LOW-TEMPERATURE SYNTHESIS OF SOME ORTHOSILICATES

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Crystalline and amorphous orthosilicates of magnesium, zinc, cadmium and copper were prepared by non-traditional sol-gel schemes connected with the use of high-boiling chemically active (HBCA) additives to prevent the polycondensation of silicate anions at early synthesis stages. Metal acetates and nitrates were used as the metal oxide precursors, tetraethoxysilane and γ-aminopropyltriethoxysilane - as the SiO_2 precursors, resorcinol and triethanolamine - as the HBCA additives, water and dimethyl formamide - as the solvents. Gelation and drying of the precursor solutions were carried out at 20 ° or 120 °C, the further thermal treatment of samples were performed in three stages up to 900 °C. Chemical evolution of the systems during the thermal treatment, was controlled using TGA-DTA and XRD techniques, the kinetic "molybdate" method, FTIR and UV-VIS spectrophotometry. The use of high-boiling chemically active additives was shown to reduce the content of free metal oxides in the synthesis products, as well as to suppress the formation of high-polymerized silicate species that could complicate the further formation of orthosilicates. The formation of amorphous Cu_2SiO_4 is particularly complicated by thermodynamic instability of the corresponding crystalline silicate and needs addition of quaternary ammonium hydroxide as the highly basic agent.

INTRODUCTION

Orthosilicates of many bivalent metals (M_2SiO_4) are widely applied in various technologies, for example, as luminescent materials (Zn_2SiO_4), ultraviolet absorbers (Zn_2SiO_4), dielectric and corrosion protective coatings (Mg_2SiO_4, Fe_2SiO_4, Zn_2SiO_4). Apart from traditional high-temperature methods, various sol-gel methods were proposed for their preparation starting usually from tetraethoxysilane (TEOS) and metal alkoxides [1 - 3] or salts [4 - 6]. However the sol-gel synthesis of orthosilicates is characterized by the high MO/SiO_2 molar ratio in precursor mixtures that often leads to the formation of crystalline metal oxides at an intermediate synthesis stage and therefore to a significant increase of silicate formation temperature.

For example, the early attempts of the forsterite synthesis from stoichiometric precursor mixtures (Kazakos et al. [4] - from TEOS+nitrate, Burlitch et al. [1] - from wholly alkoxide system) were characterized by relatively high forsterite crystallization temperatures (above 800 °C). Mitchell et al. [3] applied prehydrolysis of TEOS that allowed to reduce this temperature to 770 °C but did not guarantee complete chemical binding of MgO. Ban et al. [6] prepared MgO-free forsterite with crystallization temperature 700 °C but they started from the precursor mixture with the MgO/SiO_2 molar ratio 1.0. Khristov et al. [5] obtained ZnO-free willemite from the TEOS-nitrate stoichiometric precursor mixture after thermal treatment at 1100 °C.

The preparation of gel-derived orthosilicates is also complicated by substantial difference between intermediate and final structures of silicate anions. Indeed, their polycondensation usually proceeds during the gelation stage of the process whereas a final crystalline product must have the monomeric anion structure. This fact leads to a double-stage character of the synthesis, with the formation of metal polysilicate and free metal oxide as the intermediates [3]. Their interaction at the second stage of the process, may be complicated by various factors, for example, low chemical activity of crystalline oxide, its oxidation or reduction at elevated temperature etc. [7]. So we loose the main advantage of the sol-gel synthesis - progressive formation of the final structure beginning from the gelation stage.

Several years ago we proposed a new wet-chemistry method to prepare high-basicity silicates, including forsterite, based on the use of γ-aminopropylsilanetriol (APSTOL, $H_2N(CH_2)_3Si(OH)_3$) - a water-soluble trifunctional silica precursor with relatively low polymerizability [8, 9]. The present study describes the preparation of crystalline and amorphous orthosilicates of magnesium, zinc, cadmium and copper using modified sol-gel schemes connected with the addition of high-boiling chemically active (HBCA) agents to reduce polycondensation of silicate anions during the synthesis. The main purpose was to choose the optimum

precursor mixture permitting to decrease silicate formation temperature and the main impurities (free oxides and polysilicate anions) concentration.

EXPERIMENTAL PART

Sample preparation

Two synthesis schemes were used to prepare orthosilicate samples. The first one involved the use of prehydrolized TEOS as the SiO_2 precursor, resorcinol as the HBCA agent and dimethyl formamide (DMFA) as the solvent. In the second one APSTOL was used as the SiO_2 precursor, triethanolamine (TEOA) - as the HBCA agent, methyl triethylammonium hydroxide (MTEAH) - as the strong base and water - as the solvent. In both cases metal nitrates (Cu, Zn) or acetates (Mg, Zn, Cd) were used as the MO precursors. Copper acetate was not used because of its reduction to metal copper by reactions with resorcinol or TEOA at high temperature. Flow charts corresponding to both schemes, are shown in figure 1.

