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Preparation of $CuZr_2P_3O_{12}$ from alkoxide-derived gels: phase formation as a function of heat treatment

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The phase formation in alkoxide gels with composition corresponding to $CuZr_2P_3O_{12}$ has been studied as a function of gel preparation and heat treatment. Two preparational methods have been examined. The chemicals used include $Cu(NO)_3 \cdot 3H_2O$, $Zr(n\text{-}OC_3H_7)_4$ and either P_2O_5 or H_3PO_4, respectively. The P_2O_5 method results in the formation of di-phase gels. Heat treatment of these invariably gives multi-phase materials. Gels prepared by the H_3PO_4 method are completely amorphous and can be converted into porous glasses by heating to 500° C. Calcination in the range 650 to 750° C results in the formation of a new $CuZr_4P_6O_{24}$ phase ($R\bar{3}c$, $a = 1.762_{2\pm5}$ nm, $b = 4.39_{9\pm1}$ nm). Later, this prevents formation of mono-phase materials during heating to 1200° C. It is suggested that this behaviour is related to mixing of Cu^{2+} and Zr^{4+} in the normal copper and zirconium positions in the low-temperature $R\bar{3}c$ Cu^{2+}-Nasicon. Calcination in the range 750 to 850° C results in the formation of the normal C2/c Cu^{2+}-Nasicon which readily converts to mono-phase Cu^+-Nasicon ($CuZr_2P_3O_{12}$) above 880° C. Only gels calcined in the range 750 to 850° C are useful for the fabrication of mono-phase $CuZr_2P_3O_{12}$ ceramics.

1. Introduction

Nasicon-type phases have been extensively studied in the past decade because of their ionic conductivity and low thermal expansion. Possible applications of these materials include solid state ionics for batteries [1], ion-selective electrodes [2] and gas sensors [3–5] as well as low thermal expansion ceramics [6]. The composition of Nasicon phases can be expressed by the general formula $A_xM_2T_3O_{12}$ ($0 \leqslant x \leqslant 4$) where A represents mono- or divalent ions occupying positions in the three-dimensional network formed by TO_4 tetrahedra sharing corners with MO_6 octahedra [7, 8]. Most of the research so far has been concerned with the sodium-conducting materials for which the name was coined, i.e. $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $0 \leqslant x \leqslant 3$ [8, 9], and analogues of the phosphate end member $A_xZr_2P_3O_{12}$ in which Zr^{4+} ions have been partly or completely replaced by other octahedrally coordinated cations (M^{2+}, M^{3+}, M^{4+} and M^{5+} [7, 10–12]). Copper compounds belonging to the Nasicon family have recently received attention [13–20], and their usefulness in electrochemical cells for thermodynamic measurements has been demonstrated [20]. Copper ions can be introduced into the Nasicon structures both as Cu^+ and Cu^{2+}. The Cu^+-containing phases described are $CuTi_2P_3O_{12}$ [14, 17, 19], $CuZr_2P_3O_{12}$ [20] and $HCuZr_4P_6O_{24}$ [19] as well as the solid-solution series $Cu_{1+x}Cr_xTi_{1-x}P_3O_{12}$ and $Cu_xNb_{1+x}Ti_{1-x}P_3O_{12}$, $0 \leqslant x \leqslant 1$ [14]. The known Cu^{2+}-containing phases are $CuTi_4P_6O_{24}$ [15] and $CuZr_4P_6O_{24}$ [16]. Recently, the ion-conducting compound $NaCu_2ZrP_3O_{12}$ has also been synthesized and partly characterized [13]. This phase has a tetragonal structure which appear to be related to the Nasicon structure.

