

# The phase coexistence in the system $\text{CaO}-\text{ZrO}_2-\text{V}_2\text{O}_5$

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The phase coexistence in the subsolidus region of the system was determined by the powder diffraction. The only ternary compound present is  $\text{CaZr}(\text{VO}_4)_2$  for which its indexed powder diffraction pattern is given.

С помощью рентгеновского фазового анализа было определено существование фаз в субсолидусной области системы. Единственной тернарной фазой в этой системе является  $\text{CaZr}(\text{VO}_4)_2$ , для которой приводится порошковая дифрактограмма.

The ternary system  $\text{CaO}-\text{ZrO}_2-\text{V}_2\text{O}_5$  has not yet been studied as a whole. Only its binary subsystems  $\text{CaO}-\text{ZrO}_2$  [1],  $\text{ZrO}_2-\text{V}_2\text{O}_5$  [2], and  $\text{CaO}-\text{V}_2\text{O}_5$  [3, 4] are known. In the system  $\text{CaO}-\text{ZrO}_2$  five phases are present at subsolidus temperatures ( $\text{CaO}$ ,  $\text{CaZrO}_3$ ,  $\text{ZrO}_2$  phase of the fluorite type stabilized by  $\text{CaO}$ ,  $\text{ZrO}_2$ -monoclinic phase,  $\text{ZrO}_2$ -tetragonal phase). In the system  $\text{ZrO}_2-\text{V}_2\text{O}_5$  the only present compound is  $\text{ZrV}_2\text{O}_7$  which melts incongruently at  $750^\circ\text{C}$  [2]. In the system  $\text{CaO}-\text{V}_2\text{O}_5$  three intermediate compounds are present,  $\text{Ca}_3(\text{VO}_4)_2$ ,  $\text{Ca}_2\text{V}_2\text{O}_7$ , and  $\text{Ca}(\text{VO}_3)_2$ , melting incongruently at 1380, 1015, and  $778^\circ\text{C}$ , respectively [3].

Recently the crystal structure of the ternary compound  $\text{CaZr}(\text{VO}_4)_2$  was determined [5] but no details about the preparation of its single crystals were given. This compound was identified independently also by present authors.

This study was promoted by some questions concerning the corrosive influence of  $\text{V}_2\text{O}_5$  on the  $\text{CaO}$ -stabilized zirconia ceramics, which is used for galvanic cells for measurements of partial pressure of oxygen.

## Experimental

The samples for investigation were prepared by heating the mixtures of  $\text{CaCO}_3$  (reagent grade),  $\text{ZrO}_2$  (chem. grade), and  $\text{V}_2\text{O}_5$  (chem. grade) in the air at temperatures specified in Table 1.

The powder diffraction patterns used for the identification of phases were taken on 1540 Philips diffractometer ( $\text{CuK}\alpha$  radiation). Lattice parameters of  $\text{CaZr}(\text{VO}_4)_2$  were measured on its single crystals using Weissenberg and precession techniques and refined by the method of least squares from powder data [6]. The density of crystals was measured by flotation method.

## Results and discussion

The results of phase analysis are generalized in the form of a diagram showing the phase coexistence in the system. This diagram is shown in Fig. 1. The compositions of samples, their thermal treatment, and phases identified are listed in Table 1. Virtually all samples preserved simple molar ratios of their oxide components. Their compositions is thus expressed by abbreviated symbols C, Z, V (Table 1) representing  $\text{CaO}$ ,  $\text{ZrO}_2$ , and  $\text{V}_2\text{O}_5$ , respectively.

The composition of the sample listed in Table 1 under the No. 2 was considered as a mixture of  $\text{ZrO}_2$  stabilized by 15 mole % of  $\text{CaO}$  and  $\text{Ca}_3(\text{VO}_4)_2$  in the weight ratio 2 : 1.

The samples were heated at several temperature levels. The temperatures listed in Table 1 were found sufficient for the accomplishment of corresponding chemical reactions (the sample No. 9 is discussed separately).

The concentrations were selected such as to keep the samples in two phase regions what facilitated the identification.

Among the phases described by other investigators to be present in the system only the powder data for the compound  $\text{Ca}_2\text{V}_2\text{O}_7$  are missing in the literature. The presence of this phase was determined according to the powder pattern of a sample of corresponding composition heated at  $800^\circ\text{C}$  for 5 hrs [7]. The compound  $\text{Ca}(\text{VO}_3)_2$  was identified according to its powder pattern listed in [8]. The other compounds were identified by their powder data published elsewhere [9].

