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Sub-solidus phase relations and a structure determination of new phases in the $CaO–La_2O_3–TiO_2$ system

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Abstract

Sub-solidus phase relations in the ternary $CaO–La_2O_3–TiO_2$ system at 1400 °C in air were determined. The multi-phase samples were prepared by a solid-state reaction method, whereas the single-phase samples for the structure analysis of selected solid solutions were prepared by a wet-precipitation method in order to provide good homogeneity of the starting mixtures. The phases in the prepared samples were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The oxides form seven ternary compounds in the equilibrium state, many solid solutions (which extend across a broad concentration region), and a large, single-phase area based on the $CaTiO_3$ solid solution. The structures of several new phases – solid solutions on the tie lines $CaTiO_3–Ca_3La_4Ti_3O_{15}$ and $La_2TiO_5–Ca_3La_4Ti_3O_{15}$ – were determined in detail.

Keywords: Phase relations; $CaO–La_2O_3–TiO_2$ ternary system; Structure determination; X-ray powder diffraction; Wet precipitation synthesis

1. Introduction

The tremendous developments in wireless communications and information technology over the past two decades have relied on new ceramic materials that are used as the resonant elements. The most important requirements during the development of new, microwave dielectrics are a high permittivity (k), a high quality factor (Qxf) and a low temperature coefficient of the resonant frequency (τ_f). Thus, some compounds in the $La_2O_3–TiO_2$ system, for example, $La_2Ti_2O_7$ and $La_4Ti_9O_{24}$, have been examined as microwave dielectric ceramics [1,2], and their dielectric properties can be additionally tuned by the partial substitution of the La by Nd and/or Sm [3]. Furthermore, the addition of selected oxides to this binary system, for example, Al_2O_3 [4], Ga_2O_3 [5], CaO [6], causes the formation of an A-site-deficient perovskite $La_{2/3}TiO_3$ compound. Such a stabilized $La_{2/3}TiO_3$ compound forms solid solution with the perovskites $LaAlO_3$ and $CaTiO_3$, according to the formula $(1-x)La_{2/3}TiO_3 - xLaAlO_3$, which are stable over the range $0.04 \leq x \leq 1$ [4], and $(1-x)La_{2/3}TiO_3 - xCaTiO_3$, which is stable over the range $0.04 \leq x \leq 1$ [6,7]. Single-phase ceramics based on these solid solutions exhibit excellent microwave-dielectric properties, which can be easily tuned by changing the $La_{2/3}TiO_3$:($LaAlO_3$ or $CaTiO_3$) ratio [4,8]. Moreover, in the ternary $CaO–La_2O_3–TiO_2$ system, several compounds were identified, showing interesting microwave dielectric properties [9,10]. In our investigation we focused on a determination of the high-temperature sub-solidus phase relations in this ternary system. We also performed a structural characterization of some of the solid solutions that are formed.

Until now, all the compounds in this ternary system were mostly prepared using a solid-state preparation technique. The advantages of wet-chemical techniques are a better homogeneity, the desired particle size and shape on the nanoscale, less

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power consumption and a lower cost of preparation. After calcination and sintering, the resulting product is well defined and suitable for a structural characterization.

1.1. Literature survey

Phase relations in the La_2O_3–TiO_2 binary system are well described [11–15]. The stable compounds are $La_4Ti_9O_{24}$, $La_2Ti_2O_7$, $La_4Ti_3O_{12}$ and La_2TiO_5. Firing of the composition La_2O_3:3TiO_2 in a reducing atmosphere [16], or the addition of a small quantity of 1+ ions, such as Li, Na, K [17], or 2+ or 3+ ions, such as Ca [6], Al [4], Ga [5] or Fe [18], leads to the stabilization of the A-site-deficient perovskite compound $La_{2/3}TiO_3$. It is also documented in the literature that a minute amount of impurities, the presence of a liquid phase during sintering, or even a small amount of Ti^{4+} reduced to Ti^{3+}, may enable the formation of an otherwise unstable phase in the La_2O_3–TiO_2 system [2,19–21].

In the binary system CaO–La_2O_3 no compounds that would be stable over 1000 °C have been identified [22].

The phase relations in the system CaO–TiO_2 have been studied experimentally and calculated by numerous investigators and their results are somewhat inconsistent [23–30]. According to these results, the existence of a perovskite-type $CaTiO_3$ that is stable above 1900 °C, and a compound with the composition $Ca_3Ti_2O_7$, was confirmed [23,29,30], while others have also reported a compound with the composition $Ca_4Ti_3O_{10}$ [24–28,30].

Similarly controversial data were obtained in some investigations dealing with a sub-solidus phase-relations determination in the ternary CaO–TiO_2–M oxide systems. In the case where M = Al [31], M = Sr [32], M = Ba [32], only $CaTiO_3$ was identified, whereas in the system where M = Sn [33,34] the compounds $CaTiO_3$ and $Ca_3Ti_2O_7$ were identified, and in the system where M = In [35] the compounds $CaTiO_3$ and $Ca_4Ti_3O_{10}$ were identified.