To avoid the silica loss during the initial synthesis stages, TEOS was prehydrolized by adding concentrated HCl up to the molar ratio H_2O/TEOS = 1.0 and stirring the mixture for 5 min. APSTOL solution was prepared by mixing γ-aminopropyltriethoxysilane (APTEOS) with water, at the molar ratio H_2O/APTEOS = 8.0, and stirring the mixture for 15 - 30 min. to complete the hydrolysis process. The

resulted clear solution with pH = 11.3 contained 18.9 % of silica and was absolutely stable.

To obtain the binary precursor solutions according to the scheme I, the DMFA solution of the corresponding metal salt, prehydrolized TEOS and resorcinol were mixed at molar ratios MO : SiO_2 : $C_6H_4(OH)_2$ = = 2 : 1 : 18 and final M_2SiO_4 concentration 0.06 mol l^{-1}. The prepared solutions were stable for several months. According to the scheme II, the aqueous solution of metal nitrate, TEOA, MTEAH and APSTOL were mixed at molar ratios MO : SiO_2 : TEOA : MTEAH = = 2 : 1 : 10 : 4 and final M_2SiO_4 concentration 0.06 mol l^{-1}. The prepared solutions of pH values above 13 were absolutely stable.

Both sets of binary solutions were used for the preparation of powdered samples and deposition of thin films (for FTIR and UV-VIS spectral studies). In the first case, the solutions were dehydrated by heating in air at 125 °C for 2 hr; dark, very viscous resorcinol- or triethanolamine-based solutions formed. After further heating at 250 °C for 0.5 hr, slightly colored solids formed ("dry gels") which were converted to amorphous silicates by heating at 550 °C for 0.5 hr. The crystalline products were obtained by heating the amorphous products up to 900 °C at 10 °C/min.

Sample characterization

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were run to 900 °C at a heating rate 5 °C/min using a Paulik-Paulik-Erdey apparatus (Q-1000) with a multi-plate platinum holder. Powder X-ray diffraction (XRD) was performed by a JEOL diffractometer (JDX-10PA) using Cu Kα radiation. Diffraction peaks were identified using PDF-2 database (JCPDC-ICDD, 1993). The concentrations of free oxides were evaluated by calculating the main peaks areas using pure crystalline oxides as standards. Infrared spectra of thin films deposited on silicon wafers, were measured at 400 - 4000 cm^{-1} by FTIR spectroscopy using a Perkin Elmer 2000 apparatus. UV-VIS spectra of silicate films on glass, were measured at 320 - 850 nm using a Specord M80 spectrophotometer. The films were deposited on glass slides by dipping in binary precursor solutions at withdrawal rate 6.7 cm/min.

The extent of oxide chemical binding was evaluated from the XRD and UV-VIS spectral data using a simple expression:

$$B = (1 - I / I_0) \cdot 100\%$$

where I is an integral intensivity (peak area) of the main oxide difraction peak (XRD) or the charge transfer peak (UV-VIS) for binary samples, and I_0 is the corresponding peak area for pure metal oxide samples.

The polymeric structure of silicate anions in the samples was studied quantitatively using the molybdate analysis (MA), i.e. continuous UV-VIS spectrophotometry (λ = 410 nm) of the reaction between molybdic acid and an acid (HCl) solution of the sample [10].
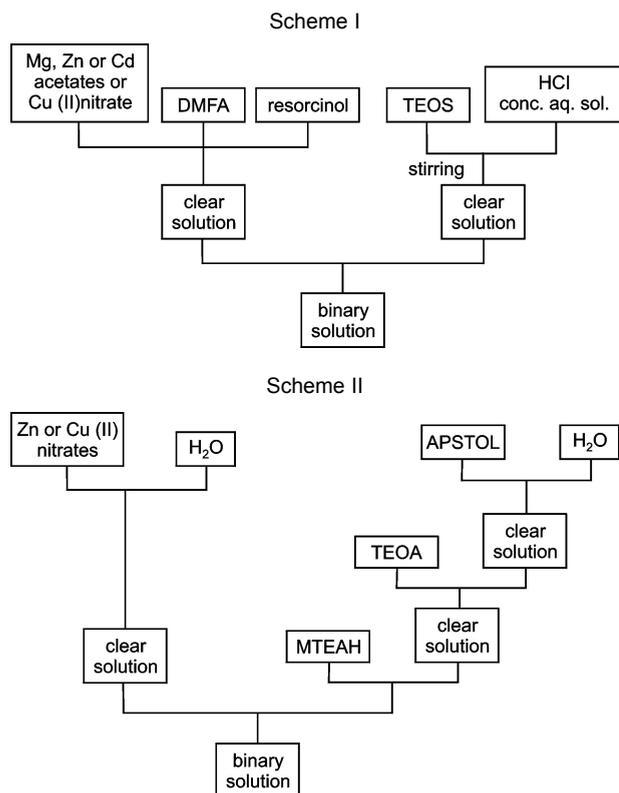
Figure 1. Flow-charts for the two preparation procedures.

