

Solid-State Reactions and Dielectric Properties in the Systems Magnesia-Zirconia-Titania and Lime-Zirconia-Titania¹

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A study of solid-state reactions and dielectric properties was made for the ternary systems $\text{MgO-ZrO}_2\text{-TiO}_2$ and $\text{CaO-ZrO}_2\text{-TiO}_2$. The compatibility relations were determined for each, and an estimate of the extent of the solid-solution areas was obtained. One ternary compound having the formula $\text{CaO-ZrO}_2\cdot 2\text{TiO}_2$ was discovered. An X-ray diffraction powder pattern of this compound is included.

Ceramic dielectric-test pieces were prepared from compositions within these systems. Data are given for the values of K and Q at 50 kilocycles per second, and at 1 and 20 megacycles per second. The variations of these values with changes in temperature were observed at a frequency of 1 megacycle per second.

1. Introduction

This is the fourth paper on a program of study of solid-state reactions occurring in various ceramic-oxide systems, and of the properties of dielectrics obtainable from those systems. It covers the systems $\text{MgO-ZrO}_2\text{-TiO}_2$ and $\text{CaO-ZrO}_2\text{-TiO}_2$. Portions of the binary boundary-systems have been studied previously by other investigators. The MgO-TiO_2 dielectrics have been described by Rieke and Ungewiss [1]² and by Shelton, et al.[2]. The properties of CaO-TiO_2 dielectrics have been determined by Bunting, et al. [3], and a limited amount of data on the $\text{ZrO}_2\text{-TiO}_2$ and MgO-ZrO_2 dielectrics have been obtained by Shelton [4]. The MgO-ZrO_2 bodies were found to have a dielectric constant (K) of less than 20 and a positive temperature coefficient of K . The $\text{ZrO}_2\text{-TiO}_2$ specimens have K values of less than 100 and have a negative temperature coefficient. Rieke and Ungewiss [1] have reported on the ceramic and dielectric properties of specimens in the $\text{MgO-ZrO}_2\text{-TiO}_2$ system, but no literature references were found pertaining to the ternary system $\text{CaO-ZrO}_2\text{-TiO}_2$.

2. Materials and Methods

2.1. Materials

The following substances were used as sources of the component oxides in the study of solid-state reactions:

MgO—Water-clear crystals of periclase of over 99-percent purity, ground to pass a 325-mesh sieve, using a mullite mortar and pestle.

CaO—Reagent grade calcium carbonate of nominal 99.5-percent purity.

TiO₂—A highly purified grade of rutile of over 99.9-percent purity.

ZrO₂—Dense zirconia of over 99-percent purity, calcined at 1,450° C, ground in a steel-ball mill, acid-treated, washed, and dried.

The substances used in the fabrication of the dielectric-test compositions were the following:

MgO—The same as used in the study of solid-state reactions.

TiO₂—The same grade as used for solid-state reactions was used in the $\text{MgO-ZrO}_2\text{-TiO}_2$ system.

TiO₂—A less highly purified grade of rutile, designated TMO, was used in the $\text{CaO-ZrO}_2\text{-TiO}_2$ system. This material had a purity of 98.7 percent, the principal impurities being SiO_2 and Al_2O_3 .

CaO:TiO₂—A commercial grade of perovskite. This material had a purity of 96.5-percent, the principal impurities being MgO , SiO_2 , and Al_2O_3 .

CaO:ZrO₂—A commercial grade of calcium zirconate. This material was about 96-percent pure, and the principal impurities were SiO_2 , Al_2O_3 , and HfO_2 .

ZrO₂—The same as used in the study of solid-state reactions.

2.2. Sample Preparation

Compositions are designated on a mole-ratio basis. No corrections were made for the percentage of purity of the raw materials.

The raw materials in sufficient amounts to yield 10-g samples were weighed to the nearest milligram, and thoroughly mixed in the dry state. The compositions were then mixed with about 5 weight percent of a 5 weight percent starch-solution binder, and 1-in.-diameter disks were formed at a pressure of 5,000 lb/in². The pressed disks, resting on platinum foil, were calcined for 4 hr at 1,000° to 1,200° C in an oxidizing atmosphere. After the calcined disks were pulverized, using a mullite mortar and pestle, the samples were ready to be used either for the solid-state studies or for forming dielectric-test specimens, depending upon the raw materials chosen.

2.3. Study of Solid-State Reactions

In the study of solid-state reactions, two methods of heat treatment were used. In many cases, a conventional platinum-wound quench furnace was used. The temperature in the furnace was measured with a Pt versus Pt-10-percent-Rh thermocouple and was

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² Figures in brackets indicate the literature references at the end of this paper.

controlled by a modified Roberts-type controller. The quenching technique was used in order that high-temperature solid solutions could be observed. For quench tests a small amount of the prepared sample was placed in a platinum envelope, which was then suspended in the furnace. The test temperature ranged from 1,200° to 1,550° C and was maintained constant for a given length of time. Equilibrium conditions were usually reached in less than 3 hr. After this reaction time, the sample was quenched, usually in air. In some cases, water or carbon tetrachloride was used as the quenching medium.

Alternatively, samples were heated to temperatures as high as 1,750° C, in an oxide-resistor furnace [5], and were cooled relatively slowly. The quenched or slowly cooled specimens were then analyzed by X-ray diffraction and petrographic methods.

These procedures and methods of sample selection are, in general, similar to those discussed by Foster [6a]. In the interpretation and plotting of the results, the discussions of Foster [6a] and Barrett [6b] were applied.

2.4. Preparation of Dielectric-Test Specimens

The calcined mixtures were moistened with about 5 weight percent of starch-solution binder, and disks about $\frac{1}{8}$ in. thick and $\frac{1}{2}$ to $1\frac{1}{2}$ in. in diameter were formed at a pressure of 10,000 to 15,000 lb/in². The pressed disks were fired for $\frac{1}{2}$ to 1 hr on platinum foil in an oxidizing atmosphere, and were cooled relatively slowly. Maturing temperatures varied from 1,400° to 1,650° C, depending upon the composition and the raw materials. For maturing temperatures up to 1,550° C, a platinum-wound resistance furnace was used. Temperatures were measured with a Pt versus Pt-10-percent-Rh thermocouple and were controlled by an automatic commercial instrument. For maturing temperatures higher than 1,550° C, an oxide-resistor furnace [5] was used. This furnace was manually controlled, and temperatures were measured with a calibrated optical pyrometer.

