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Phase stability and equilibria in the La_2O_3–TiO_2 system

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Abstract

XRD, electron probe wavelength and energy dispersive X-ray analyses were used to reexamine the phase relations in the La_2O_3–TiO_2 system. The diagram was redrawn to include the compound $La_4Ti_3O_{12}$ in addition to $La_4Ti_9O_{24}$, $La_2Ti_2O_7$ and La_2TiO_5. Above 1455°C a cation deficient perovskite $La_{2/3}TiO_3$ is stabilized by a small number of Ti^{3+} ions and remains stable on cooling in air. The proposed diagram represents a section through the system at the normal oxygen pressure in air at 1 atm, compositions being expressed in terms of the oxide components stable at room temperature. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ceramics based on the La_2O_3–TiO_2 system exhibit interesting dielectric properties. Over fifty years ago Ehlers and Roup patented mixtures of rare-earth oxides, including lanthana, with titania as low temperature coefficient capacitors.[1] More recently, lanthanum titanate ceramics were examined as microwave frequency dielectrics.[2] $La_2Ti_2O_7$ exhibits an unusually high Curie temperature and was reported to be a promising candidate for high temperature piezoelectric and electro-optic devices.[3,4]

To optimize the properties of La_2O_3–TiO_2 ceramics, it is important to know the temperature and phase stability of phases in the system. The binary La_2O_3–TiO_2 diagram, published in 1962,[5] has to be modified to include the later identified $La_4Ti_3O_{12}$.[6,7] There is also uncertainty about the stability of the A-site deficient $La_{2/3}TiO_3$ perovskite compound.

Thus the purpose of the present investigation was to propose a revised phase diagram of the La_2O_3–TiO_2 system. Besides XRD, semiquantitative microstructural analysis was extensively employed together the experimental evidence.

2. Literature survey

MacChesney and Sauer[5] in their study of phase relations in the system La_2O_3–TiO_2 included three compounds: $La_4Ti_9O_{24}$ (frequently written as $2La_2O_3$:$9TiO_2$ and abbreviated as L_2T_9), which melts incongruently at 1455°C, $La_2Ti_2O_7$ (LT_2) and La_2TiO_5 (LT), which melt congruently at 1790 and 1700°C, respectively. Later on, Ismailzade and Mirishli[6] reported a fourth compound in the system, $La_4Ti_3O_{12}$ (L_2T_3). Fedorov et al. determined that the compound has a perovskite-like 12 layer hexagonal crystal structure and decomposes at 1450°C to La_2TiO_5 and $La_2Ti_2O_7$.[7] A modified part of the phase diagram in the region 30–50 mol% La_2O_3 was proposed. The existence of the $La_4Ti_3O_{12}$ compound was confirmed by German et al.[8] and Saltikova et al.,[9] but not by Jonker and Havinga.[10]

Early investigators reported the existence of $La_2Ti_3O_9$ (LT_3).[11–13] The compound was described as a defect perovskite containing up to 1/3 vacant A sites, as expressed by the formula $La_{2/3}TiO_3$. The slightly oxygen deficient compound was synthesized under reduced oxygen pressure at 1300°C.[14] Later on, monocrystals were grown in an air atmosphere from a flux of the KF–$Na_2B_4O_7$ system at 950–1000°C.[15] The authors concluded that $La_2Ti_3O_9$ can exist in stable form in the La_2O_3–TiO_2 system at around 1000°C in a higher oxygen pressure than reported in Ref. 14.

The cubic compound $La_2Ti_3O_9$ has also been synthesized by calcining coprecipitated hydroxides in the temperature region 400–800°C;[16] however it was established that it decomposes into $La_2Ti_2O_7$ and TiO_2 at higher temperatures. The compound was further detected after calcination of oxides in an oxidizing atmosphere at 1450–1500°C.[17] At present, it is generally accepted that the $La_{2/3}TiO_3$ structure may be stabilized by the presence of minute amounts of Ti^{3+} ions possessing a larger ionic size

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(0.067 nm) than Ti^{4+} ions (0.060 nm) and that it decomposes at lower temperatures in an air atmosphere following the oxidation of Ti^{3+}. This may be the reason that the compound $La_2Ti_3O_9$ was not included in the existing La_2O_3–TiO_2 diagram published in Ref. 5.

