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PHASE EQULIBRIA IN THE SYSTEM BaO-TiO_2-Gd_2O_3*

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Abstract

The phase diagram BaO-TiO_2-Gd_2O_3 has been determined for an isothermal subsolidus section at 1300°C. In contrast with other BaO-TiO_2-R_2O_3 systems (R = La, Nd), it contains only 2 previously reported ternary compounds, $Ba_6Gd_2Ti_4O_{17}$ and $Ba_{6-x}Gd_{8+2/3x}Ti_{18}O_{54}$ solid solution. The solid solution range has been determined as 1.1 < x < 1.65.

Introduction

Ceramics based on the ternary BaO-TiO_2-R_2O_3 system (R = rare earth) are extensively used for manufacturing passive electronic components. Of particular interest are compositions in the vicinity of $BaTiO_3$. $BaTiO_3$ slightly doped with rare earth oxides (up to a concentration of around 0.3 - 0.5 at %) is semiconductive with a large PTCR effect, and is used for the preparation of a wide variety of switching, heating and regulating devices. With higher amounts of rare earths, $BaTiO_3$ exhibits high electrical conductivity and is used for manufacturing highly temperature stable ceramic capacitors ("NPO" type). Ceramics in the vicinity of BaO:R_2O_3:TiO_2 = 1:1:4 are used in the manufacture of high permittivity microwave resonators.

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*Dedicated to the memory of Prof. Dr. Jože Šiftar

The electrical properties of $BaO-TiO_2-R_2O_3$ ceramics strongly depend on their crystal structure, stoichiometry, grain size and phase composition. Therefore, to optimize their properties and assure reproducibility, phase equilibrium data are of great importance.

In the present work, equilibrium phases in the $BaO-TiO_2-Gd_2O_3$ were studied by microanalysis of sintered specimens in combination with electron microscopy and X-ray diffractometry. From the results, the subsolidus phase diagram at 1300° was constructed.

Literature survey

The phase equilibrium diagram $Gd_2O_3-TiO_2$ was, according to the authors' knowledge, not described. Two compounds are known to exist: Gd_2TiO_5 (Due to the Gd_2O_3 : TiO_2 ratio 1 : 1 abbreviated to "GT") [1] and $Gd_2Ti_2O_7$ ("GT_2") [2]. In the absence of firm data on the $Gd_2O_3-TiO_2$ system, some conclusions may be drawn from the expected similarity with the other rare earth oxide - TiO_2 systems. In the $La_2O_3-TiO_2$ system, 5 compounds have been confirmed: $La_4Ti_9O_{24}$ ("L_2T_9"), $La_2Ti_2O_7$ ("LT_2"), $La_4Ti_3O_{12}$ ("L_2T_3") and La_2TiO_5 ("LT") [3-4].

The system $BaO-TiO_2$ has been extensively investigated and high temperature equilibrium diagrams have been reported by several groups [5-9]. Although details vary, it is generally accepted that five stable binary compounds exist: Ba_2TiO_4 ("B_2T"), $Ba_6Ti_{17}O_{40}$ ("B_6T_{17}"), $Ba_4Ti_{13}O_{30}$ ("B_4T_{13}") $BaTi_4O_9$ ("BT_4") and $Ba_2Ti_9O_{20}$ ("B_2T_9"). The compounds B_6T_{17}, B_4Ti_{13} and BT_4 decompose to liquid and solid phases at approximately 1350°C, 1365°C and 1446°C, respectively. B_2T_9 decomposes peritectoidaly into BT_4 and TiO_2 at 1420°C [9].

The phase equilibrium diagram $BaO-Gd_2O_3$ was not published, according to the authors' knowledge. The compound $BaGd_2O_4$, "BG" is registered in the XRD powder file [10]. The compound is reported to be stable up to 1860°C. A similar rare-earth system, BaO-La_2O_3 has been reported in [11], with only the $BaLa_2O_4$ ("BL") compound melting incongruently at 1845°C. In the same article, another family of rare-earth titanates with composition $Ba_3R_4O_9$ is briefly mentioned. The $Ba_3Sm_4O_9$ was reported to exist above 1550°C.