In the systems M = Gd [36] and M = Y [37], all three compounds, $CaTiO_3$, $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$, were confirmed.

Moreover, in the system CaO–MgO–TiO_2, Coughanour et al. [33] identified $CaTiO_3$ and $Ca_3Ti_2O_7$, but Shultz [38] found $CaTiO_3$, $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$.

In the ternary system CaO–La_2O_3–TiO_2 Nanot et al. [39] reported a perovskite-related series of compounds with the general formula $(CaLa)_nTi_nO_{3n+2}$, where $n = 4.5$, 5, and 6 along the compositional line $CaTiO_3$–$La_2Ti_2O_7$. Thus, the stable compounds are: with $n = 4.5$ $CaLa_8Ti_9O_{31}$ (**149**), with $n = 5$ $CaLa_4Ti_5O_{17}$ (**125**) and with $n = 6$ $Ca_2La_4Ti_6O_{20}$ (**226**). Additionally, the crystal structures of the compounds **149**, **125**, and **226** were determined by Demšar et al. [9] and Stare et al. [40]. The binary phase diagram of the system was reported by Pivovarova et al. [41], showing the stability of the three compounds **149**, **125** and **226** above 1400 °C.

On the compositional line $CaTiO_3$–$La_4Ti_3O_{12}$ two trigonal compounds with a known structure and the general formula $La_{n-x}Ca_xTi_{n-1}O_{3n}$ were identified [42–44], with $n = 5$ and $x = 1$ $CaLa_4Ti_4O_{15}$ (**124**) and $n = 6$ and $x = 2$ $Ca_2La_4Ti_5O_{18}$ (**225**). A phase diagram of the binary system was published by Pivovarova et al. [19], where the existence and the thermal stability of the compounds **124** and **225** above 1400 °C were confirmed. She reported that the compound **124** dissolves approximately 5 mol % of $La_4Ti_3O_{12}$ in the temperature range 1200–1400 °C.

Saltykova et al. [20] and Pivovarova [45] reported perovskite-type solid solution on the tie line $CaTiO_3$–$Ca_3La_4Ti_3O_{15}$ (**323**) with the formula $Ca_{1-x/2}La_xTi_{1-x/2}O_3$ (at 1200 °C up to the melting point), where the compounds with $x < 0.2$ were supposed to be cubic and the other ones orthorhombic. The end member of this solid solution, **323**, was identified, but the structure was not determined. Later on Vanderah et al. [46] denied the existence of the compound **323** and claimed that $CaTiO_3$ dissolves only up to 38 mol % La_2O_3. The structure of only one composition from this part of the phase diagram, with the formula $Ca_{2/3}La_{2/3}Ti_{2/3}O_3$, is known [47]. It crystallizes in a monoclinic unit cell in the $P2_1/n$ space group. However, this is not in agreement with Pivovarova [45], where powder patterns were indexed in more symmetrical crystal systems. To clarify these disagreements, this paper reports the crystal structures of solid solution over the whole compositional range on the tie line $CaTiO_3$–**323**. Furthermore, the solid solubility of **323** in La_2TiO_5 was identified and structurally characterized.

2. Experimental

2.1. Synthesis

For the structure determination the wet-precipitation method for the synthesis of samples was used since this method enables a better homogeneity and a higher crystallinity compared to the solid-state method. In all the precipitation experiments weighed amounts of $Ca(CH_3COO)_2{\cdot}H_2O$ (99%, Alfa Aesar) and $La(NO_3)_3{\cdot}6H_2O$ (99.9%, Alfa Aesar) were dissolved in 10 mL of distilled water. Separately, the $Ti[OCH(CH_3)_2]_4$ (97%, Aldrich Chemical Company Inc.) was pre-diluted in 10 mL of distilled water, acidified with HNO_3 (>65%, Aldrich Chemical Company Inc.), to obtain a stable solution. Both solutions were mixed and evaporated at approximately 100 °C, while mixing with a magnetic stirrer. The white solids were additionally heated up to 210 °C for 2 h. The product was crushed and well homogenized in an agate pestle and mortar and calcined at 750 °C in air for 1 h. The so-prepared powder was uniaxially pressed into pellets and finally sintered at 1400 °C from 20 h to 100 h. After the heat treatment the samples were cooled by quenching in air to room temperature.

The majority of the samples used for the high-temperature phase-relation determination were prepared by a solid-state reaction method from the oxides TiO_2 (Alfa Aesar, 99.8%), La_2O_3 (Alfa Aesar, 99.99%) and $CaCO_3$ (Alfa Aesar, 99.5%). Due to the reactivity of the La_2O_3 with the environmental moisture and CO_2, the oxide was routinely analyzed before weighing using a firing test at 1300 °C. The starting reagents were mixed in the proper molar ratio and homogenized in a planetary YTZ ball mill for 0.5 h in ethanol media. The dried powders were biaxially pressed into pellets and fired in a tube furnace in air at 1400 °C for 20 h. The air-quenched samples were ground and