Contrary to the above data, stable $La_2Ti_3O_9$ was observed as a second phase in La_2O_3–TiO_2 and La_2O_3–Nb_2O_5–TiO_2 compositions fired in air at temperatures in the range 1300–1400°C.[4]

These conflicting data may arise from the strong influence of minute amounts of impurities on the stability of $La_2Ti_3O_9$. The perovskite structure was stabilized in the form of a solid solution with other ferroelectric perovskites, i.e. $PbTiO_3$,[18,19] $SrTiO_3$[20] and $BaTiO_3$.[13] It was also stabilized by partial filling of A-site vacancies with M^{1+} ions (M = Li, Na, K).[21] Recently it was reported that the structure may be stabilized by small additions of $LaAlO_3$[22] or $LaGaO_3$.[23]

3. Experimental

Samples were prepared from reagent grade La_2O_3 and TiO_2. Prior to weighing, the La_2O_3 content in the partially hydrated oxide was determined by weight loss after calcination. Two preparation routines were used to make samples for compound identification: (I) The required amounts of both oxides were well mixed in an agate mortar and pestle with acetone. The dried and pressed powder was fired on a Pt foil at 1400°C for about 60 h with intermittent air-quenching, crushing and repressing to assure equilibrium. (II) Prereacted ground powders were heated in a sealed Pt tube in the temperature range 1460–1690°C for 20 h and then quenched in liquid nitrogen. Prepared samples were analyzed by X-ray diffraction (XRD) analysis (Enraf-Nonius, Model FR 590). Polished surfaces of samples were examined by a scanning electron microscope (SEM) (JEOL, Model JXA 840 A) equipped with electron probe wavelength (WDS) and energy-dispersive X-ray (EDS) analyzers.

Monocrystals of tetragonal $La_{2/3}TiO_3$ were prepared following the same procedure as described in Ref. 15. Separated crystals were washed in boiled nitric acid for 10 h and further in boiled distilled water for more than 20 h.

Samples for electrical measurements were sintered on a Pt foil at 1500° for 5 h. The capacitance and dielectric losses were measured with a Hewlett Packard 4192A LF impedance analyzer.

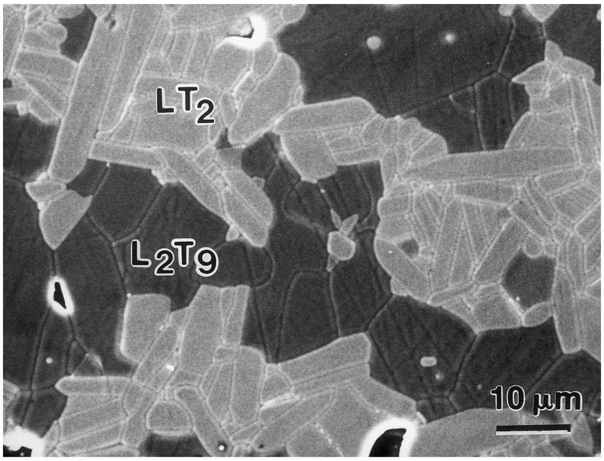
4. Results and discussion

4.1. $La_{2/3}TiO_3$ monocrystals

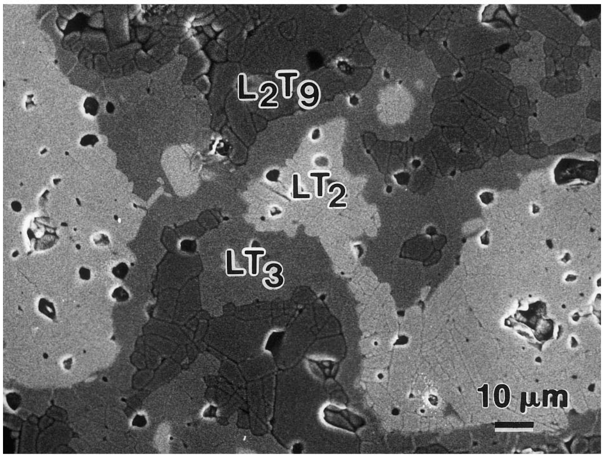
Following Ref. 15, $La_{2/3}TiO_3$ monocrystals were prepared from a KF–$Na_2B_4O_7$ flux at ~950°C in air. The crystals grew with a predominant cubic form and were up to 0.4 mm large. According to XRD, the crystals were tetragonal. Detailed SEM analysis of several monocrystals showed a high Na content and traces of K. The calculated composition of the monocrystals agreed well with the results of Belous et al.,[21] i.e. $(La_{2/3-x}Na_{3x})TiO_3$ with $x \sim 0.165$. Therefore it may be concluded that the stability of $La_{2/3}TiO_3$ at around 1000°C in air is due to a high Na impurity content.