The present work concerns phase formation as a function of heat treatment of alkoxide-derived gels with an equivalent oxide composition corresponding to $CuZr_2P_3O_x$. Yao and Fray [20] prepared ceramics of composition $CuZr_2P_3O_{12}$ from Cu_2O, ZrO_2 and $NH_4H_2PO_4$ using a conventional powder technique, and a firing schedule including calcination in air at 300° C for 4 h followed by 16 h at 850° C and a final sintering in air at 1200° C for 3 to 16 h. Jazouli *et al.* [16] prepared the Cu^{2+} analogue, $CuZr_4P_6O_{24}$, by oxidation of the Cu^+ compound at 500° C in oxygen. Excess CuO was removed by a brief washing in diluted warm nitric acid. The final product was dried at 600° C for 15 h. Heating of $CuZr_4P_6O_{24}$ to 400° C for 15 h under hydrogen results in the formation of $HCuZr_4P_6O_{24}$ [19]. Hence, the transformations of the alkoxide-derived gels are expected to depend critically on details in the thermal treatment.

2. Experimental procedure

The $CuZr_2P_3O_x$ gels used in the present study were prepared from $Cu(NO_3)_2 \cdot 3H_2O$ (Merck, p.a., Darmstadt), $Zr(n\text{-}OC_3H_7)_4$ (Alfa Chemicals, 95 wt %) and solid H_3PO_4 (Merck, p.a.) or P_2O_5 (Merck, p.a., Karlsruhe) using methanol, MeOH (> 99.7 vol %) and *n*-propanol, Pr^nOH (> 99.8 vol %) as solvents.

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For both alcohols the water content was determined by Karl Fischer titration.

In each case the exact content of copper, zirconium and phosphorus in the raw materials was determined by chemical analysis in order to obtain the desired composition of the final product.

All weighings of $Zr(OPr^n)_4$, H_3PO_4 and P_2O_5 were performed in a dry air filled glove box (dew point $<$ $-50°$ C). Stock solutions of the $Zr(OPr^n)_4$, the copper salt, H_3PO_4 and "P_2O_5" were prepared by dissolving these components in Pr^nOH ($333\,g\,l^{-1}$), MeOH ($83\,g\,l^{-1}$) Pr^nOH ($25\,g\,l^{-1}$) and Pr^nOH ($18\,g\,l^{-1}$), respectively. Dissolution of P_2O_5 in Pr^nOH results in the following (strongly exothermic) reaction [21]

$$P_4O_{10} + 5Pr^nOH \rightarrow H_2P_2O_5(OPr^n)_2 + H_2PO_3OPr^n + HPO_2(OPr^n)_2$$

Thus, the average number of reactive groups (i.e. OH groups) per phosphorus atom is 1.25 in this solution, compared to 3 for the H_3PO_4 solution (where no chemical reaction takes place).

Gels were prepared in polypropylene bottles using two different methods based on either the H_3PO_4 or the P_2O_5 solutions. In the H_3PO_4 method the chosen amounts of the Zr(IV) and Cu(II) solutions were mixed first. The homogenized solution was then added to a H_3PO_4 solution while stirring vigorously. This resulted in inhomogeneous gelation when roughly half the Zr(IV)–Cu(II) solution had been added. In order to facilitate homogenization, the resulting materials were dried first in a rotary evaporator (50 to 90° C) and finally in a vacuum drier (100° C). In the P_2O_5 method the Zr(IV) and Cu(II) solutions were also mixed first. The "P_2O_5" solution was slowly added to the homogeneous mixture. The result was a dark blue solution which gelled homogeneously after about 75 min. These gels were dried directly in the vacuum drier (50 to 100° C, 800 to 15 mbar). The dried gels were ball milled for approximately 5 days in polypropylene bottles using rounded zirconia cylinders (1 cm × 1 cm) as grinding media, and then as a standard procedure calcined at 500° C for 48 h. The calcined powders were further heat treated to different temperatures in the range 550 to 1600° C and the resulting materials characterized.

Thermal analyses (differential thermal analysis/thermogravimetry, DTA/TG) were carried out in dry CO_2-free air on dried gels and calcined powders using alumina crucibles and either a Mettler TA1 instrument or a Stanton Redcroft 780 Thermal Analyser.

Electron spin resonance (ESR) spectra were recorded on a Jeol JES-ME-1X instrument.

X-ray diffraction (XRD) powder data for the dried and heat-treated materials were collected as step scan (step size 0.1°, 25 sec/step) on a Philips PW 1050/25 diffractometer equipped with graphite monochromator and continuous divergence slit using Cu$K\alpha$ radiation. Low-temperature α-quartz was used as internal standard.

