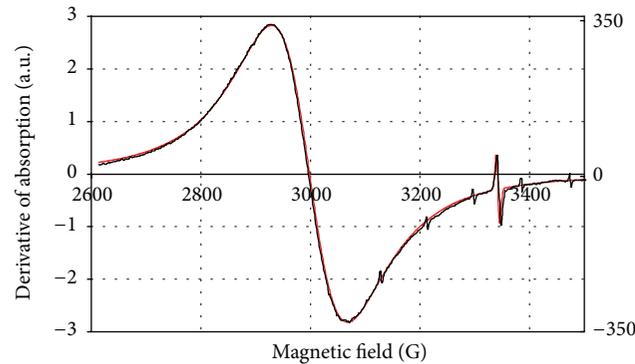


FIGURE 7: EPR spectrum type II (10–30 mol% CuO). Black spectrum experimental, red spectrum calculated.

with antiferromagnetic interactions between the Cu^{2+} ions, which do not contribute to the EPR spectra. The metaphosphate glasses were melted under oxidising atmosphere (air), so the reduction from the Cu^{2+} of $\text{Cu}_2\text{P}_4\text{O}_{12}$ to Cu^0 and Cu^{1+} is very unlikely. Besides Cu^0 would change the colour of the glasses to red [22]. The ultraphosphate glasses were melted under vacuum (in sealed ampoules), so the reduction of Cu^{2+} to Cu^{1+} is principally possible. But the formation of Cu^0 is unlikely, due to the colour of the glasses. Ultraphosphate glasses with a copper concentration in a middle range (between 10 and 30 mol% CuO) exhibit a very narrow single symmetric Lorentzian line of the type II spectra with $g = 2,227 - 2,244$ and $\Delta H_{\text{pp}} = 240 - 300$ G (Figure 7). The shape and width of this line indicate the exchange interactions among Cu^{2+} ions in a common spin system. Here, the number of Cu^{2+} ions contributed to the EPR spectra adds up to 20–30%. The highest number was obtained for a glass containing 10 mol% H_2O . Hence, additional water increases the number of Cu^{2+} ions which contribute to the spectra.

The structure of spectrum type III (Figure 8) lies between the types I and II. It shows a single line broadened because of spin-spin interactions in a united spin system with higher Cu^{2+} concentrations. This type occurs for copper ultraphosphate glasses with a higher copper content (>30 mol% CuO). The number of Cu^{2+} ions contributed to the EPR spectra increases to >45 %. The g -factor is with $g = 2,224$ slightly smaller than that for spectrum type II and bigger than that

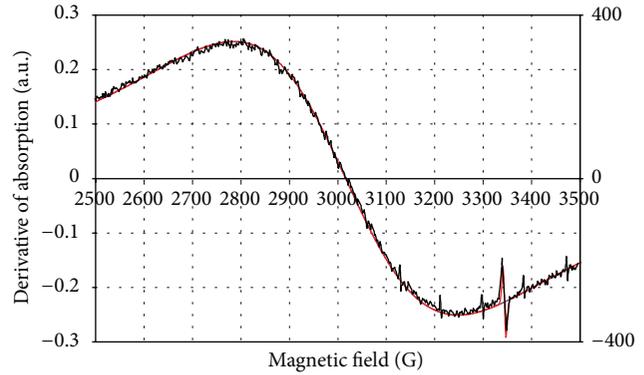


FIGURE 8: EPR spectrum type III (>30 and <50 mol% CuO).