RESULTS AND DISCUSSION

As was mentioned above, the sol-gel synthesis of orthosilicates is always complicated by the formation of condensed silicate structures at intermediate synthesis stages. In order to increase the synthesis efficiency by suppressing the polycondensation process, we used the HBCA agents: resorcinol and TEOA. The chemical mechanism of their action is following:

1. They react with the silica precursors by ester exchange, blocking the Si-OH or Si-OR groups and substantially decreasing their ability to polycondensation [11, 12]:

$$Si(OEt)_4 + 4C_6H_4(OH)_2 \rightarrow$$
$$\rightarrow Si(OC_6H_4OH)_4 + 4EtOH \uparrow \qquad (1)$$

$$H_2N(CH_2)_3Si(OH)_3 + (HOC_2H_4)_3N \rightarrow$$
$$\rightarrow H_2N(CH_2)_3Si(OC_2H_4)_3N + 3H_2O \uparrow \qquad (2)$$
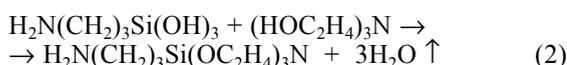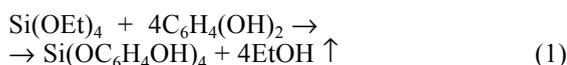
The formed substances dissolve in the excess of resorcinol or TEOA and remain stable during further thermal treatment up to the solvents evaporation (280 °C and 360 °C respectively). The product of reaction (1) may participate in condensation processes through its hydroxyls, not forming siloxane bonds. In the synthesis scheme II, the depolymerizing ability of TEOA was amplified by adding of a strong base (MTEAH) active in both aqueous and triethanolamine solutions.

2. All the used MO precursors (acetates and nitrates) react with liquid resorcinol or TEOA forming metal resorcinates or triethanolaminates soluble in the corresponding solvents.

3. The equilibrium of the formation of siloxane bond is displaced toward depolymerization at elevated temperatures (280 - 360 °C) because of substantially exothermic character of the polycondensation reaction [13].

The efficiency of the HBCA agents may be evaluated by the analysis of polymeric structure of silicate anions in amorphous samples after the second stage of thermal treatment at 550 °C (see below).

Thermogravimetry and Differential thermal analysis

Figure 2 shows TGA and DTA curves for the Mg-, Zn- and Cd-containing dry gels prepared according to the scheme I. The corresponding curves for the Cu-containing gel had the same shape, but the intensity of the DTA exothermic peak near 400 °C, is extremely high because of a red-ox process between nitrate residues and organics. The following observations can be summarized:

1. Thermal decomposition of the orthosilicate gels proceeds in the temperature range 300 - 580 °C and is accompanied with broad DTA exotherms at 360 - 470 °C. They are very intensive (the total mass loss is 40 - 60 %) and includes the oxidative decomposition of both precursors and the oxidation of all the residual organics. After this stage, the summary mass loss does not exceed 3% (magnesium orthosilicate).

2. In the range 600 - 700 °C all the samples (excluding Cu-containing one) should exist as amorphous silicates (or intimate oxide - silicate mixtures) with the total chemical composition corresponding to orthosilicates.

3. The chemical evolution of the systems above 700 °C lies mainly in the crystallization processes accompanied with weak DTA exotherms. So the Mg-containing system shows crystallization of forsterite (720 °C), Zn-containing system - willemite (820 °C). DTA curve of the Cd-containing system does not show any crystallization peak, probably because of the complex phase composition in the final material (see below). Finally, the absence of the crystallization peaks for the Cu-containing sample is due to the impossibility of the crystallization of copper orthosilicate. Simultaneously, the oxidation of the last carbon residues proceeded (the mass loss from 0.5 to 1.8 %). The samples which were dark brown when heated to 550 °C, became white (Mg, Zn), yellowish (Cd) or black (Cu).
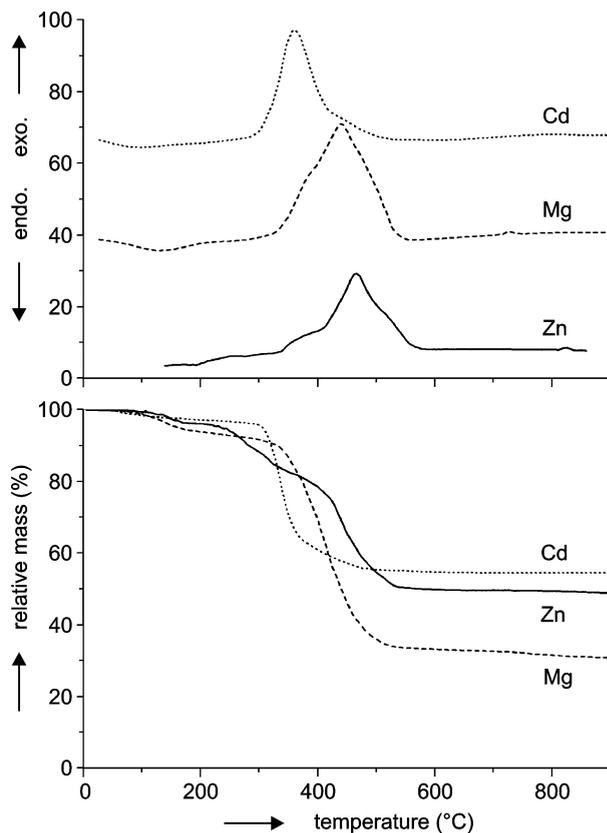