For electron micrographs and energy dispersive analysis of X-rays (EDAX) a Philips SEM 505 equipped with an EDAX analyser was used.

3. Results and discussion

The two routes used for the preparation of the $CuZr_2P_3O_x$ gels gave quite different results (Table I). It is known that $Zr(OPr^n)_4$ reacts quickly with both H_2O and H_3PO_4. However, because there are more than enough reactive groups present to ensure complete hydrolysation of the alkoxide ($3H_2O$ + 9OH groups to react with 8OR groups), it is not surprising that premature inhomogeneous gelation is observed when the H_3PO_4 method is used. However, the resulting dried gels are completely X-ray amorphous (see Fig. 2). The apparent density (helium-pycnometry) and specific surface area (BET) of the dried gel are $2.52\,g\,cm^{-3}$ and $256\,m^2\,g^{-1}$, respectively (Table II). Homogeneous gelation is easily achieved when the P_2O_5 method is used. However, upon drying at 100° C and 1 torr, di-phase xerogels containing crystals of $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ are obtained. This salt is the decomposition product of $Cu(NO_3)_2 \cdot 3H_2O$, after heating to 100° C under vacuum. This result indicates that some of the copper ions remain in solution when the gels are formed. In contrast to what happens when H_3PO_4 is added, the gelation process in the P_2O_5 method is controlled by the slow and incomplete hydrolysation of the OR groups on the phosphorus atoms. The number of OH groups formed will therefore be smaller than when the H_3PO_4 method is used. It is concluded that the ion-exchange capacity of the gel produced by the P_2O_5-method is insufficient to form bonds to all the copper ions. The remaining Cu^{2+} ions precipitate more or less homogeneously during drying in the nanometre-sized pores of the gel.

The inhomogeneous nature of the P_2O_5-derived gels persists to temperatures above 1000° C. Thus, the XRD spectra show that crystalline CuO is present after calcination to 450° C for 48 h, and after heating to 750° C for 1 h, the rhombohedral phase discussed below is found together with CuO. In materials heated to 1000° C for 5 h, cubic ZrP_2O_7 and an unidentified phase occur together with $CuZr_2P_3O_{12}$. It should be noted that no CuO could be detected by X-ray diffraction after this treatment.

TABLE I Compositions and preparation route of the gels obtained

Gel no.	Oxide composition (mol %)			Preparation of gels		Crystalline phases in gels dried at 100° C
	Cu_2O	ZrO_2	P_2O_5	Route	Gelation	
CZP-84-5	13.49	46.34	40.18	H_3PO_4	Inhomogeneous	None
CZP-87-1	13.48	46.42	40.11	H_3PO_4	Inhomogeneous	None
CZP-86-2	13.54	46.31	40.15	P_2O_5	Homogeneous	$Cu(NO_3)_2 \cdot 3Cu(OH)_2$
CZP-86-3	13.49	46.41	40.10	P_2O_5	Homogeneous	$Cu(NO_3)_2 \cdot 3Cu(OH)_2$

TABLE II Properties and ESR parameters for CZP-87-1 heat treated at different temperatures compared with literature values

Heat treatment		Apparent density (g cm^{-3})	Theoretical density of main phase (g cm^{-3})	Specific surface (m^2 g^{-1})	ESR Parameters			Crystalline phases	Reference
(° C)	(h)				$g_{\parallel}$	$g_{\perp}$	$g^{*\dagger}$		
100	–	2.52	–	256	–	–	–	None	
500	48	3.21	–	91	–	–	–	None	
650‡	16	3.55	3.36	17	2.31	2.16	2.21	R$\bar{3}$c phase	
750‡	16	3.33	3.31	8	2.36	2.10	2.19	$Cu_{1+x}Zr_4P_6O_{24}$¶ ‖	
850‡	16	3.33	3.30	8	2.35	2.10	2.19	$Cu_{1+x}Zr_4P_6O_{24}$‖	
1200††	16	3.41	3.48	–		traces§		$CuZr_2P_3O_{12}$	
					2.37	2.08	2.18	$CuZr_4P_6O_{24}$	[16]
					2.32	2.07	2.16	$CuTi_4P_6O_{12}$	[15]

† Note $g^* = [(g_{\parallel}^2 + 2g_{\perp}^2)/3]^{1/2}$

‡ After calcination to 500° C for 48 h.