4.2. High temperature stability of $La_{2/3}TiO_3$ phase

Our experiments confirmed that $La_{2/3}TiO_3$ is not stable in pure form in air at 1400°C, in accordance with Refs. 5 and 26. The microstructure of a sample with composition $La_{2/3}TiO_3$ fired at 1400°C in air in a clean (previously unused) Al_2O_3 tube showed the presence of L_2T_9 and LT_2 only (Fig. 1a). However, minute amounts of impurities may stabilize the compound $La_{2/3}TiO_3$. Fig. 1b shows a SEM micrograph of a composition corresponding to $La_{2/3}TiO_3$, fired three times at 1400°C

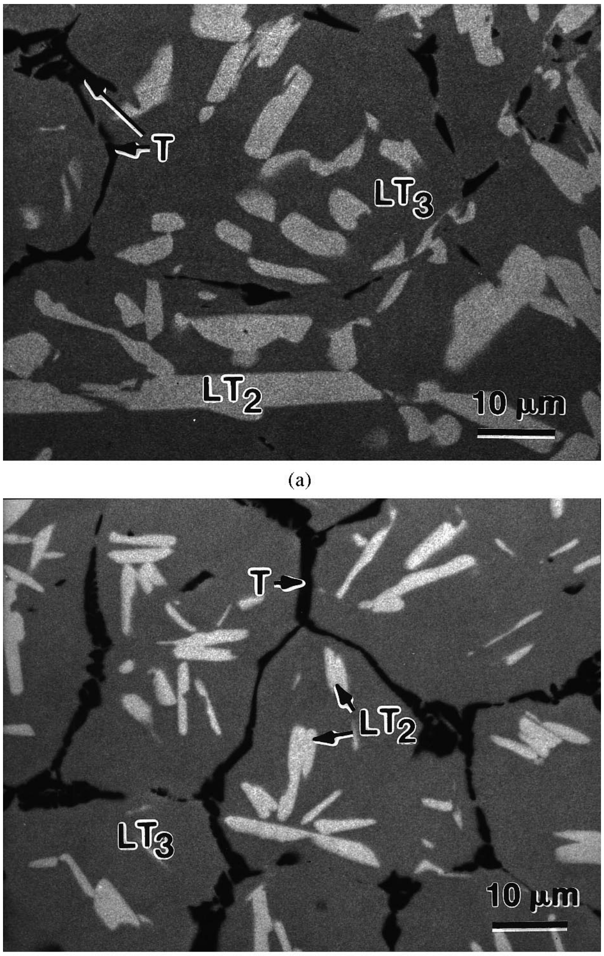


(a)



(b)

Fig. 1. SEM photomicrographs of ceramics with the starting composition La_2O_3:$3TiO_2$ equilibrated at 1400°C: (a) sample fired in a clean furnace exhibiting LT_2 (bright) phase and L_2T_9 (dark) phase; (b) sample fired in a contaminated furnace exhibiting LT_2, L_2T_9 and LT_3 (grey) phase on the LT_2–L_2T_9 phase boundary.



(a)

(b)

Fig. 2. Backscattered electron SEM images of a quenched sample with nominal composition La_2O_3:3TiO_2 fired at: (a) 1480°C and (b) 1540°C. Both microstructures show the same phases, namely a thermally stabilized LT_3 matrix, needle-like crystallites of LT_2 phase and solidified liquid-like TiO_2 phase.

in a furnace, contaminated from previous firing of other samples. The microstructure reveals the presence of the $La_{2/3}TiO_3$ phase at the boundaries between LT_2 and L_2T_9 grains.

In contrast to the sample fired at 1400°C, a quenched pure sample with composition $La_{2/3}TiO_3$ fired above 1455°C, i.e. above the melting temperature of $La_4Ti_9O_{24}$, always exhibits a three-phase microstructure (Fig. 2a). The picture shows a bright, needle-like $La_2Ti_2O_7$ phase and a solidified dark, liquid-like TiO_2 rich phase embedded in a grey matrix of stabilized $La_{2/3}TiO_3$ phase. The sample was fired at 1480°C. With increasing firing temperature the amount of the LT_2 phase decreases and the amount of $La_{2/3}TiO_3$ and TiO_2 rich phases increase, as demonstrated by comparing microstructures after firing at 1480°C (Fig. 2a) and 1540°C (Fig. 2b).