Figure 2. DTA and TGA curves for Mg-1, Zn-1 and Cd-1 dry gels, 5 °C/min.

Table 1. Characteristics of the orthosilicate samples prepared using two synthesis schemes.

Parameters	Determ. method	Systems and synthesis schemes					
		Mg-Si (I)	Zn-Si (I)	Cd-Si (I)	Cu-Si (I)	Zn-Si (II)	Cu-Si (II)
Decomposition temperature (°C)	TGA	530	580	500	590	570	600
Crystallization temperature (°C)	DTA	720	810	?	-	810	-
SA basicity at 550 °C	MA	1.41	1.61	1.40	1.26	1.43	1.58
SA basicity at 700 °C	MA	1.45	1.64	1.72	1.18	1.62	1.38
	MA	70	80	70	63	72	79
Oxides binding at 550 °C (%)	UV-VIS	-	80	-	25	60	85
	XRD	78	85	69	10	69	80
Oxides binding at 700 °C (%)	MA	72	82	86	59	81	69
Main crystalline phase at 900 °C	XRD	Forsterite	Willemite	Cd_2SiO_4	CuO	Willemite	(am.)
Accomp. crystalline phases at 900 °C	XRD	MgO, $MgSiO_3$	ZnO	CdO, Cd_3SiO_5	-	ZnO	CuO
Oxides binding at 900 °C (%)	XRD	80	87	72	-	80	-

SA = silicate anions, MA = "molybdate" analysis

The temperatures of final decomposition and silicate crystallization are displayed in table 1. As compared with the corresponding temperatures for the samples prepared without use of resorcinol, the decomposition temperatures are 100 - 150 °C higher, but the crystallization temperatures are 20 °C (Zn) and 120 °C (Mg) lower (in comparison with recently published data - ca. 50 °C lower in both cases [3, 14]). This is probably connected with higher structural homogeneity of intermediate amorphous solids formed in the systems prepared using HBCA agents.

The Zn- and Cu-containing dry gels prepared according to the scheme II, showed the similar character of DTA and TGA curves. Their principal parameters are also displayed in table 1.

X-ray diffraction

All the two-component samples after being heated to 550 °C, were mostly amorphous, with low (Mg-I, Zn-I, Zn-II, Cd-I, Cu-II) or high (Cu-I) content of crystalline oxides. After the final thermal treatment (900 °C) the samples were well-crystallized, corresponding orthosilicates in the stable forms (forsterite Mg_2SiO_4, willemite Zn_2SiO_4 and ortho-rhombic Cd_2SiO_4) were the main crystalline phases except for the Cu-containing systems where CuO was the main phase. Figure 3 shows XRD patterns obtained for four binary samples heated to 900 ºC and the Cu-contained samples heated to 550 °C. The main types of crystalline impurities are oxides MgO, ZnO and CdO, oxide-orthosilicate (tricadmium silicate $Cd_3(SiO_4)O$) and metasilicate (enstatite $MgSiO_3$). The phase compositions of binary samples and the values of extent of oxides chemical binding in silicate structures, as percentages in relation to pure oxides, are displayed in table 1.

As for the Cu-containing systems, their XRD patterns indicate the presence of the unique crystalline phase - tenorite CuO. Its concentration in the sample
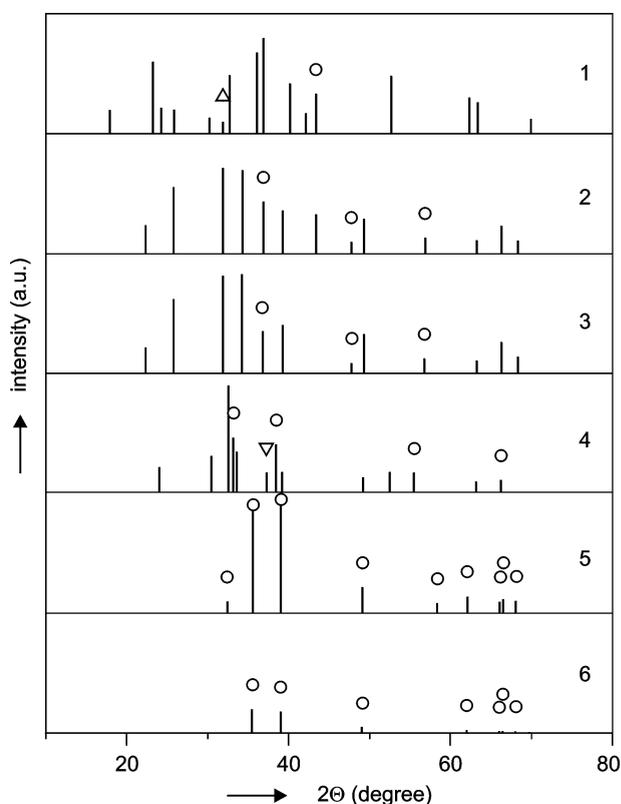