§ Close to detection limit for Cu^{2+}.

¶ Also small amounts of the R$\bar{3}$c phase.

‖ Also small amounts of an unidentified phase.

†† Sintered pellet.

From thermogravimetric analysis (TGA) of a dried gel it is concluded that the evolution of oxygen associated with the reduction of Cu^{2+} to Cu^+ occurs in the temperature range from 770 to 1000° C.

The behaviour as a function of thermal treatment has been studied in more detail for the $CuZr_2P_3O_x$ gels prepared by the H_3PO_4 method. The DTA and TG curves for the dried gel are shown in Fig. 1. The sharp exotherm peak at approximately 110° C reflects the decomposition of the nitrate groups, and the broad exotherm maximum in the interval 200 to 300° C corresponds to the decomposition of the major part of the residual organic groups in the gel. At 500° C the major part of the weight loss has occurred and the gel has been converted into an oxide glass. The small exotherm peak between 650 and 700° C reflects the crystallization of the amorphous phase when heated at 2° C min^{-1}. Constant weight is first obtained at temperatures in excess of 875° C (Fig. 1). The DTA/TG response upon crystallization can be seen more clearly in the thermal analyses of powder previously heat treated to 550° C (see Fig. 3).

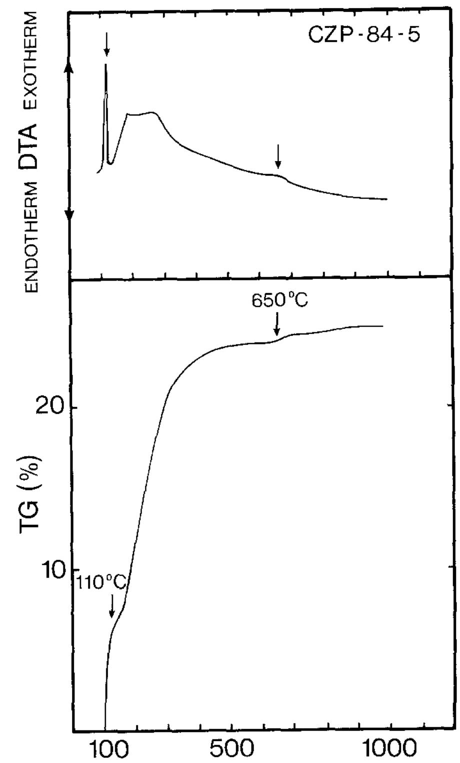

Figure 1 Thermal analysis of the gel CZP-84-5 dried at 100° C. Heating rate 2° C min^{-1}.

The XRD spectra of CZP-87-1 treated first at 500° C for 48 h and then heated to different temperatures in air for 16 h are shown in Fig. 2. The samples were not quenched, but were allowed to cool to room temperature over a period of 8 to 10 h. No special precautions were taken to avoid reoxidation of Cu^+ formed at high temperatures. Under these