A specimen was considered to be properly matured when its equivalent water absorption was 0.1 percent or less of the dry weight. The absorption was determined by placing the weighed sample in carbon tetrachloride. The liquid was boiled for 5 hr and allowed to cool; the specimen was removed from the liquid, quickly surface-dried, and weighed in a stoppered bottle. From the gain in weight, the equivalent water absorption was calculated.

Some compositions could not be properly matured, in which case, dielectric tests were performed on test pieces having the lowest obtainable absorption value.

2.5. Determination of Dielectric Properties

The test specimens were coated on each side with a silver paste and fired to 750° C to give silver elec-

trodes about 3 to 5 mils thick. The specimens were then cooled overnight. Preliminary determinations were made at a temperature of $25^\circ \pm 0.5^\circ$ C, and at a controlled relative humidity of 40 percent or less.

At frequencies between 50 kc and 20 Mc and at temperatures between 25° and 250° C, the dielectric constant (K) and the Q -value (when greater than 10, the Q -value is very nearly equal to the reciprocal of the power factor) were determined by measurements on a Q -meter.

For measurements at temperatures greater than 25° C, the specimens were placed on an electric hotplate covered by a muffle and were connected to the Q -meter by 10-in. leads. The temperature was controlled by means of a variable autotransformer and was measured by means of a thermocouple inserted into a silvered ceramic disk adjacent to the specimen. Correction factors for the capacitance and inductance of the lead wires were applied.

For measurements in the temperature range between -50° and 0° C, the specimens were placed in an insulated chamber cooled by dry ice. The temperature was controlled by a thermostat and was measured by means of a liquid-in-glass thermometer. The measurements were made at a frequency of 1 Mc and were obtained by using a type 820A twin-T impedance circuit combined with a model HRO-50T radio receiver. Corrections were applied for the capacitance and inductance of the lead wires.

3. Results of Solid-State Reaction Studies

3.1. The MgO-ZrO₂-TiO₂ System

The four binary compounds occurring in the boundary systems are 2MgO·TiO₂, MgO·TiO₂, MgO·2TiO₂ [7], and ZrO₂·TiO₂ [8]. There are no binary compounds in the MgO-ZrO₂ system [9]. For the study of the ternary fields, 31 selected compositions were subjected to suitable heat treatment and, after quenching or cooling, were analyzed by X-ray and petrographic methods. The data resulting from these tests are listed in table 3. The compatibility relations derived from these data, together with the location of the compositions, are indicated in figure 1. No ternary compounds were observed, and the binary joins established for the subsolidus equilibrium relations are MT₂-ZT,³ MT₂-ZrO₂, MT-ZrO₂, and M₂T-ZrO₂. The estimated solid-solution areas are indicated in figure 2. No attempt was made to locate the solid-solution limits with a high degree of accuracy. The heat treatment of samples was not uniform from one part of the system to another; therefore, figure 2 is not to be considered an isothermal section of the diagram. The figure does, however, indicate the general trends of solid-solution formation within the system at temperatures below the solidus.

³ M = MgO, C = CaO, Z = ZrO₂, and T = TiO₂. Thus, in this shorthand notation, MT₂ = MgO·2TiO₂.

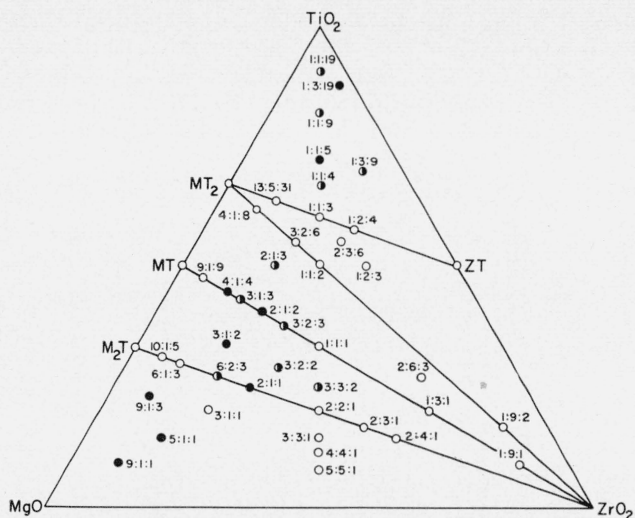


FIGURE 1. Compatibility relations in the system MgO-ZrO₂-TiO₂.

The prepared compositions are indicated and plotted according to mole ratios.
 O, Compositions used in the study of solid-state reactions;
 ●, compositions used in the study of dielectric properties;
 ○, compositions used for both studies.

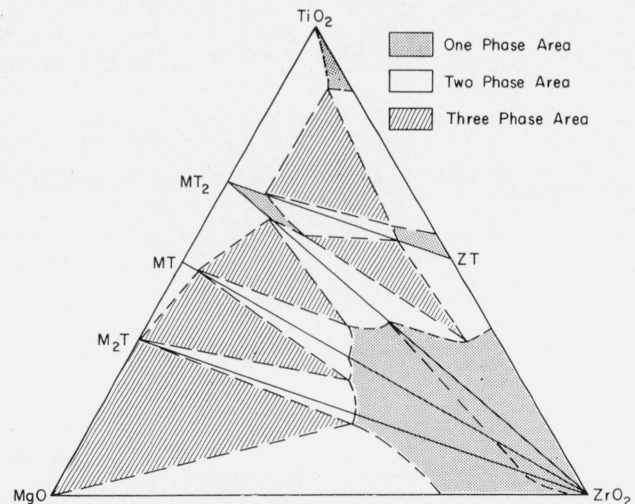


FIGURE 2. Estimated trends of solid-solution development in the system MgO-ZrO₂-TiO₂ over the temperature range 1,400° to 1,750° C.

The dashed line near the ZrO₂ apex of the figure indicates the approximate location of a two-phase area, which theoretically would separate the cubic ZrO₂ field on the left from the tetragonal ZrO₂ field on the right in a true isothermal section of the phase diagram.