The reaction which takes place above the melting temperature of $La_4Ti_9O_{24}$ may be described in the following way: On peritectic melting, $La_4Ti_9O_{24}$ decomposes into $La_2Ti_2O_7$ and a TiO_2-rich melt. The reduction of Ti^{4+} to Ti^{3+} is facilitated in the melt. It was already noted[12,14] that small amounts of Ti^{3+} stabilize the $La_{2/3}TiO_3$ phase, which is a solid at the peritectic temperature of $La_4Ti_9O_{24}$ and precipitates from the melt. Stabilized $La_{2/3}TiO_3$ remains stable during cooling in air to room temperature, producing a three-phase structure.

The study of Abe and Uchino[14] on the effect of a reducing atmosphere on the crystal structure of $La_{2/3}TiO_3$ during heating showed that only 1.4 at% Ti^{3+} was necessary to stabilize the compound.

XRD analysis revealed that thermally stabilized $La_{2/3}TiO_3$ has a doubled unit cell, as is evident from the (001) peak in the X-ray diffraction pattern, at $2\Theta = 11.5°$ (Fig. 3). Inserted in Fig. 3 is the profile of the pseudo-cubic (200) peak, which is actually split into three (004), (020) and (200) lines, characteristic of an orthorhombic crystal structure. The result is in accordance with Ref. 14.

The estimated melting temperature of the starting composition La_2O_3:3TiO_2 determined by a optical heating microscope is 1660 ± 10°C.

4.3. Electrical measurements as evidence of the presence of Ti^{3+} ions in the $La_{2/3}TiO_3$ structure

Electrical measurements were used to ascertain the presence of Ti^{3+} ions in $La_{2/3}TiO_3$. The electrical resistivity of a sample with nominal composition $La_{2/3}TiO_3$, fired at 1500°C, was approximately $\rho = 10^8 - 10^9 \Omega$ cm, which is about two orders of magnitude lower than that of the monophase $La_{2/3}TiO_3$, stabilized with 4 mol% $LaAlO_3$. Low resistivity is indirect evidence for the transition $Ti^{4+} \rightarrow Ti^{3+}$ caused by oxygen deficiency.

Further indirect evidence for the presence of Ti^{3+} ions in the high temperature fired $La_{2/3}TiO_3$ samples was provided by dielectric measurements. The relative permittivity was calculated from capacitance measurements at 100 Hz to 1 MHz over the temperature range 20–110°C (under heating conditions). The dielectric constant at 20°C and 100 Hz was $\varepsilon_r \approx 73$ and at 1 MHz $\varepsilon_r \approx 68$. These values are similar to those reported by Nenasheva et al.[17] and Kim et al.[25] The difference in dielectric constant at 20°C over this frequency range was ~7%; however at 110°C the dielectric constant was about 3 times higher at 100 Hz than at 1 MHz. This difference probably arises from the contribution of space-charge polarization due to the existence of movable charge carriers in the sample fired to over 1455°C.

4.4. High temperature phase relations in the TiO_2-rich part of the La_2O_3–TiO_2 system

Microstructural examination, supported by EDS and WDS analysis, was extensively used to determine the high temperature phase relations in the 96–70 mol% TiO_2 composition region. Samples with 96 to 88 mol% TiO_2, quenched from 1500°C exhibited similar microstructures, consisting of primary TiO_2 crystals embedded in a solidified pseudo-binary eutectic containing $La_{2/3}TiO_3$ and $La_2Ti_2O_7$ phases (Fig. 4). WDS analysis performed on 5–10 TiO_2 grains could not detect dissolved La_2O_3 in TiO_2. The detection limit was estimated to be 300 ppm. The sample with 83 mol% TiO_2 after firing at 1500°C showed a pseudo-binary eutectic consisting of the same three phases, however with a much smaller number of TiO_2 crystals (Fig. 5). With further decrease in TiO_2, the microstructures exhibited increasing amounts of $La_{2/3}TiO_3$ and $La_2Ti_2O_7$ crystals in the solidified eutectic (Fig. 6). The microstructure of a sample with 70 mol% TiO_2 was composed of $La_{2/3}TiO_3$ and $La_2Ti_2O_7$ phases only, without a detectable eutectic phase (Fig. 7).