Ternary system BaO-Gd_2O_3-TiO_2 has not been recorded. In similar ternary systems with other rare earth oxides, several ternary compounds are known. The data with references are collected in recently published phase diagrams, determined in the authors' laboratory [12,13]. Of particular industrial importance for microwave applications is the compound $BaR_2Ti_4O_{12}$ ("114") with solid solubility range, expressed by the formula $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$. The solid solubility range varies with the rare earth element, being within $0 < x < 3$ (14). For the Gd 114 compound, reported data are in disagreement over the composition. Stoichiometry of $x = 0$ [14], $0 \leq x \leq 1.5$ [15] and $x = 1.5$ [16,17] was reported. Other ternary compounds, confirmed in the La-based system, include Ba $La_2Ti_3O_{10}$ ("113") Ba $La_2Ti_2O_8$ ("112") and $Ba_2La_4Ti_5O_{18}$ ("225"). Recently, a new Ba-rich compound was identified in BaO-R_2O_3-TiO_2 systems, with composition (54-55) BaO . 10 R_2O_3 [34-35] TiO_2 (18). The compound is registered in the JCPDS file as $Ba_{12}Gd_{4.67}Ti_8O_{35}$ [19]. Compounds with similar composition BaO:R_2O_3:TiO_2 = 6:1:4 were also reported by Chen at al [20].

Experimental procedure

Samples were prepared by solid state reaction in air from high purity Gd_2O_3, TiO_2, $BaTiO_3$ and $BaCO_3$. Prior to weighing, the weight loss of Gd_2O_3 was checked by ignition at 1300°C. Weighed batches were wet mixed in acetone using an agate mortar and pestle. The dried mixtures were pelleted and reacted on Pt foil at 1300°C for approximately 20 hours and rapidly cooled. To ensure the attainment of equilibrium, the sintered samples were crushed, repressed and fired several times. The prepared samples were examined by X-ray powder diffractometry (XRD). Polished surfaces of the pellets were examined by optical and scanning electron microscopy, and quantitative analysis was performed by energy dispersive X-ray analysis (EDS).

Results and Discussion

Results of heating experiments on BaO-TiO_2-Gd_2O_3 compositions are given in Tables 1-3; Only those results in which the samples were deemed to have reached equilibrium have been included.

Table 1: Results of heating experiments in the binary Gd_2O_3-TiO_2 system at 1300°C

Composition, mol %		Phases detected by XRD
Gd_2O_3	TiO_2	
33.3	66.6	GT_2
18.2	81.8	GT_2, T
40.0	60.0	GT, GT_2
60.0	40.0	GT, G
50.0	50.0	GT

Key: Abbreviations are explained in table 2

The system TiO_2-Gd_2O_3

As noted in the literature survey, 5 compounds are known to exist in the similar rare-earth containing system TiO_2-La_2O_3. To verify the possible existence of analogous compounds in the TiO_2 - Gd_2O_3 system, samples listed in table 1 were prepared and submitted for XRD. Only two previously known compounds could be detected, $Gd_2Ti_2O_7$ and Gd_2TiO_5. Results are consistent with [1].

Table 2: Results of heating experiments in the system BaO-TiO_2-Gd_2O_3 (1300°C, 40 h)