In the binary system MgO-ZrO₂, single-phase cubic ZrO₂ solid solutions are obtained by quenching the specimens from a temperature in excess of 1,400° C, as indicated in table 1. Relatively slow cooling from the same temperature results in an exsolution process giving cubic ZrO₂ and some monoclinic ZrO₂, and MgO. Very slow cooling from high temperatures, or quenching from 1,200° C, results in only MgO and monoclinic ZrO₂ with no cubic ZrO₂. No quenched specimens contained both the cubic and monoclinic ZrO₂. It is assumed that the tetragonal ZrO₂ modification cannot be retained at room temperature by quenching and that all monoclinic ZrO₂ found in the

TABLE 1. Results of study of solid-state reactions in the system MgO-ZrO₂-TiO₂

Mole ratio M:Z:T	Binary join or ternary field	Heat treatment ^a		Phases identified by X-ray and/or petrographic means (all in solid-solution form, unless otherwise indicated)
		Time	Temperature	
13:5:31	MT ₂ -ZT	2	1,500	MT ₂ +ZT+trace TiO ₂ .
1:1:3	do	1	1,550	MT ₂ +ZT.
1:2:4	do	1	1,600	Do.
4:1:8	MT ₂ -ZrO ₂	2	1,500	MT ₂ +trace MT (no ZrO ₂ at all).
3:2:6	do	2	1,500	MT ₂ +monoclinic ZrO ₂ +trace ZT.
1:1:2	do	28	^b 1,500	Do.
1:1:2	do	2	1,525	MT ₂ +monoclinic ZrO ₂ .
1:9:2	do	1	1,670	monoclinic ZrO ₂ +trace MT ₂ .
9:1:9	MT-ZrO ₂	2	1,500	MT+trace monoclinic ZrO ₂ .
3:1:3	do	2	1,525	MT+monoclinic ZrO ₂ +trace MT ₂ .
3:2:3	do	1	1,610	MT+monoclinic ZrO ₂ +trace cubic ZrO ₂ .
1:1:1	do	1/2	1,625	MT+monoclinic ZrO ₂ .
1:1:1	do	72	^b 1,400	MT+cubic ZrO ₂ .
1:3:1	do	1/2	1,750	Cubic ZrO ₂ +monoclinic ZrO ₂ +trace MT.
1:9:1	do	1/2	1,700	Monoclinic ZrO ₂ +trace cubic ZrO ₂ .
10:1:5	M ₂ T-ZrO ₂	2	1,500	M ₂ T ^e +small amount cubic ZrO ₂ .
6:1:3	do	2	1,500	M ₂ T ^e +cubic ZrO ₂ .
6:2:3	do	1	1,610	Do.
2:2:1	do	1/2	1,750	M ₂ T ^e +cubic ZrO ₂ .
2:2:1	do	72	^b 1,200	M ₂ T ^e +monoclinic ZrO ₂ .
2:3:1	do	1/2	1,700	Cubic ZrO ₂ +trace M ₂ T ^e .
2:4:1	do	1/2	1,750	Cubic ZrO ₂ .
1:1:4	MT ₂ -ZT-TiO ₂	1	1,425	MT ₂ +ZT+TiO ₂ .
1:1:9	do	1	1,425	MT ₂ +TiO ₂ +trace ZT.
1:1:19	do	2	1,550	TiO ₂ +MT ₂ .
1:3:9	do	1	1,425	TiO ₂ +MT ₂ +ZT.
2:3:6	MT ₂ -ZT-ZrO ₂	2	1,500	MT ₂ +ZT.
1:2:3	do	5	1,450	MT ₂ +ZT+monoclinic ZrO ₂ .
2:1:3	MT-MT ₂ -ZrO ₂	4	1,450	MT ₂ +cubic ZrO ₂ +MT.
2:6:3	do	16	^b 1,500	Cubic ZrO ₂ +monoclinic ZrO ₂ .
3:2:2	M ₂ T-MT-ZrO ₂	1/2	1,625	M ₂ T ^e +MT+cubic and monoclinic ZrO ₂ .
3:3:2	do	1	1,610	M ₂ T ^e +cubic ZrO ₂ .
3:3:1	MgO-M ₂ T-ZrO ₂	1/2	1,650	Cubic ZrO ₂ +MgO ^e +trace M ₂ T ^e .
5:5:1	do	1/2	1,650	Cubic ZrO ₂ +MgO ^e .
1:9:0	MgO-ZrO ₂	1	1,670	Cubic ZrO ₂ +monoclinic ZrO ₂ .
1:9:0	do	72	^b 1,490	Cubic ZrO ₂ .
1:9:0	do	80	^b 1,200	Monoclinic ZrO ₂ +small amount MgO ^e .
1:4:0	do	1	1,610	Cubic ZrO ₂ +small amounts of MgO ^e and monoclinic ZrO ₂ .
1:1:0	do	1	1,610	Cubic ZrO ₂ +monoclinic ZrO ₂ +MgO ^e .
1:1:0	do	48	^b 1,515	Cubic ZrO ₂ +MgO ^e .
1:1:0	do	80	^b 1,200	Monoclinic ZrO ₂ +MgO ^e .

^a Each sample had been calcined at least once prior to the recorded heat treatment and cooled slowly, unless otherwise indicated.

^b The specimen was quenched from the temperature indicated.

^c No solid-solution formation was noted in this substance.

X-ray patterns is actually tetragonal ZrO₂ at temperatures above 1,000° C. Data were obtained by the quenching technique for compositions in the MgO-ZrO₂ system. These data indicate that for compositions higher in MgO content than 10 mole percent, there is no two-phase region of tetragonal and cubic ZrO₂ at temperatures above 1,500° C. The apparent disagreement of these results with those of Duwez, Odell, and Brown [9a] is believed to be due to their having obtained their data from "rapidly cooled," but not quenched, specimens.

Within the ternary system, cubic ZrO₂ solid solutions can be found which are stable to a greater or lesser extent, depending on the TiO₂ content of the specimen. Samples on the M₂T-ZrO₂ join show cubic ZrO₂ solid solutions with stability relations similar to those in the MgO-ZrO₂ system. However, compositions on the MT-ZrO₂ join must be cooled faster than those on the MgO-ZrO₂ and M₂T-ZrO₂ joins in order to maintain the cubic solid solutions. Furnace-cooled specimens, although actually cooled fairly rapidly, show little or no cubic ZrO₂, but the same materials, when quenched, show only cubic ZrO₂ solid solutions, with no monoclinic ZrO₂. All samples in the two-phase region of the MT₂-ZrO₂ join showed MT₂ and monoclinic ZrO₂. Even quenched samples did not contain cubic ZrO₂.

3.2. The CaO-ZrO₂-TiO₂ System

The binary compounds occurring in the boundary-systems are CaO-TiO₂ and 3CaO·2TiO₂ [10,8b], ZrO₂·TiO₂ [8], and CaO·ZrO₂ [11].