Figure 3. XRD patterns for the samples: Mg-I (1), Zn-I (2), Zn-II (3), Cd-I (4) heated to 900 °C, Cu-I (5), Cu-II (6) heated to 550 °C. All peaks are characteristic of corresponding orthosilicates (forsterite, willemite and Cd_2SiO_4 respectively) except those indicated that are characteristic of accompanying crystalline phases: oxides (circles), tricadmium silicate (down triangles), enstatite (up triangles).

Cu-I at 550 °C corresponds to the practical absence of the chemical binding of CuO to any silicate structure. As contrary, in the sample Cu-II the free oxide

concentration is found to be 10 % that corresponds to 80 % binding of CuO. It is characteristic that without use of TEOA and MTEAH (precursor mixture $Cu(NO_3)_2$ + APSTOL + HNO_3 + H_2O) one can achieve merely 55 % binding of copper oxide.

As follows from figure 3 and table 1, the synthesis scheme I is highly efficient for the synthesis of forsterite and willemite and less efficient in the case of crystalline Cd_2SiO_4 and absolutely inefficient for the preparation of amorphous high-basicity copper silicates. However, such silicates may be prepared using the scheme II which is rather efficient also for willemite (70 - 80 % oxide binding evidents the formation of silicate structures with MO/SiO_2 molar ratio 1.4 - 1.6).

Formation of the silicate structure

The thermal evolution of the binary MO - SiO_2 systems in the temperature region 250 - 700 °C was additionally studied using FTIR data for the samples prepared according to the scheme I. Figure 4 shows FTIR spectra (in the characteristic region 400 - 2000 cm^{-1}) for the two characteristic binary systems representing successful (Cd) and unsuccessful (Cu) synthesis, heated up to three different temperatures. The development of the silicate structure may be understood mainly by following the thermal evolution of the O-Si-O stretching bond position.

At 250 °C the samples present a single broad peak centered at 1000 - 1100 cm^{-1} of a shape that is rather typical for amorphous silicates. Unlike the Cu-containing system, in the Cd-containing one this peak has a very intensive shoulder at 900-980 cm^{-1} that indicates the presence of a significant fraction of low-polymerized silicate species. As temperature increases, the peak width in both systems decreases and the peak position shifts towards lower (Cd) or higher (Cu) wave numbers, reflecting general trends to the depolimerization or polycondensation of silicate network. For the Cd-containing sample, at 700 °C the peak maximum reaches 930 cm^{-1} that is characteristic for the mono- or dimeric silicate anions. In the CuO-SiO_2 system, the corresponding peak is centered at 1100 cm^{-1} that is characteristic for highly condensed silicate species.

The thermal evolution of FTIR spectra for the Mg- and Zn-containing systems are similar to that for the Cd-containing one and differ from the latter only by the extents of peak broadening and splitting. For Mg silicate, the peak position shifts from 1060 to 970 cm^{-1}, for Zn silicate - from 1050 to 910 cm^{-1} as temperature increased from 250 to 700 °C.

For the Cu- and Zn-based samples, the yield of amorphous orthosilicates at an intermediate synthesis stage can be evaluated also comparison of UV-VIS spectra of thin films heated up to 550 °C. If amorphous or crystalline oxides form in the systems instead of (or together with) orthosilicates, wide and intensive charge-transfer bands near 350 nm (3.5 eV) arise in the spectra [15, 16]. The value of this peak area should be
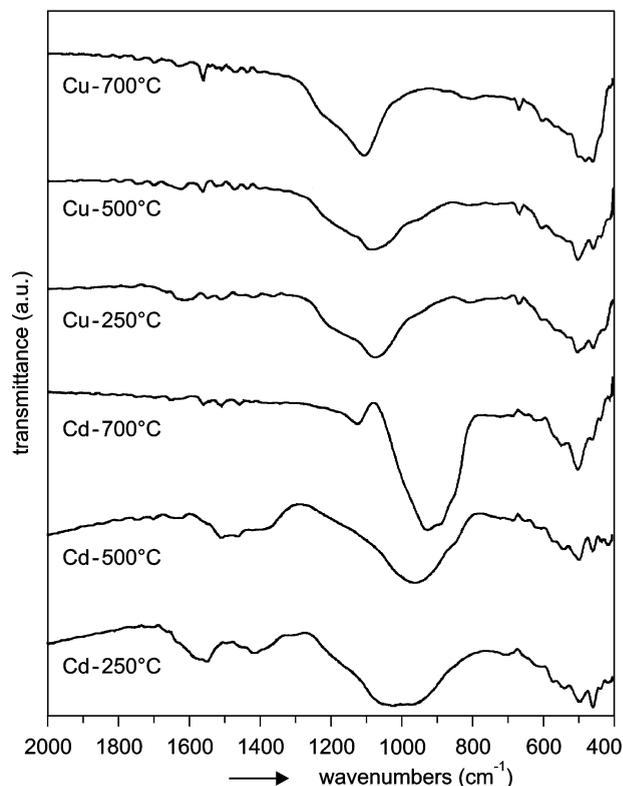