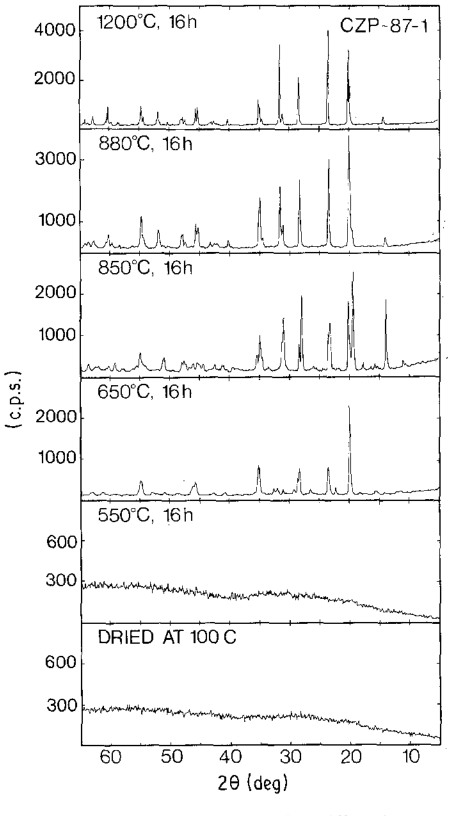

Figure 2 Room-temperature XRD powder diffraction patterns of CZP-87-1 as a function of heat treatment. Except for the gel dried at 100° C, all samples where first calcined to 500° C for 48 h. The spectra of the samples heated to 100 and 550° C were recorded with a continuous divergence slit, whereas the spectra of the samples heated to 650, 850, 880 and 1200° C were recorded with fixed slit.

TABLE III Unit cell dimensions (confidence interval 2σ) for copper-containing Nasicon compounds

Composition	Calcination (°C, h)	Unit cell dimensions (nm) *a*	*b*	*c*	*β*	Vol. (nm^3)	Space Group	Reference
CZP-87-1†	650, 16	$1.762_{2\pm5}$		$4.39_{9\pm1}$		11.830	R$\bar{3}$c	
	750, 16	$1.51_{2\pm1}$	$0.878_{3\pm1}$	$1.78_{9\pm2}$	$12.26_{4\pm5}$	2.000	C2/c	
	850, 16	$1.518_{2\pm7}$	$0.878_{9\pm3}$	$1.79_{0\pm1}$	$12.28_{2\pm2}$	2.007	C2/c	
	1200, 16*	$0.889_{2\pm2}$		$2.21_{7\pm1}$		1.518	R$\bar{3}$c	
$CuZr_2P_3O_{12}$		0.887		2.219		1.512	R$\bar{3}$c	[20]
$HCuZr_4P_6O_{24}$		$1.53_{8\pm4}$	$0.88_{4\pm2}$	$0.90_{6\pm2}$	$12.31_{8\pm2}$		C2/c or Cc	[19]
$CuZr_4P_6O_{24}$		$1.52_{1\pm4}$	$0.88_{4\pm2}$	$1.82_{9\pm5}$	$12.39_{0\pm2}$		C2/c or Cc	[16]

*Sintered pellet.
†See Table I.

conditions crystallization begins somewhere in the interval 550 to 650° C (Fig. 2). Depending on the heat treatment, three different Nasicon-type phases are observed in the crystallized samples.

For samples heated to temperatures above 880°C the main phase is $CuZr_2P_3O_{12}$ (Fig. 2). The pure phase is obtained after sintering to 1200° C for 5 h or more (Fig. 2). The unit cell dimensions found (Table III) correspond closely to the data reported by Yao and Fray [20]. The ESR spectrum of this sample shows only minute traces of Cu^{2+}, which probably results from a slight surface oxidation during cooling. (Thermal analysis of a powder heated to 880° C showed no significant weight loss, i.e. no oxygen evolution.)

The main phase detected in samples heat treated to between 750 and 850° C is Nasicon-like with a composition close to $CuZr_4P_6O_{24}$ (Tables III and IV). Surprisingly no crystalline CuO could be detected, and the XRD spectra give no evidence for the presence of any substantial amount of a glassy phase in these samples (Fig. 2). Thermal analysis of the 850° C sample shows an endothermic reaction associated with a weight loss of 1.21 wt % between 500 and 700° C, and no further weight change in the range up to 1200° C (Fig. 3). This is a little less than the calculated 1.48 wt % assuming that the reaction corresponds to the evolution of oxygen associated with a complete reduction of Cu^{2+} to Cu^+. Thus, the indication is that the $CuZr_2P_3O_{12}$ was originally formed at 850° C. During cooling this phase was subsequently oxidized to $CuZr_4P_6O_{24}$ or perhaps $Cu_{1+x}Zr_4P_6O_{24}$. Some weak lines from an unidentified crystalline phase also appear in the XRD spectrum as discussed below. The