For the investigation of the ternary fields, 22 selected samples were quenched from various temperatures and were examined by X-ray diffraction and petrographic means. From the results of these tests, which are listed in table 2, a ternary compound, CZT₂, was discovered and the arrangement of composition triangles was determined. The binary joins

TABLE 2. Results of study of solid-state reaction in the system CaO-ZrO₂-TiO₂

Mole ratio C:Z:T	Binary join or ternary field	Heat treatment ^a		Phases identified by X-ray and/or petrographic means (ss=solid solution)
		Time	Temperature	
		hr	°C	
1:1:2	CT-CZT ₂ -----	24	1,450	CZT ₂ .
2:1:3	do-----	2.5	1,450	CT+CZT ₂ (little or no ss).
1:2:3	CZT ₂ -ZT-----	24	1,450	CZT ₂ +ZT (small amount ss).
1:4:5	do-----	3	1,450	Do.
1:1:4	CZT ₂ -TiO ₂ -----	3	1,450	CZT ₂ ss+TiO ₂ ss.
1:4:2	CZT ₂ -ZrO ₂ -----	3	1,500	CZT ₂ ss+monoclinic ZrO ₂ ss.
1:1:1	CT-ZrO ₂ -----	3	1,550	CT+cubic ZrO ₂ ss.
1:4:1	do-----	3	1,550	Cubic ZrO ₂ ss.
2:1:1	CT-CZ-----	5	1,550	(CT-CZ) ss.
5:2:2	C ₃ T ₂ -CZ-----	5	1,550	(C ₃ T ₂ -CZ) ss+small amount CaO.
9:6:2	do-----	3	1,550	(C ₃ T ₂ -CZ) ss.
7:1:4	do-----	3	1,550	C ₃ T ₂ +(C ₃ T ₂ -CZ) ss+small amount CaO.
3:1:6	CT-CZT ₂ -TiO ₂ ---	3	1,400	CT ss+CZT ₂ ss+TiO ₂ ss.
1:3:6	CZT ₂ -ZT-TiO ₂ ---	14	1,450	CZT ₂ ss+ZT ss+TiO ₂ ss.
2:2:3	CT-CZT ₂ -ZrO ₂ ---	16	1,450	CZT ₂ ss+CT+monoclinic ZrO ₂ ss.
2:9:6	CZT ₂ -ZT-ZrO ₂ ---	43	1,450	CZT ₂ +ZT ss+monoclinic ZrO ₂ ss.
2:2:1	CT-CZ-ZrO ₂ -----	16	1,450	(CT-CZ) ss+cubic ZrO ₂ ss.
3:4:1	do-----	3	1,550	Do.
2:4:1	do-----	3	1,550	Small amount (CT-CZ) ss+ cubic ZrO ₂ ss.
6:1:4	CT-CZ-C ₃ T ₂ -----	3	1,550	(CT-CZ) ss+small amount C ₃ T ₂ .
4:1:1	C ₃ T ₂ -CZ-CaO-----	3	1,550	(C ₃ T ₂ -CZ) ss+CaO.
16:1:4	do-----	3	1,550	C ₃ T ₂ +(C ₃ T ₂ -CZ) ss+CaO.

^a Each sample was quenched, in air, from the temperature indicated. Each sample had been previously calcined at least once.

found to exist in the subsolidus temperature range were CT-CZT₂, CZT₂-TiO₂, CZT₂-ZT, CZT₂-ZrO₂, CT-ZrO₂, CT-CZ, and C₃T₂-CZ. These compatibility relations, together with the location of pre-

TABLE 3. X-ray powder diffraction pattern of the compound CaO·ZrO₂·2TiO₂, using Cu Kα₁ radiation

2θ	d	R.I. ^a	2θ	d	R.I. ^a
14.28	6.2	7	74.98	1.27	3
15.68	5.6	6	75.63	1.26	10
16.99	5.2	8	76.19	1.25	5
19.53	4.5	4	76.74	1.24	3
20.41	4.35	4	80.96	1.18	4
22.42	3.96	14	81.72	1.177	9
23.54	3.78	5	82.38	1.169	16
24.59	3.62	3	82.70	1.166	15
25.16	3.57	2	84.50	1.146	7
25.87	3.44	3	84.62	1.144	7
26.76	3.33	14	85.28	1.137	17
27.59	3.23	26	85.70	1.133	7
29.04	3.07	2	86.84	1.121	8
29.39	3.04	3	87.00	1.119	8
30.51	2.93	100	87.49	1.114	5
30.75	2.91	78	87.81	1.111	8
32.07	2.79	56	88.09	1.108	7
33.26	2.69	3	88.46	1.104	7
35.83	2.50	54	90.69	1.083	2
36.03	2.49	19	91.83	1.072	3
37.68	2.39	5	92.57	1.066	5
38.48	2.34	4	94.83	1.046	5
39.39	2.29	21	95.97	1.037	5
39.55	2.28	14	96.25	1.036	6
40.57	2.22	4	96.58	1.032	7
40.77	2.21	3	96.94	1.029	7
42.23	2.14	7	97.25	1.026	10
42.74	2.11	4	97.87	1.022	6
43.50	2.08	5	98.49	1.017	4
44.32	2.04	8	100.99	0.9983	3
44.48	2.04	10	101.32	.9959	5
45.07	2.01	16	101.76	.9928	5
47.76	1.90	13	102.98	.9843	4
48.05	1.89	9	103.68	.9796	10
48.37	1.88	6	104.92	.9714	7
48.82	1.86	7	105.76	.9659	5
50.23	1.81	27	106.17	.9634	4
50.72	1.79	67	107.88	.9528	5
51.32	1.78	10	108.33	.9501	5
51.63	1.77	15	109.82	.9413	2
52.28	1.75	7	110.96	.9348	4
52.52	1.74	66	113.76	.9197	5
52.64	1.74	58	115.53	.9106	5
52.99	1.73	4	115.90	.9085	5
53.47	1.71	7	117.11	.9028	9
54.01	1.69	5	119.16	.8932	6
55.39	1.66	6	120.09	.8890	5
55.74	1.65	4	120.37	.8878	6
56.12	1.64	3	122.88	.8769	4
57.57	1.59	4	125.19	.8676	12
58.06	1.59	5	126.28	.8634	11
58.20	1.58	7	126.45	.8628	9
59.69	1.55	8	127.61	.8584	5
59.97	1.54	32	128.00	.8569	7
60.57	1.53	12	128.79	.8541	7
60.78	1.52	20	129.95	.8501	6
61.22	1.51	42	131.26	.8456	6
62.76	1.48	17	132.82	.8405	7
62.94	1.48	24	133.02	.8379	7
63.26	1.47	14	143.76	.8104	5
63.81	1.46	15	145.92	.8056	4
65.33	1.43	3	146.35	.8047	2
65.88	1.42	6	147.53	.8022	9
66.87	1.39	2	148.59	.8001	10
69.25	1.36	8	148.96	.7994	7
69.69	1.35	7	149.71	.7979	9
70.44	1.34	4	160.63	.7815	6
71.93	1.31	7	163.75	.7781	4