In samples with nominal composition 90% TiO_2, eutectic melting was observed at 1445 ± 3°C, which is in accordance with the reported eutectic temperature of 1445°C for the eutectic composition of about 83 mol% TiO_2, reported in Ref. 5. The microstructure of the sample quenched from 1450°C showed only primary TiO_2 grains in a solidified eutectic consisting of

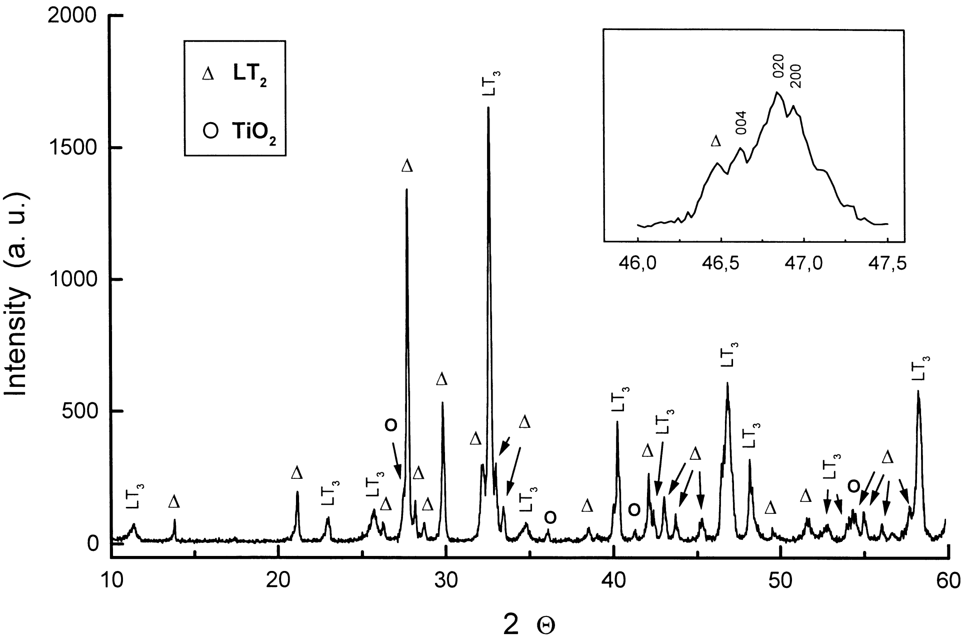


Fig. 3. X-ray pattern of the La_2O_3:$3TiO_2$ composition fired at 1500°C in air. The sample is composed of three phases: LT_3, LT_2 and TiO_2. The pseudo-cubic (200) XRD line of the thermally stabilized LT_3 phase which is split into three lines (004), (020) and (200) is inserted.

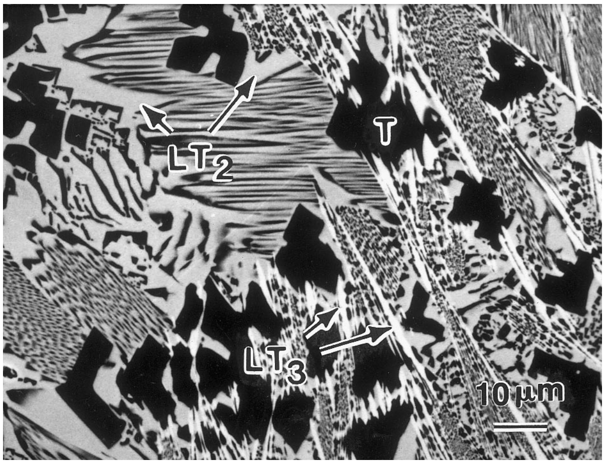


Fig. 4. Backscattered electron SEM image of a quenched sample with 12 mol% La_3O_3 heated at 1500°C. The microstructure shows primary TiO_2 crystals and a solidified pseudo-binary eutectic containing thermally stabilized LT_3 and LT_2 phases.

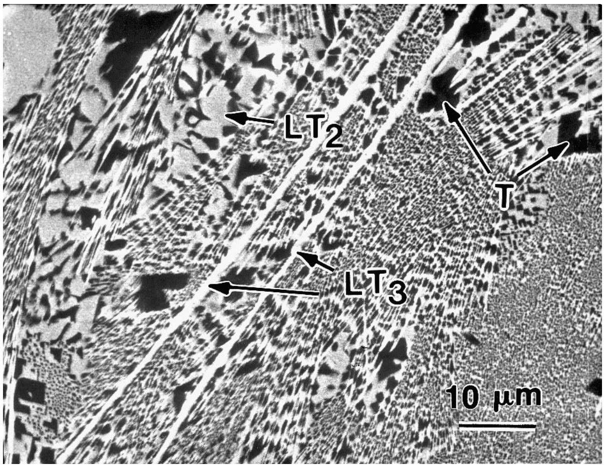


Fig. 5. Backscattered electron SEM image of a quenched sample with 17 mol% La_3O_3 heated at 1500°C showing a solidified pseudo-binary eutectic.