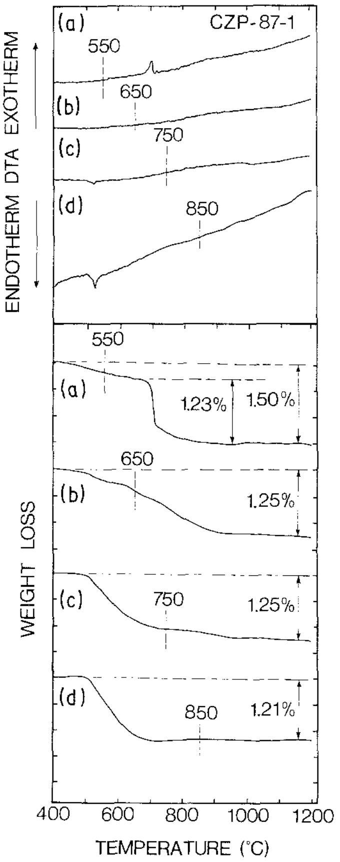

Figure 3 Thermal analysis of CZP-87-1 calcined to different temperatures. The dried gel powder was first heated for 48 h to 500° C and then for 16 h to: (a) 550° C, (b) 650° C, (c) 750° C and (d) 850° C. During thermal analysis, the samples were heated to 400° C until constant weight was obtained (in order to remove absorbed water). Afterwards they were heated in the 400 to 1200° C range at a heating rate of 2° C min^{-1}.

TABLE IV Powder X-ray diffraction data of the monoclinic phase obtained after heating to 850° C

d_{obs}(nm)	d_{calc}(nm)	*hkl*	I/I_0(%)
0.64	0.64	20 0	71
0.456	0.456	11 2	100
0.438	0.438	31 −2	70
0.384	0.383	31 0	49
0.319	0.319	40 0	78
0.313	0.314 0.313	11 −5 22 −4	26
0.289	0.289	31 2	54
0.267	0.267	20 4	6
0.257	0.257	13 2	36
0.252	0.253 0.252	60 −4 11 5	15
0.232	0.232	51 −7	19
0.219	0.219	62 −4	22
0.2167	0.2168 0.2163	42 2 22 −7	8
0.2037	0.2038	51 2	8
0.1965	0.1964	40 4	9
0.1918	0.1917	24 2	11
0.1907	0.1907	11 7	33
0.1892	0.1893	71 −1	11
0.1788	0.1795	33 4	15
0.1759	0.1760	24 −6	16
0.1692	0.1692	82 −3	30
0.1656	0.1656	91 −6	73
0.1595	0.1596 0.1595	40 6 80 0	24
0.1558	0.1560 0.1558	91 −9 15 −5	39
0.1497	0.1496	55 −5	30
0.1484	0.1484	53 4	29
0.1463	0.1463	55 −6	40

TABLE V Powder X-ray diffraction data of rhombohedral low-temperature phase. Indexed with hexagonal parameters