^a R.I. is the intensity of the diffraction peaks relative to the strongest peak.

pared compositions, are shown in figure 3. The compound CZT₂ forms large well-developed crystals when heated. Its optical properties are biaxial negative with optic axial angle (2V)=80° to 85°, and indices of refraction $\alpha \approx 2.23$, $\beta \approx 2.27$, and $\gamma \approx 2.30$. It has a distorted pyrochlore-type structure, with orthorhombic or lower symmetry. Its X-ray powder pattern is given in table 3. The composition of this compound may be written as (Ca, Zr)Ti₂O₇ to show its relation to the pyrochlore structure [12], which is (Na, Ca)(Nb, Ta)O₆F or A₂B₂X₇. This is believed to be the first published paper on a compound having a pyrochlore-type structure with no pentavalent ions as essential elements in the B position of the structure.

The indexed powder pattern for CaZrO₃ is given in table 4. It has been indexed as orthorhombic with:

$$\begin{aligned} a &\approx \sqrt{2} \times \text{pseudo cube} = 5.587 \text{ \AA}, \\ b &\approx 2 \times \text{pseudo cube} = 8.008 \text{ \AA}, \\ c &\approx \sqrt{2} \times \text{pseudo cube} = 5.758 \text{ \AA}, \end{aligned}$$

in a manner similar to that done for CaTiO₃ and CaSnO₃ [13].

The estimated solid-solution limits for this system are shown in figure 4. Here, also, the figure is not intended to represent an isothermal section of the diagram, but to show only approximate solid-solution areas, as samples within the system are heated to subsolidus temperatures.

The relative stability relations of the cubic ZrO₂ solid solutions within this system are essentially similar to those in the MgO-ZrO₂-TiO₂ system. The cubic solid solution in the CaO-ZrO₂ system is more stable than that in the MgO-ZrO₂ system. Its stability also decreases with increasing TiO₂ content.

Quenched specimens on the CT-ZrO₂ join show cubic ZrO₂ solid solution, while those on the CZT₂-ZrO₂ join show only monoclinic ZrO₂.

TABLE 4. Indexed X-ray powder pattern of the orthorhombic compound CaO·ZrO₂, using CuK α_1 radiation

2 θ	d	R.I. ^a	hkl	2 θ	d	R.I. ^a	hkl
22.19	4.00	84	101	75.60	1.26	4	402
24.84	3.58	5	111	75.82	1.25	4	252
31.06	2.88	40	002	78.39	1.22	3	224
31.56	2.83	100+	121	79.92	1.20	4	422/153
32.02	2.79	50	200	82.44	1.169	4	044
35.73	2.51	4	201	84.50	1.146	3	440
37.30	2.41	6	130	86.13	1.128	2	314
37.50	2.40	6	211	88.40	1.125	2	105
38.42	2.34	2	022	87.70	1.112	4	343/262
39.30	2.29	3	220	90.40	1.086	3	125
40.62	2.22	5	131	91.16	1.078	4	244
41.88	2.16	4	122	91.49	1.075	8	163
45.22	2.00	74	202/040	92.49	1.066	9	361
46.34	1.96	4	032	92.62	1.065	8	442
46.67	1.94	3	212	93.42	1.058	5	521
50.23	1.81	14	103	100.43	1.002	3	404
50.91	1.79	24	222	100.70	1.000	2	080
50.93	1.79	26	141	103.20	0.9828	4	145
51.57	1.77	9	301	103.70	.9795	3	305
55.54	1.65	29	123	104.78	.9723	4	424
55.89	1.64	26	042	105.18	.9697	3	181
56.50	1.63	16	240	108.11	.9514	4	305
56.78	1.62	40	321	109.10	.9455	4	106
61.75	1.50	3	133	109.23	.9448	5	363
64.70	1.44	4	004	109.62	.9425	4	280
65.87	1.42	20	242	110.25	.9359	4	523
66.93	1.40	5	400	111.60	.9313	2	182
69.32	1.35	4	024	118.55	.8960	5	444
69.89	1.34	8	143	119.02	.8939	3	282
70.50	1.33	2	060	120.86	.8856	3	226
70.97	1.33	4	341	122.70	.8777	2	143/471
71.50	1.32	3	420	126.74	.8617	3	165
73.99	1.28	4	204	130.67	.8476	6	501/316
74.82	1.27	14	323	137.35	.8269	3	246
74.89	1.27	16	161	143.86	.8102	6	642

^a R.I. is the intensity of the diffraction peaks relative to the strongest peak.

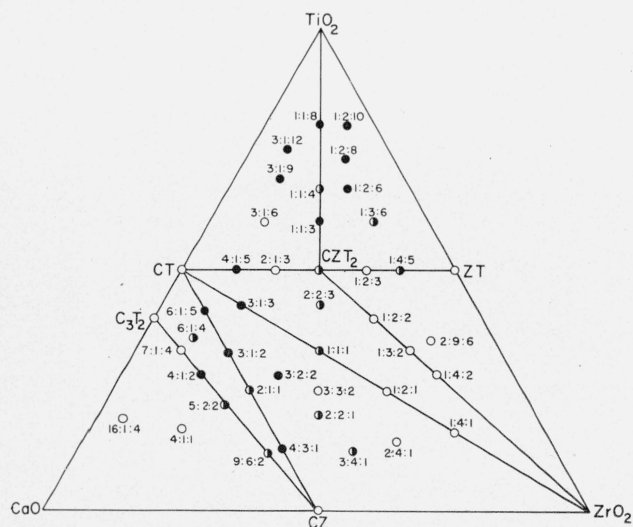


FIGURE 3. Compatibility relations in the system CaO-ZrO₂-TiO₂.

The compositions studied are indicated and plotted according to mole ratios.
 ○, Compositions used in the study of solid-state reactions;
 ●, compositions used in the study of dielectric properties;
 ⊙, compositions used for both studies.