Sample	Composition, mol % BaO	Gd_2O_3	TiO_2	Phases detected (XRD, EDS)
1	70.0	15.0	15.0	B_2T, BG, B
2	53.0	30.0	17.0	G, BG, B_2T
3	53.0	17.0	30.0	G, 614, B_2T
4	57.0	5.0	38.0	BT, B_2T, 614
5	25.0	45.0	30.0	G, GT, 614
6	35.0	20.0	45.0	614, GT, BT
7	20.0	17.5	62.5	GT_2, BT, 114
8	20.0	20.0	60.0	GT_2, BT
9	20.0	25.0	55.0	GT, GT_2, BT
10	32.5	6.0	61.5	BT, B_6T_{17}, 114
11	44.0	3.0	53.0	BT, 114
12	7.0	7.0	86.0	T, GT_2, B_2T_9
13	16.5	5.0	78.5	GT_2, BT_4, B_2T_9
14	12.0	13.0	75.0	BT_4, GT_2
15	15.0	15.0	70.0	GT_2, BT_4, 114
16	18.0	5.0	77.0	GT_2, 114, BT_4
17	20.0	5.0	75.0	BT_4, B_4T_{13}, 114
18	22.0	5.0	73.0	B_4T_{13}, B_6T_{17}, 114

Key:

B : BaO
BT : $BaTiO_3$
B_2T_9: $Ba_2Ti_9O_{20}$
B_6T_{17}: $Ba_6Ti_{17}O_{40}$
BT_4: $BaTi_4O_9$
B_4T_{13}: $Ba_4Ti_{13}O_{30}$
T : TiO_2

G: Gd_2O_3
BG: $BaGe_2O_4$
GT: Gd_2TiO_5
GT_2: $Gd_2Ti_2O_7$
114: $BaGd_2Ti_4O_{12}$ ($Ba_{6-x}Gd_{8+2/3x}Ti_8O_{54}$ss)
614: $Ba_6Gd_2Ti_4O_{17}$

Table 3: Results of heating experiments of compositions corresponding to $Ba_{6-x}Gd_{8+2/3x}TiO_{18}$ solid solution

Composition, mol %				
BaO	Gd_2O_3	TiO_2	x	Phases detected (XRD, EDS)
19.9	15.1	65.0	0.5	114, BT
18.3	15.8	65.9	1.0	114, BT
17.6	16.2	66.2	1.2	114
17.3	16.3	66.4	1.3	114
17.0	16.5	66.5	1.4	114
16.7	16.7	66.6	1.5	114
16.4	16.8	66.8	1.6	114
16.0	17.0	67.0	1.7	114, GT_2
15.0	17.5	67.5	2.0	114, GT_2, BT_4

Key: Abbreviations are explained in table 2

The ternary system BaO - Gd_2O_3-TiO_2

The results listed in table 2 were used to construct the phase diagram at 1300°C shown in Fig. 1. Two ternary compounds were confirmed: $Ba_6Gd_2Ti_4O$ ("614") and $Ba_{4.5}Gd_9Ti_{18}O_{54}$ ("114"). The family of rare earth 114 compounds are known to form extensive solid solutions, represented by the formula $Ba_{6-x}R_{8+2/3x}Ti_{18}O_{54}$, where the range of x varies with rare earth. To determine the extension of x in the case of the Gd 114 compound, a series of compositions with $0.5 < x < 2.0$ were examined. After prolonged firing at 1300°C the samples were analysed by SEM and XRD. Results, given in table 3, confirmed a single phase structure in the composition region $1.2 < x < 1.6$. Representative microstructures are shown on Figs. 2-6. Microstructures of compositions with x = 1.0 and x = 1.7 exhibit the presence of second phases, $BaTiO_3$ and $GdTi_2O_7$, respectively. The microstructure of the composition with x = 1.2 exhibits a single-phase solid solution. These data are in disagreement with published results [14-17], indicating that the solid solubility range strongly depends on processing conditions.