The phase analysis made it possible to determine the composition of the only ternary phase in the system as  $\text{CaZr}(\text{VO}_4)_2$  in spite of the fact that in the sample of this composition a small amount of monoclinic  $\text{ZrO}_2$  (up to 5%) was found. This accompanying phase manifested by two strongest diffractions (the rest of them was

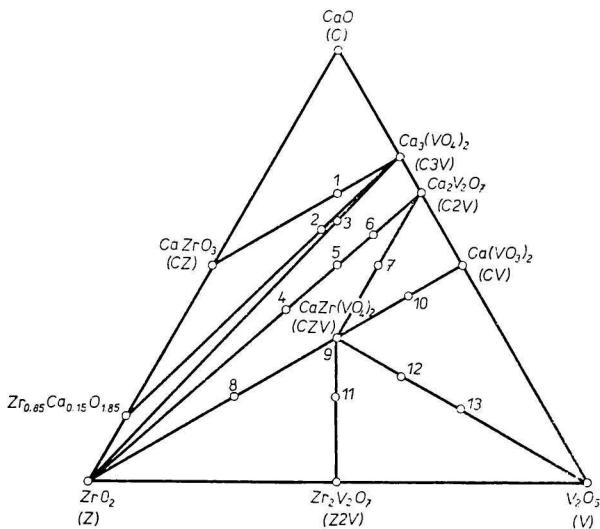


Fig. 1. The phase coexistence diagram for the system  $\text{CaO}-\text{ZrO}_2-\text{V}_2\text{O}_5$ .

Table 1

Results of the phase analysis in the system  $\text{CaO}-\text{ZrO}_2-\text{V}_2\text{O}_5$ 

Sample	Composition (molar ratio of oxides)*	Thermal treatment °C/hr	Identified phases
1	C4ZV	1050/2	CZ, C3V
2	C3.05Z1.28V	1200/3	Z (c), C3V
3	C3ZV	1050/2	Z (m), C3V
4	C2Z2V	700/16	Z (m), C2V
5	C2ZV	1000/1	Z (m), C2V
6	C4ZV2	900/1	Z (m), C2V
7	C3ZV2	900/1	CZV, C2V
8	CZ3V	850/5	CZV, Z (m)
9	CZV	850/5	CZV, Z (m)**
10	C3ZV3	750/2	CZV, CV
11	CZ2V2	650/20	CZV, ZV
12	CZV2	600/4	CZV, V
13	CZV4	600/4	V, CZV

\* C = CaO, Z =  $\text{ZrO}_2$ , V =  $\text{V}_2\text{O}_5$ ; C4ZV =  $4\text{CaO} \cdot \text{ZrO}_2 \cdot \text{V}_2\text{O}_5$ .\*\* The monoclinic  $\text{ZrO}_2$  in the amount up to 5%.m — monoclinic  $\text{ZrO}_2$ , c— cubic  $\text{ZrO}_2$ .

Table 2

The list of diffraction lines of  $\text{CaZr}(\text{VO}_4)_2$ 

<i>hkl</i>	$d_{\text{obs}}$	$d_{\text{calc}}$	$I/I_0$	$I_{\text{calc}}$
101	4.6586	4.6583	2	3
200	3.4933	3.4936	100	100
112	2.6408	2.6410	50	55
220	2.4688	2.4703	10	12
202	2.3280	2.3291	6	8
301	2.1822	2.1826	6	8
103	1.9961	1.9965	4	5
321	1.8511	1.8510	4	4
312	1.8033	1.8041	35	50
400	1.7461	1.7468	13	14
004 } 420 }	1.5619	1.5624	10	2 8
332	1.4566	1.4569	8	14
204	1.4260	1.4263	7	8
224	1.3207	1.3205	4	7
512	1.2550	1.2549	4	6
440	1.2353	1.2352	1	2
404 } 600 }	1.1648	1.1646 1.1645	3	3 3
532	1.1186	1.1189	2	5
424 } 620 }	1.1049	1.1048 1.1048	4	5 3

under detection limit) was present also after prolonged heating and pressing the sample into pellets after rehomogenization. An increase of temperature above 900°C resulted in the formation of melt.

Single crystals of the ternary compound were obtained by a slow cooling of the melt of the composition  $3\text{CaO} \cdot \text{ZrO}_2 \cdot 5\text{V}_2\text{O}_5$ . The corresponding sample lies in the three phase region including  $\text{CaZr}(\text{VO}_4)_2$ ,  $\text{Ca}(\text{VO}_3)_2$ , and  $\text{V}_2\text{O}_5$ . The crystals were of a gray colour and of an isometric cube-like shape up to the magnitude of 0.2–0.4 mm. The colour of accompanying crystals varied from orange-brown to black.

The powder diffraction pattern of  $\text{CaZr}(\text{VO}_4)_2$  taken from the sample No. 9 (Table 1) is shown in Table 2. The scanning rate was  $1/4^\circ 2\theta/\text{min}$ . In the last column of Table 2 the intensities of  $hkl$  diffractions are listed, calculated on the basis of the known crystal structure of  $\text{CaZr}(\text{VO}_4)_2$  [5]. The procedure of such calculation was described in [10].

The lattice parameters of  $\text{CaZr}(\text{VO}_4)_2$  refined from powder data are shown in Table 3 and compared with the parameters of  $\text{CaZr}(\text{VO}_4)_2$  described in [5].

Table 3  
Crystallographic data for  $\text{CaZr}(\text{VO}_4)_2$

Tetragonal symmetry $I4_1/amd$ $Z = 2$	
This work	Ref. [5]
$a = 6.9872(7) \text{ \AA}$	$a = 6.992(3) \text{ \AA}$
$c = 6.2499(11) \text{ \AA}$	$= 6.255(3) \text{ \AA}$
$D_x = 3.93 \text{ g cm}^{-3}$	
$D_m = 3.96 \text{ g cm}^{-3}$	$D_m = 3.81 \text{ g cm}^{-3}$
$V = 305.1 \text{ \AA}^3$	

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