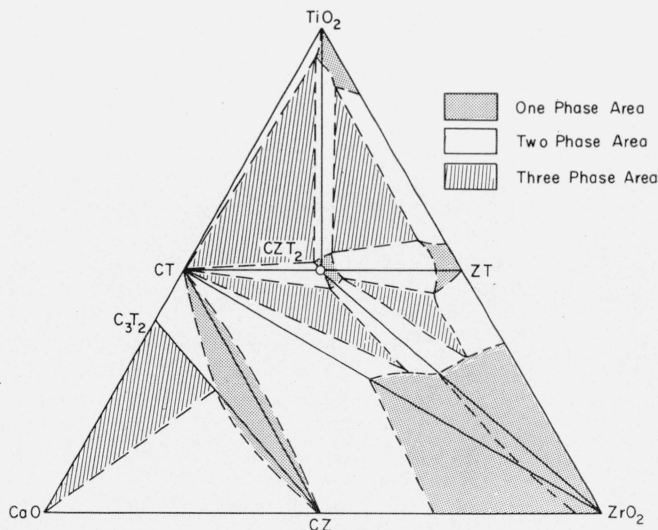


FIGURE 4. Estimated trends of solid-solution development in the system CaO-ZrO₂-TiO₂ over the temperature range 1,450° to 1,550° C.

The dashed line near the ZrO₂ apex of the figure indicates the approximate location of a two-phase area which theoretically would separate the cubic ZrO₂ field on the left from the tetragonal ZrO₂ field on the right in a true isothermal section of the phase diagram.

4. Results of Dielectric Testing

4.1. The System MgO-ZrO₂-TiO₂

The dielectric properties obtained for test specimens from the MgO-ZrO₂-TiO₂ system are listed in tables 5, 6, and 7.

In the MT₂-ZT-TiO₂ field of the system, *K* varied from 40 to 80, and the average temperature coefficients of the dielectric constant (*TCK*) were found

to be negative. In the other areas of the system, *K* was found to vary between 15 and 20 and the *TCK*-values were positive and between 100 and 200 ppm/°C. The *Q*-values were, for the most part, high in all parts of the system. These results are in general agreement with those reported by Riecke and Ungewiss [1]. The values of the observed properties for any given specimen composition, as expected, seemed to be an average of the values for the appropriate end members.

TABLE 5. Results of dielectric testing in the system MgO-ZrO₂-TiO₂

Mole ratio M:Z:T	Binary join or ternary field	Heat treatment		Linear shrinkage	Equivalent water absorption	Dielectric constant, <i>K</i> , at 25° C and—			Reciprocal, <i>Q</i> , of power factor at 25° C and—		
		Time	Temperature			50 kc	1 Mc	20 Mc	50 kc	1 Mc	20 Mc
4:1:4	MT-ZrO ₂	2	1,500	13.2	0.06	17	18	18	500	5,000	6,000
3:1:3	do.....	1	1,550	13.0	.13	18	18	17	30	400	4,000
2:1:2	do.....	1	1,550	13.0	.04	17	18	17	200	3,000	10,000
3:2:3	do.....	2	1,560	11.6	.21	18	17	17	200	3,000	5,000
6:2:3	M ₂ T-ZrO ₂	1/2	1,625	11.2	.00	19	19	19	400	1,000	800
2:1:1	do.....	1/3	1,625	10.0	.00	20	20	20	300	1,000	600
1:1:19	MT ₂ -ZT-TiO ₂	2	1,425	14.8	.10	76	76	76	700	10,000	1,000
1:1:9	do.....	2	1,425	16.4	.00	75	75	75	6,000	10,000	1,400
1:1:5	do.....	2	1,425	15.6	.00	52	52	52	4,000	10,000	3,000
1:1:4	do.....	2	1,425	15.5	.10	42	41	41	150	2,000	3,000
1:3:19	do.....	1	1,500	14.6	.23	80	79	79	200	1,300	4,000
1:3:9	do.....	1	1,500	13.8	.10	65	64	65	70	700	2,000
2:1:3	MT-MT ₂ -ZrO ₂	1	1,550	13.2	.55	18	18	18	500	2,000	820
3:1:2	M ₂ T-MT-ZrO ₂	1	1,550	11.0	.04	16	17	17	170	1,000	1,000
3:2:2	do.....	1/2	1,650	11.0	.12	21	21	21	400	700	600
3:3:2	do.....	1/2	1,650	9.6	.02	28	28	28	400	700	500
9:1:3	MgO-M ₂ T-ZrO ₂	1/2	1,625	11.0	.15	14	14	14	100	2,000	3,000
9:1:1	do.....	1	1,550	11.6	.08	13	13	13	80	1,000	2,000
5:1:1	do.....	1	1,610	11.2	.09	15	16	15	200	1,000	1,000
3:1:1	do.....	1	1,635	16.3	.05	20	20	20	1,000	960	430

TABLE 6. Variation of dielectric constant with temperature of some specimens in the system MgO-ZrO₂-TiO₂

Mole ratio M:Z:T	Binary join or ternary field	Value of <i>K</i> at 1 Mc and—							Average temperature coefficient of <i>K</i> from -50° to 250° C
		-50° C	0° C	50° C	100° C	150° C	200° C	250° C	
2:1:1	M ₂ T-ZrO ₂	19.4	19.5	19.7	19.8	19.9	20.1	20.2	ppm/° C +135
1:1:4	MT ₂ -ZT-TiO ₂	41.9	41.3	40.7	40.0	39.3	39.0	38.6	-280
1:1:5	do.....	53.5	52.5	51.3	50.2	49.2	49.2	47.5	-410
1:1:9	do.....	78.5	76.2	73.2	70.7	68.6	66.4	64.7	-650
2:1:3	MT-MT ₂ -ZrO ₂	17.5	17.7	17.8	17.9	18.1	18.2	18.3	+150
3:1:1	MgO-M ₂ T-ZrO ₂	19.4	19.5	19.6	19.8	19.9	20.0	20.2	+130
9:1:1	do.....	14.6	14.9	15.0	15.1	15.2	15.3	15.4	+180
9:1:3	do.....	17.8	17.9	18.1	18.2	18.3	18.4	18.6	+150

TABLE 7. Variation of *Q* with temperature of some specimens in the system MgO-ZrO₂-TiO₂

Mole ratio M:Z:T	Binary join or ternary field	Value of <i>Q</i> at 1 Mc and—						
		-50° C	0° C	50° C	100° C	150° C	200° C	250° C
2:1:1	M ₂ T-ZrO ₂	570	620	470	580	630	430	280
1:1:4	MT ₂ -ZT-TiO ₂	5,000	5,000	5,000	5,000	5,000	3,000	800
1:1:5	do.....	10,000	10,000	5,000	8,000	8,000	6,000	3,000
1:1:9	do.....	10,000	10,000	8,000	5,000	4,000	3,500	3,000
2:1:3	MT-MT ₂ -ZrO ₂	4,000	4,000	3,000	2,500	2,200	1,700	850
3:1:1	MgO-M ₂ T-ZrO ₂	840	930	970	940	840	690	520
9:1:1	do.....	1,400	1,400	1,400	1,950	1,400	900	710
9:1:3	do.....	1,900	1,900	2,400	1,610	1,950	1,090	700

4.2. The System CaO-ZrO₂-TiO₂

The dielectric properties obtained for specimens from this system are given in tables 8, 9, and 10.