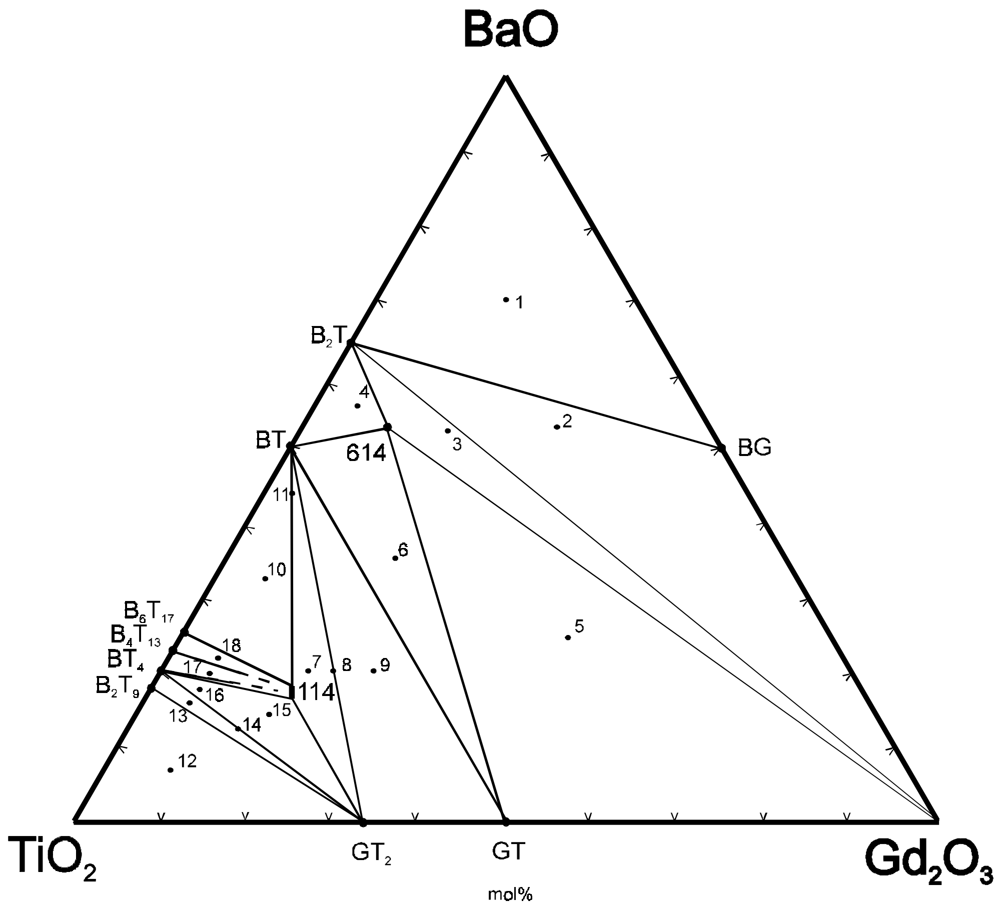

Fig. 1: Subsolidus phase diagram of the BaO-TiO_2-Gd_2O_3 system in air at 1300°C.

The ternary diagram should be self-explanatory. It is divided into a number of two-phase and three-phase regions. The tie-lines connecting the 114 solid solution with the various barium polytitanates were not drawn with certainty because the exact composition of the 114 solid solution in equilibrium with the corresponding polytitanate could not be determined.

In contrast with other similar systems BaO-TiO_2-R_2O_3 (R = La, Nd, Sm), the system BaO-TiO_2-Gd_2O_3 does not include the tie-line $Ba_2Ti_9O_{20}$ - 114 ss. Instead, analysis of samples No. 12, No. 13 and No. 16 confirmed the existence of compatibility triangles TiO_2-$Gd_2Ti_2O_7$-$Ba_2Ti_9O_{20}$, $Gd_2T_2O_7$-$Ba_2Ti_9O_{20}$-$BaTi_4O_9$ and $Gd_2Ti_2O_7$-$BaTi_4O_9$ - 114 ss, respectively.