d_{obs}(nm)	d_{calc}(nm)	$h\,k$	l	I/I_0(%)
0.77	0.76	0 1	5	2
0.76	0.76	0 2	1	3
0.73	0.73	0 0	6	2
	0.72	0 2	2	
0.621	0.627	0 2	4	3
0.562	0.571	1 2	1	4
	0.564	1 1	6	
	0.558	1 2	2	
0.480	0.481	0 3	3	3
0.442	0.441	2 2	0	100
0.396	0.395	1 3	4	11
0.377	0.378	2 2	6	36
	0.376	0 4	2	
0.313	0.313	0 4	8	44
0.311	0.309	0 2	13	25
0.304	0.304	0 5	1	8
	0.303	1 4	6	
0.297	0.297	0 3	12	2
0.293	0.294	3 3	0	12
0.288	0.288	2 4	1	10
0.282	0.282	2 2	12	3
0.279	0.279	2 4	4	11
0.275	0.275	1 4	9	14
	0.275	0 5	7	
0.256	0.255	2 4	8	52
0.241	0.241	3 4	5	3
	0.241	2 4	10	
	0.241	2 5	3	
0.221	0.222	0 2	19	8
	0.221	1 3	17	
0.2151	0.2149	1 2	19	3
0.2032	0.2033	2 5	12	3
	0.2031	1 3	9	
0.1969	0.1970	1 4	18	23
0.1877	0.1877	2 5	15	6
0.1859	0.1860	3 6	6	5
	0.1858	2 7	2	
0.1841	0.1841	4 5	8	2
0.1794	0.1794	2 6	13	10
	0.1791	3 5	14	
0.1743	0.1743	1 3	23	4
0.1724	0.1724	0 3	24	9
0.1707	0.1708	3 5	16	3
	0.1708	0 7	16	
	0.1703	3 6	12	
0.1695	0.1696	0 9	0	4
0.1675	0.1677	2 6	16	46
0.1605	0.1606	1 4	24	4
	0.1604	4 6	11	
0.1570	0.1571	1 3	26	5
	0.1569	1 5	23	
0.1558	0.1559	4 5	17	6
	0.1558	1 7	18	
0.1521	0.1521	3 4	23	4
0.1510	0.1510	0 1	29	10
0.1477	0.1478	1 6	23	11
	0.1477	4 6	16	
0.1471	0.1471	0 10	8	10

sample heated to 750° C shows a similar behaviour, except for a second small weight loss observed between 750 and 950° C (Fig. 3). This behaviour shows that two categories of Cu^{2+} must be present. The indication is that the sample still contains some of the low-temperature rhombohedral phase discussed below, and this is confirmed by the X-ray data.

Unit cell dimensions calculated for the $CuZr_4P_6O_{24}$ phase assuming space group C2/c (Table III) are slightly smaller than the unit cell dimensions reported by Jazouli *et al.* [16]. When comparing the data, the possibility of a partial protonization of the samples examined by Jazouli *et al.* [16] should be borne in mind. The spectra contain some weak lines (0.801, 0.562, 0.535, 0.499, 0.403, 0.269 and 0.194 nm with I/I_{100} 4, 5, 4, 7, 3, 6 and 6, respectively, in the spectrum of the sample heated to 850° C) which could not be assigned to the $CuZr_4P_6O_{24}$ phase even assuming a primitive monoclinic cell. These lines were assumed to be associated with a second unidentified phase formed as an oxidation product during cooling.

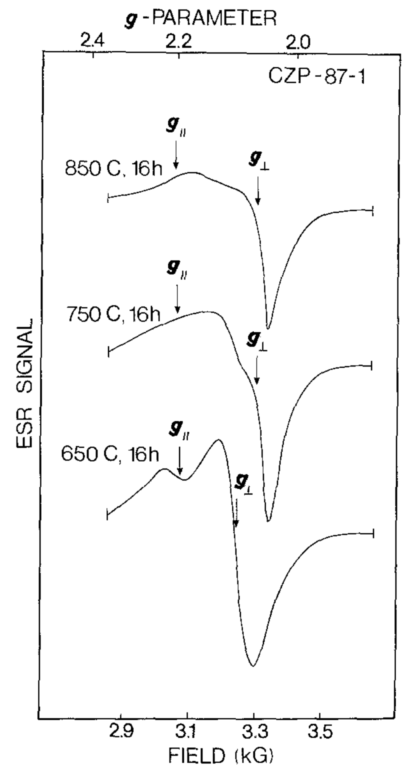

Figure 4 ESR spectra recorded at room temperature of CZP-87-1 calcined to 500° C for 48 h and then heated to 650, 750 and 850° C for 16 h, respectively. Microwave frequency 9.42 GHz.

The ESR spectra of these samples also show a variation with temperature (Fig. 4, Table III), but the spectrum of the sample heated to 850° C is essentially similar to the spectrum reported by Jazouli *et al.* [16] for $CuZr_4P_6O_{24}$. The differences can be explained by assuming that the spectrum of the sample heated to 750° C is a combination of the spectrum of $CuZr_4P_6O_{24}$ and the spectrum of the rhombohedral phase.