The value of K varied from about 164 for the compound CT to about 24 for the compound CZ. The ternary compound CZT₂ was found to have a K of about 48. The TCK varied from large negative values for compositions high in CT to small positive values for compositions high in CZT₂ or CZ. Bodies having a low TCK can be obtained by proper adjustment of the composition. This fact is illustrated in figure 5 for some specimens along the CZT₂-TiO₂ join. It is probable that more precise adjustment of the ratio of TiO₂ to CZT₂ would result in a body having a zero average TCK value. The Q -values of specimens in this system are generally lower than those of specimens in the MgO-ZrO₂-TiO₂ system. In this system also, the properties of a specimen of given composition seemed to be an average of the properties of the end members of the appropriate join or composition triangle.

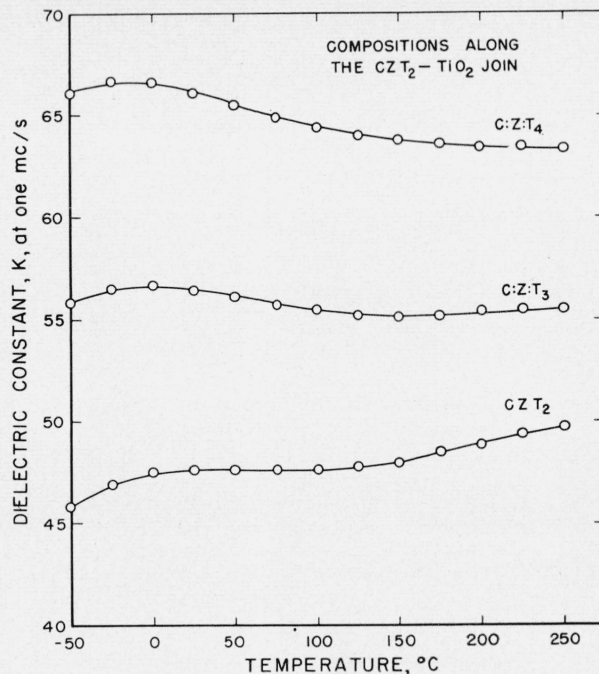


FIGURE 5. Effect of temperature variations on the dielectric constant of some compositions on the CZT₂-TiO₂ join.

TABLE 8. Results of dielectric testing in the system CaO-ZrO₂-TiO₂

Mole ratio C:Z:T	Binary join or ternary field	Heat treatment		Equivalent water absorption	Linear shrinkage	Dielectric constant K , at 25° C and —			Reciprocal, Q , of power factor, at 25° C and —		
		Time	Temperature			50 kc	1 Mc	20 Mc	50 kc	1 Mc	20 Mc
4:1:5	CT-CZT ₂	1	1,475	.01	16.2	99	98	97	300	260	50
1:1:2	do	1	1,425	.08	13.9	47.8	47.6	47.6	200	190	30
1:1:2	CZT ₂ -TiO ₂	1	1,425	.08	13.9	47.8	47.6	47.6	200	190	30
1:1:3	do	1	1,425	.06	15.9	56.5	56.4	55.6	320	230	30
1:1:4	do	1	1,400	.01	14.1	68	66	65	330	250	70
1:1:8	do	1	1,425	.04	12.2	86	86	86	600	300	60
1:1:2	CZT ₂ -ZT	1	1,425	.08	13.9	47.8	47.6	47.6	200	190	30
1:4:5	do	1	1,450	.14	13.5	39.9	39.6	39.6	330	440	70
1:0:1	CT-ZrO ₂	1	1,500	.08	16.8	16.4	16.4	16.4	2,000	9,000	600
3:1:3	do	1	1,400	.00	16.4	88	87	86.5	340	350	110
1:1:1	do	1	1,450	.00	15.8	64.7	64.6	64.4	200	560	240
1:0:1	CT-CZ	1	1,500	.08	16.8	164	164	154	2,000	9,000	600
6:1:5	do	1	1,500	.05	13.8	106	106	106	1,000	3,000	2,000
3:1:2	do	1	1,550	.00	12.1	86	86	86	2,000	1,500	2,000
2:1:1	do	1	1,500	.02	13.3	64	63	63	2,000	2,000	980
4:3:1	do	1	1,500	.04	11.2	40	40	40	1,000	2,000	1,000
1:1:0	do	1	1,500	.17	15.0	24	24	24	130	100	1,000
4:1:2	C ₃ T ₂ -CZ	1	1,550	.16	18.0	74.4	74.3	74.2	1,000	1,300	510
5:2:2	do	1	1,550	.13	14.9	68.6	68.4	68.1	1,000	2,000	380
9:6:2	do	1	1,500	.04	13.5	44	44	44	8,000	10,000	2,000
3:1:9	CT-CZT ₂ -TiO ₂	1	1,350	.35	13.9	92	91	89	50	110	55
3:1:12	do	1	1,350	.10	13.8	98	97	96	120	310	80
1:3:6	CZT ₂ -ZT-TiO ₂	1	1,450	.03	16.6	56.6	56.4	56.1	440	440	66
1:2:6	do	1	1,450	.00	14.4	63.3	62.9	62.5	480	380	40
1:2:8	do	1	1,425	.03	15.7	79	78	78	600	500	70
1:2:10	do	1	1,450	.03	13.7	77	76	76	800	600	90
2:2:3	CT-CZT ₂ -ZrO ₂	1	1,475	.04	12.8	38.6	38.0	37.1	100	130	30
3:2:2	CT-CZ-ZrO ₂	1	1,450	.09	13.7	62.2	61.7	61.7	700	750	440
3:4:1	do	1	1,460	.13	13.7	39	38	37	100	250	250
2:2:1	do	1	1,450	.00	17.1	59.0	58.6	58.4	380	380	320
6:1:4	CT-CZ-C ₃ T ₂	1	1,500	.00	15.9	97.2	97.1	97.0	1,000	960	330