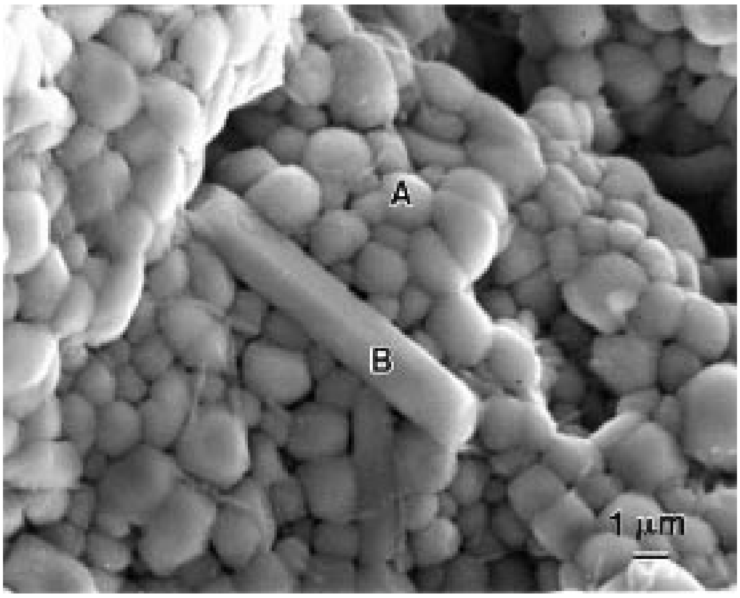

Fig. 2: Microstructure of composition 44 m/o BaO, 3 m/o Gd_2O_3, 53 m/o TiO_2 located on tie-line BT - BGT_4 showing the two phase structure: A = $BaTiO_3$, B = $BaGd_2Ti_4O_{12}$ss.

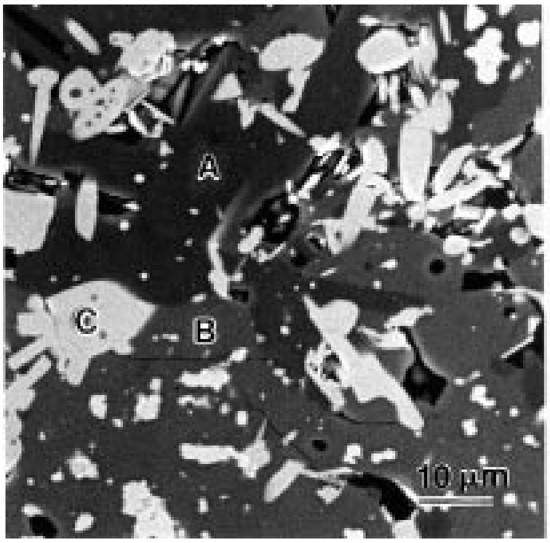

Fig. 3: Microstructure of composition 20 m/o BaO, 5 m/o Gd_2O_3, 75 m/o TiO_2 located in the compatibility triangle B_4T_{13}-114-BT_4 showing three phase structure: A = BT_4, B = B_4Ti_{13}, C =114.

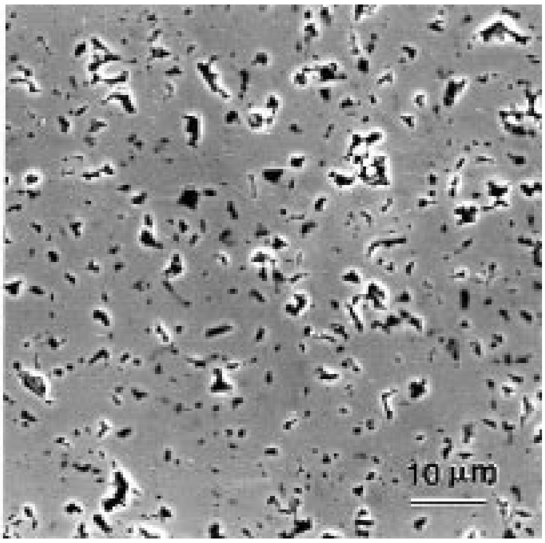

Fig. 4: Microstructure of composition $Ba_{6-x}Gd_{8+2/3x}Ti_{18}O_{54}$ with x = 1.2. Single-phase structure.