Figure 4. Thermal evolution at 250 - 700 °C of FTIR spectra for the samples Cd-I and Cu-I.

proportional to the integral oxide concentration in the sample.

In figure 5, UV-VIS spectra of the Zn- and Cu-contained samples prepared according to both schemes, are shown in comparison with the spectra of samples prepared in the same way but without corresponding silica precursors, i.e. containing only oxides. It is obvious that both ways of preparation of Zn orthosilicates were efficient (the extents of oxide binding are 80 % and 60 %). For the Cu-containing systems, the UV-VIS spectra show inefficiency of the scheme I (oxide binding is about 25 %) and the excellent productivity of the scheme II (oxide binding is about 85 %). All these results are in a good agreement with those of XRD and FTIR experiments.

The results obtained using the molybdate analysis give a more direct information on the polymerization state of the samples and therefore on their phase composition, especially for amorphous samples. In table 1, the values of average basicity of silicate anions (SA), are displayed for all the samples treated at 550 and 700 °C. For the present case, the basicity (x) means the molar ratio MO/SiO_2 in silicates and indicates the polymerization degree of the silicate anions. For example, $x = 2$ for the monomer (orthosilicate), $x = 1.5$ for the dimer, $x = 1.0$ for the wollastonite-like linear polymer and $x = 0$ for pure silica. For the linear oligomers the basicity is connected with the polymeri-
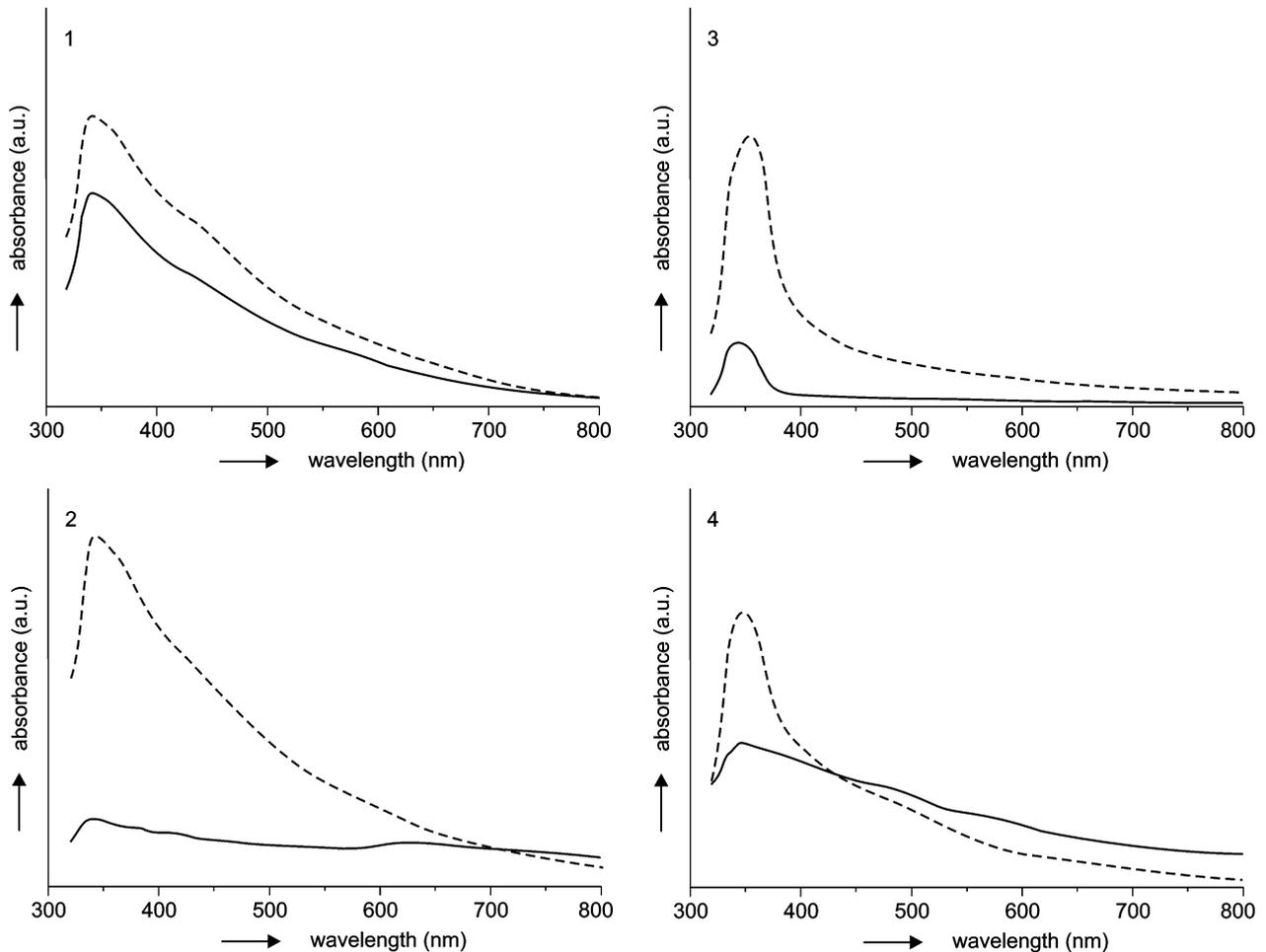
Figure 5. UV-VIS spectra for the samples: Cu-I (1), Cu-II (2), Zn-I (3) and Zn-II (4).
1, 2 - - - - - Si/Cu = 0, ——— Si/Cu = 0.5; 3, 4 - - - - - Si/Zn = 0, ——— Si/Zn = 0.5;