TABLE 9. Variation of K with temperature in the system $\text{CaO-ZrO}_2\text{-TiO}_2$

Mole ratio C:Z:T	Binary join or ternary field	Value of K at 1 Mc and—							Average temperature coefficient of K from -50°C to 250°C
		-50°C	0°C	50°C	100°C	150°C	200°C	250°C	
4:1:5	CT-CZT ₂	104	100	96	93	90	87	85	<i>ppm/°C</i>
1:1:2	do.....	45.8	47.5	47.6	47.6	48.0	48.9	49.7	-670
1:1:2	CZT ₂ -TiO ₂	45.8	47.5	47.6	47.6	48.0	48.9	49.7	+270
1:1:3	do.....	55.8	56.7	56.1	55.5	55.1	55.7	55.5	-----
1:1:4	do.....	66.1	66.6	65.5	64.4	63.8	63.5	63.4	-140
1:1:8	do.....	68.0	86.7	62.5	82.2	80.4	78.9	77.6	-420
1:4:5	CZT ₂ -ZT.....	39.0	39.6	39.6	39.6	39.7	39.9	40.1	+90
1:0:1	CT-ZrO ₂	184	172	152	141	133	125	120	-1,350
3:1:3	do.....	75	90	84	80	78	76	74	-820
1:1:1	do.....	66	65	64	62	62	61	60	-300
6:1:5	CT-CZ.....	120	110	102	96	91	87	84	-1,200
3:1:2	do.....	96	89	83	78	74	71	68	-780
4:3:1	do.....	42.1	40.7	39.4	38.2	37.5	36.7	36.2	-500
1:1:0	do.....	23.6	23.7	23.8	23.9	24.0	24.1	24.2	+85
4:1:2	C ₃ T ₂ -CZ.....	80	76	72	69	67	65	63	-800
5:2:2	do.....	73	69	63	65	63	61	59	-790
9:6:2	do.....	47	45	44	43	42	41	40	-480
3:1:9	CT-CZT ₂ -TiO ₂	95	92	89	86	83	81	79	-610
3:1:12	do.....	103	99	95	92	88	86	84	-670
1:3:6	CZT ₂ -ZT-TiO ₂	56.6	56.8	56.1	55.5	55.2	55.1	55.1	-90
1:2:6	do.....	64.1	63.5	62.5	61.1	60.4	60.0	59.7	-250
1:2:8	do.....	80.8	79.1	77.0	75.0	73.4	72.4	71.5	-410
1:2:10	do.....	79	77	75	73	71	69	69	-470
2:2:3	CT-CZT ₂ -ZrO ₂	36.2	37.7	38.2	38.5	39.0	39.8	40.6	+390
3:2:2	CT-CZ-ZrO ₂	68	64	61	59	57	55	54	-810
3:4:1	do.....	39.3	38.6	38.0	37.6	37.3	37.2	37.3	-170
2:2:1	do.....	63	60	58	56	55	54	53	-600
6:1:4	CT-CZ-C ₃ T ₂	108	100	94	90	86	82	80	-990

TABLE 10. Variation of Q with temperature in the system $\text{CaO-ZrO}_2\text{-TiO}_2$

Mole ratio C:Z:T	Binary join or ternary field	Value of Q at 1 Mc and—						
		-50°C	0°C	50°C	100°C	150°C	200°C	250°C
4:1:5	CT-CZT ₂	60	140	280	230	130	90	70
1:1:2	do.....	25	90	240	140	60	50	60
1:1:2	CZT ₂ -TiO ₂	25	90	240	140	60	50	60
1:1:3	do.....	30	110	300	210	80	70	90
1:1:4	do.....	40	110	320	200	100	80	100
1:1:8	do.....	50	120	370	450	280	150	100
1:4:5	CZT ₂ -ZT.....	60	210	490	300	140	110	100
1:0:1	CT-ZrO ₂	760	4,000	3,500	2,500	1,700	170	40
3:1:3	do.....	180	240	260	180	120	100	100
1:1:1	do.....	310	390	390	100	50	100	230
6:1:5	CT-CZ.....	2,000	2,000	3,000	2,000	2,000	2,000	500
3:1:2	do.....	1,000	870	1,100	1,100	890	570	190
4:3:1	do.....	800	1,000	2,000	2,000	2,000	900	900
1:1:0	do.....	800	800	700	900	600	500	400
4:1:2	C ₃ T ₂ -CZ.....	1,100	760	880	650	320	120	35
5:2:2	do.....	1,200	1,000	900	480	400	180	60
9:6:2	do.....	1,000	2,000	3,000	3,000	3,000	3,000	2,000
3:1:9	CT-CZT ₂ -TiO ₂	70	120	260	330	210	160	110
3:1:12	do.....	110	180	380	400	270	210	140
1:3:6	CZT ₂ -ZT-TiO ₂	60	200	510	300	130	100	100
1:2:6	do.....	60	180	360	250	120	90	90
1:2:8	do.....	70	230	520	380	160	130	120
1:2:10	do.....	90	290	440	350	190	140	140
2:2:3	CT-CZT ₂ -ZrO ₂	30	60	110	100	60	40	40
3:2:2	CT-CZ-ZrO ₂	690	600	480	390	300	240	140
3:1:1	do.....	270	250	240	210	18	140	90
2:2:1	do.....	420	380	340	280	260	200	120
6:1:4	CT-CZ-C ₃ T ₂	560	590	820	740	330	110	30

5. Summary

An investigation of solid-phase reactions in the systems $\text{MgO-ZrO}_2\text{-TiO}_2$ and $\text{CaO-ZrO}_2\text{-TiO}_2$ was conducted. Compatibility relations were established and solid-solution areas were estimated for each system. No ternary compounds were observed in the $\text{MgO-ZrO}_2\text{-TiO}_2$ system. In the $\text{CaO-ZrO}_2\text{-TiO}_2$ system, a ternary compound having the formula $\text{CaO}\cdot\text{ZrO}_2\cdot 2\text{TiO}_2$ was discovered, and its optical properties and X-ray diffraction pattern were determined.

The X-ray diffraction powder pattern for the compound $\text{CaO}\cdot\text{ZrO}_2$ was obtained and indexed as orthorhombic.

Dielectric-test samples were prepared and tested in each system. The dielectric constant varied between 15 and 165, depending upon the composition of the specimen. The average temperature coefficient of K between -50° and 150° C varied from large negative values to small positive values, also depending upon the composition of the fired piece.

6. References

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