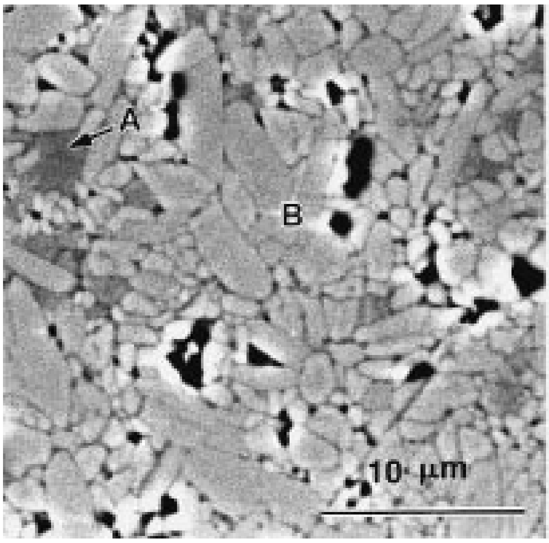

Fig. 5: Microstructure of composition $Ba_{6-x}Gd_{8-2/3x}Ti_{18}O_{54}$ with x = 1.0. Two-phase structure: A = BT, B = 114.

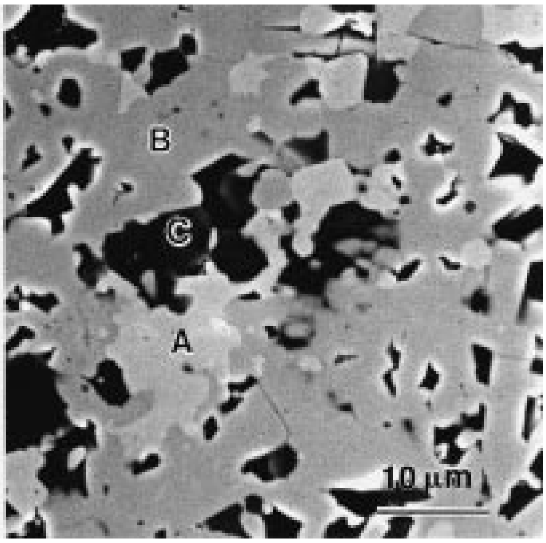

Fig. 6: Microstructure of composition $Ba_{6-x}Gd_{8+2/3x}Ti_{18}O_{54}$ with x = 2.0. Three-phase structure: A = GT_2, B = 114, C = BT_4.

Conclusions

A subsolidus ternary BaO-TiO_2-Gd_2O_3 equilibrium diagram at 1300°C has been constructed. Nine stable previously reported binary compounds and 2 ternary compounds, $Ba_{12}Gd_{4.67}Ti_8O_{35}$ (possibly $Ba_6Gd_2Ti_4O_{17}$) and $Ba_{6-x}Gd_{8+2/3x}Ti_{18}O_{54}$ ("114" compound) have been confirmed. The solid solubility range of the 114 compound has been determined as $1.1 < x < 1.65$. In contrast with other BaO-TiO_2-R_2O_3 systems (R = La, Nd), the tie line 114 - TiO_2 does not exist in the Gd containing system. Instead, the tie lines $Ba_2Ti_9O_{20}$-$Gd_2Ti_2O_7$ and $BaTi_4O_9$-$Gd_2Ti_2O_7$ were confirmed.

Acknowledgments

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Povzetek

Določen je bil ravnotežni fazni diagram sistema BaO-TiO_2-Gd_2O_3 pri 1300°C. Sistem se razlikuje od sorodnih sistemov z drugimi oksidi redkih zemelj (La, Nd) v tem, da vsebuje le dve že opisani ternarni spojini, $Ba_6Gd_2Ti_4O_{17}$ in $Ba_{6-x}Gd_{8+2/3x}Ti_{18}O_{54}$ trdno raztopino. Obseg trdne raztopine pri 1300°C je 1.1 < x< 1.65.