Samples which had been heated to 650° and 700° C show the presence of the light green rhombohedral $R\bar{3}c$ phase (Fig. 2, Tables III and IV). No other crystalline phases have been detected, and there is no evidence for the presence of substantial amounts of a glass phase. The dimensions of the hexagonal unit cell of the rhombohedral phase are $a = 1.7622 \pm 0.0005$ nm, $c = 4.399 \pm 0.001$ nm. This indicates a similarity to the rhombohedral high-temperature form of $CuZr_4P_6O_{24}$ reported to be stable above 520° C by Jazouli *et al.* [16]. At 800° C the hexagonal unit cell for this phase is very similar except for the doubling of the axes ($a = 0.884 \pm 0.004$ nm, $c = 2.277 \pm 0.005$ nm).

Thermal analysis of the 650° C sample shows a gradual weight loss of 1.25 wt % between 500 and

900° C, and then no further weight change up to 1200° C (Fig. 3). Roughly half the weight loss occurs at temperatures below 650° C and must thus be related to reduction of Cu^{2+} formed during the prior cooling to room temperature. The weight loss above 650° C indicates the presence of Cu^{2+} in a crystal position where it is more difficult to reduce than is normally the case in $CuZr_4P_6O_{24}$ (cf. 850° C sample, Fig. 3). Thus, the indication is that the rhombohedral low-temperature phase might have a Nasicon-like structure showing mixing of Cu^{2+} and Zr^{4+} in the normal copper and zirconium positions. Some support for this view can be drawn from the single crystals of $NaCu_2ZrP_3O_{12}$ reported by Byrappa *et al.* [13] and the XRD-data for $Zr_3P_4O_{16}$ [22]. The general shape of the ESR spectrum for the sample heated to 650° C (Fig. 4, Table III) is more closely related to the spectrum reported for $CuTi_4P_6O_{24}$ [15] than to the spectrum for $CuZr_4P_6O_{24}$ [16].

The pellets of powder containing $CuZr_4P_6O_{24}$ were readily converted to a light green essentially mono-phase $CuZr_2P_3O_{12}$ material when heated to 1200° C, no other phases could be detected, either by XRD or by SEM. In contrast, amorphous powders and powders containing the rhombohedral low-temperature phase gave rise to a very dark green multiphase material containing both CuO and $CuZr_2P_3O_{12}$ when heated to 1200° C for 5 h or more. This behaviour is probably related to the increased temperature needed for the complete reduction of Cu^{2+} to Cu^{+} in these powders (Fig. 3).

4. Conclusions

The phase formation in alkoxide-derived gels with composition corresponding to $CuZr_2P_3O_{12}$ (in the final material) depend critically on the homogeneity of the gel and on details in the heat treatment employed.

The P_2O_5 method results in the formation of di-phase gels. Heat treatment of these invariably results in multi-phase materials. The crystalline phases observed are $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ (110° C), CuO (450° C), CuO + R$\bar{3}$c $CuZr_4P_6O_{24}$ (750° C, 1 h) and finally ZrP_2O_7 + C2/c $CuZr_2P_3O_{12}$ + X-phase (1000° C, 5 h).

Gels prepared by the H_3PO_4 method are completely amorphous and can be converted into porous glasses by heating to 500° C. Calcination in the range 650 to 750° C results in the formation of a new R$\bar{3}$c $CuZr_4P_6O_{24}$ phase (Table III). Later, this prevents formation of mono-phase materials during heating to 1200° C. It is suggested that this behaviour is related to mixing of Cu^{2+} and Zr^{4+} in the normal copper and zirconium positions in the low-temperature R$\bar{3}$c Cu^{2+}-Nasicon. This leads to inhomogeneity because of a two-step reduction of Cu^{2+} to Cu^{+} upon further heating. Calcination in the range 750 to 850° C results in the formation of the normal C2/c $CuZr_4P_6O_{24}$ (Table III) which readily converts to mono-phase $CuZr_2P_3O_{12}$ (Table III) above 880° C. Only gels calcined in the range 750 to 850° C are useful for the fabrication of mono-phase $CuZr_2P_3O_{12}$ ceramics.

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