zation degree (*n*) according to the expression $x = 1 + 1/n$. For the studied samples of the orthosilicate composition, the extent of metal oxide chemical binding can be determined as $(0.5\ x) \cdot 100\ \%$.

The obtained basicity values evident that silicate structures formed at 550 °C, right after the precursors decomposition, are relatively low polymerized, excluding the case Cu-I. The average basicity values (1.40 - 1.61) correspond to various mixtures of monomeric, dimeric and trimeric anions with a predomination of the dimeric one. The result for the system Cu-II seems to be especially interesting because up to now, the preparation of copper silicates with so low polymerization grade has not been described. As temperature increased to 700 °C, the *x* values rise for all the systems excluding Cu-containing ones, that is in a good agreement with the FTIR data.

On the base of the MA results, the values of percentage of oxides bonded in silicate structures (provided that the samples are two-component between decomposition and crystallization temperatures) were calculated. These results are also displayed in table 1 in comparison with those evaluated using UV-VIS spectral

and XRD data. In most cases, the results obtained by different methods, are in a satisfactory agreement. In the case of the sample Cu-I, some discordance between MA and other methods, can be seen caused probably by low percentage of silica that may be dissolved in HCl during the molybdate analysis (about 10 % compared with 44-91 % in other systems) and therefore by reduced representativity of the MA data in this case.

Thus, the probable general scheme of the formation of orthosilicates in the studied systems, can be written as follows:

Scheme I (M = Mg, Zn, Cd):
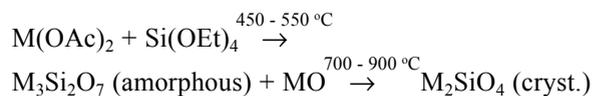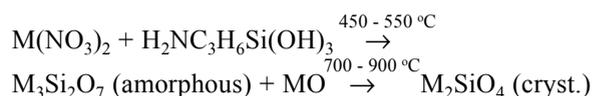
$$M(OAc)_2 + Si(OEt)_4 \xrightarrow{450 \text{ - } 550\ ^\circ C}$$

$$M_3Si_2O_7 \text{ (amorphous)} + MO \xrightarrow{700 \text{ - } 900\ ^\circ C} M_2SiO_4 \text{ (cryst.)}$$

Scheme II (M = Zn):

$$M(NO_3)_2 + H_2NC_3H_6Si(OH)_3 \xrightarrow{450 \text{ - } 550\ ^\circ C}$$

$$M_3Si_2O_7 \text{ (amorphous)} + MO \xrightarrow{700 \text{ - } 900\ ^\circ C} M_2SiO_4 \text{ (cryst.)}$$

Scheme II (M = Cu):

$$M(NO_3)_2 + H_2NC_3H_6Si(OH)_{34} \xrightarrow{450 - 550\ ^oC}$$
$$M_3Si_2O_7 \text{ (amorphous)} + MO \xrightarrow{700 - 900\ ^oC} 2MO + SiO_2$$
$$\text{(amorphous)}$$
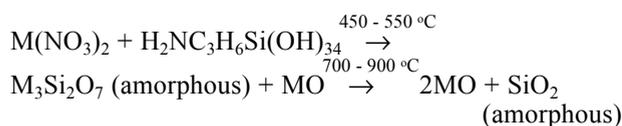
The formation of amorphous copper silicate with near-diorthosilicate structure in the temperature range 550 - 700 °C, is extremely important because of thermodynamic instability of anhydrous crystalline high-basicity copper silicates which have not been synthesized up to now. Previously the sol-gel synthesis was used to prepare amorphous silicates in the systems where stable silicate phases do not exist (for example, in the system Fe_2O_3 - SiO_2 [17]). The present synthesis way (Scheme II) seems to be rather promising for the preparation of crystalline copper orthosilicate by modifying crystallization conditions and possibly using suitable catalyzers.