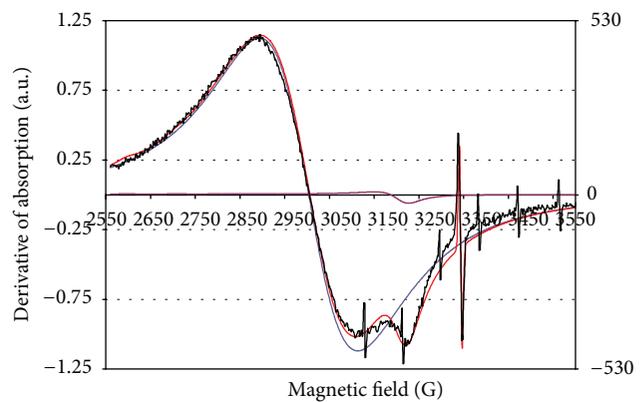


FIGURE 9: EPR spectrum type IV (<10 mol% CuO).

for type I and the peak-to-peak width $\Delta H_{\text{pp}} = 800 - 900$ G is bigger than that for type II and smaller than that for type I. Subsequently the g -factor decreases with increasing the copper content, and the peak-to-peak width decreases.

Ultraphosphates with a small copper content (<10 mol% CuO) change the shape of their spectra in comparison to the other glasses (Figure 9). Spectrum type 4 is the superposition of two spectra. Both spectra belong to Cu^{2+} , but probably in different coordination states, which could be different kinds of octahedrally distortion or another coordination like square pyramidal.

One of the spectra exhibits a four-component hyperfine structure (HFS) for parallel orientation and a structureless peak for perpendicular orientation. The second spectrum is Lorentzian single line similar to spectrum type II. The measured data vary for the g -factor only slightly between $g = 2,232$ and $g = 2,236$ and for the peak-to-peak width between $\Delta H_{\text{pp}} = 220$ G and $\Delta H_{\text{pp}} = 380$ G. The ratio (R) of the integrated intensity of the structureless line to that of the HFS spectrum of the last HFS spectrum accounts to 71 : 1 for a turquoise glass without water and to 167 : 1 for a green glass with about 1 mol% water and a certain amount of Cu^{1+} .

The experimental spectra were fitted to simulated ones to determine the spectral parameters of Cu^{2+} [23, 24]. The simulated spectra were calculated computing spin Hamiltonian

of an axial symmetry with electron spin $S = 1/2$ and nuclear spin $I = 3/2$ [25]

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta (H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y). \quad (1)$$

The best HFS fit parameters of all samples were $A_{\parallel} = 120 \cdot 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = 10 \cdot 10^{-4} \text{ cm}^{-1}$, $g_{\parallel} = 2,435$, and $g_{\perp} = 2,093$.

The EPR investigations are much more accurate and higher resolving for small copper contents. Therefore, only for glasses with less than 10 mol% CuO, different Cu^{2+} coordinations could be detected.

4. Summary

The crystals of CuHPO_4 , $\text{Cu}_2\text{P}_4\text{O}_{12}$, and $\text{Cu}_2\text{P}_8\text{O}_{22}$ were compared to copper phosphate glasses. Some of the glasses were prepared in crucibles and the others in evacuated and sealed silica ampoules. The glasses show similar optical properties to the crystals. The Cu^{2+} band in the UV-VIS-spectra was investigated for square-pyramidal and octahedrally coordinated structures. These structures were compared to the glasses, which show different parts of both coordinations. The colours of the glasses differ from green to turquoise, depending on the coordination, Cu^{1+} concentration, water content, and cooling procedure of the glasses.

The IR-spectra of the crystals and the glasses can be compared with each other, in spite of the fact that the glasses show much broader bands. The metaphosphate structure is similar in the crystals and the glasses. The same can be observed for the ultraphosphate structure. The most interesting changes from the metaphosphate to the ultraphosphate structure can be found in the range between 1400 cm^{-1} and 850 cm^{-1} , where the ultraphosphate crystals show much more bands than the metaphosphate crystals. The EPR spectra change with the decreasing copper content, and at least two different coordinated Cu^{2+} ions were found for glasses with less than 10 mol% CuO.

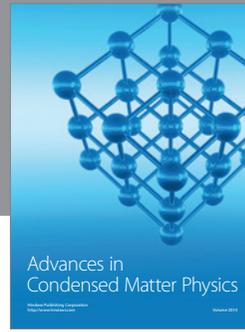
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