CONCLUSION

We propose two synthesis schemes suitable for the preparation of crystalline orthosilicates of bivalent metals such as Mg, Zn, Cd. The method involves the use of simple, low-cost and moisture resistant precursors (metal acetates and nitrates, TEOS, APTEOS), the precursor solutions are highly stable. The precursor mixtures contain also high-boiling chemically active (HBCA) additives such as triethanolamine or resorcinol to prevent early polycondensation of silicate anions. The use of HBCA additives was shown also to reduce the content of free metal oxides in the synthesis products and to decrease temperature of orthosilicates crystallization. One of two synthesis schemes proposed here is shown to be efficient for the preparation of amorphous copper silicate with near-diorthosilicate structure, and seems to be suitable for synthesis of crystalline copper orthosilicate. Such an approach may find also rather wide practical applications especially for the preparation of protection glass and glass-ceramic coatings on metal substrates.

References

1. Kazakos A., Komarneni S., Roy R.: Mater. Letters *9*, 405 (1990).
2. Burlitch J.M., Beeman M.L., Riley B., Kohlstedt D.L.: Chem. Mater. *3*, 692 (1991).
3. Mitchell M.B.D., Jackson D., James P.F.: J. Sol-Gel Sci. and Technol. *13*, 359 (1998).
4. Srank Z., Sysala O., Hajek B.: Silikaty *29*, 79 (1985).
5. Khristov Ts., Popovich N.V., Galactionov S.S., Soshchin N.P.: Inorg . Mater. (Russia) *32*, 89 (1996).
6. Ban T., Ohya Y., Takahashi Y.: J. Amer. Ceram. Soc. *82*, 22 (1999).
7. Svegl F., Orel B., Hutching M.: J. Sol-Gel Sci. and Technol. *8*, 765 (1997).
8. Maliavski N.I., Dushkin O.V., Tchekounova E.V., Markina J.V., Scarinci G.: J. Sol-Gel Sci. and Technol. *8*, 571 (1997).
9. Maliavski N.I., Dushkin O.V., Markina J.V., Scarinci G.: AIChE J. *43*, 2832 (1997).
10. Maliavski N.I., Tchekounova E.V., Dushkin O.V.: J. Sol-Gel Sci. and Technol. *2*, 503 (1994).
11. Schwarz R., Kuchen W.: Z. Anorg. Allgem. Chem. *266*, 185 (1951).
12. Voronkov M.G., Dyakov V.M.: *Silatranes*, p.206, Nauka, Novosibirsk 1978.
13. Feuston B.P., Garofalini S.H.: J. Phys. Chem. *94*, 5351 (1990).
14. Chung-Chern Lin, Pouyan Shen: J. Non-Cryst. Solids *171*, 281 (1994).
15. Sukhorukov Y.P.: J. Magn. Magn. Mater. *183*, 356 (1998).
16. Subrhamanian P.: Indian J. Phys. *72A*, 99 (1998).
17. Guglielmi M., Principi G.: J. of Non-Cryst. Solids *48*, 161 (1982).

NÍZKOTEPLOTNÍ SYNTÉZA NĚKTERÝCH ORTHOKŘEMIČITANŮ

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Krystalické a amorfní hořečnaté, kademnaté, zinečnaté a meďnaté orthokremičitany byly připraveny netradičními sol-gel postupy s použitím chemicky aktivních přísad s vysokým bodem varu (HBCA) s cílem zamezit polykondenzaci křemičitanových aniontů v počátečních stádiích syntézy. Octany a dusičnany kovu byly použity jako prekurzory oxidu kovu, tetrasiloxan a γ-aminopropyltriethoxysilan jako prekurzor SiO_2, resorcinol a triethanolamin jako HBCA přísada a voda a dimethylformamid jako rozpouštědlo. Tvorba gelu a sušení roztoku prekurzoru probíhala při 20 nebo 120 °C. Další ohřev byl třístupňový do teploty 900 °C. Chemický vývoj systému během ohřevu byl sledován TGA, DTA s XRD metodami, kinetickou „molybdenanovou" metodou, FTIR a UV-VIS spektrometrií. Ukázalo se, že použití chemicky aktivních přísad s vysokým bodem varu snižuje obsah volných oxidů kovu a potlačuje tvorbu vysoce polymerizovaných křemičitanových jednotek, které by mohly komplikovat další tvorbu orthokřemičitanů. Zejména tvorba amorfního Cu_2SiO_4 je komplikována termodynamickou nestabilitou odpovídajících krystalických orthokřemičitanů a vyžaduje proto přídavek amoniaku jako vysoce bazického činidla.