$La_4Ti_9O_{24}$ and fine TiO_2 grains, resulting from incongruent melting of $La_4Ti_9O_{24}$. $La_{2/3}TiO_3$ phase was not found in the microstructure of this sample. However, $La_{2/3}TiO_3$ appeared after refiring the sample at 1450°C in an argon atmosphere. Firing in an argon atmosphere has the same effect as increasing the temperature, i.e. increases the concentration of Ti^{3+} ions, which stabilize the $La_{2/3}TiO_3$ phase.

It may be concluded, that in compositions with 0–17 mol% La_2O_3, the temperature necessary to form $La_{2/3}TiO_3$ in air exceeds 1445°C.

4.5. *Low temperature phase relations in the TiO_2-rich part of the La_2O_3–TiO_2 system*

$La_{2/3}TiO_3$, stabilized by the presence of Ti^{3+} ions, also remains stable on prolonged heating in air or oxygen at lower temperatures. Fig. 8 shows the microstructure of a sample fired at 1500°C and afterwards annealed at 1300°C in air for 100 h. The presence of three phases, $La_2Ti_2O_7$, $La_4Ti_9O_{24}$ and $La_{2/3}TiO_3$ is clearly evident. It is obvious that the reaction $1/3\ (La_2O_3+3TiO_2) \rightleftarrows La_{2/3}(Ti^{4+}_{1-x}Ti^{3+}_{x})O_{3-1/2x}+1/4xO_2$ was not completely reversible. Several possible reasons can be listed:

a. Impurities originally present in the starting oxides concentrate in the melt during heating above 1455°C and they locally stabilize the perovskite $La_{2/3}TiO_3$ even at low temperatures.
b. Once formed, the microstructure above 1455°C, consisted mainly of the phases $La_2Ti_2O_7$ with $\rho = 5.782$ g/cm^3 (Ref. 3) and $La_{2/3}TiO_3$ with $\rho = 5.365$ g/cm^3 (calculated from the lattice parameters reported in Ref. 14 and similar to those reported in Ref. 18) represents an almost insurmountable obstacle to the formation of $La_4Ti_9O_{24}$ phase with $\rho = 4.984$ g/cm^3 (calculated from the lattice parameters reported in Ref. 24) which is appreciably lower than that of the other phases.

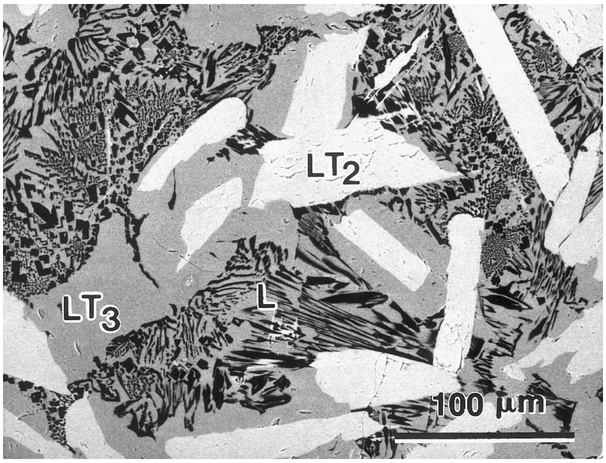


Fig. 6. Backscattered electron SEM image of a quenched sample with 23 mol% La_3O_3 heated at 1500°C showing primary LT_3 and LT_2 phases and a pseudo-binary eutectic.

4.6. *The compound $La_4Ti_3O_{12}$*

The existence of the compound $La_4Ti_3O_{12}$, reported in Refs. 6 and 7, is confirmed. In Ref. 7, it was also reported that the compound melts incongruently at 1450°C. We noted a higher decomposition temperature, 1590 ± 10°C, regardless of the preparation method, i.e. synthesis of the compound at 1400°C or heating of an oxide mixture with a La_2O_3–TiO_2 ratio of 2:3. On melting, the compound decomposes to La_2TiO_5 and $La_2Ti_2O_7$.

The phase diagram of the La_2O_3–TiO_2 is shown in Fig. 9. It reflects the fact that $La_{2/3}TiO_3$, once formed at

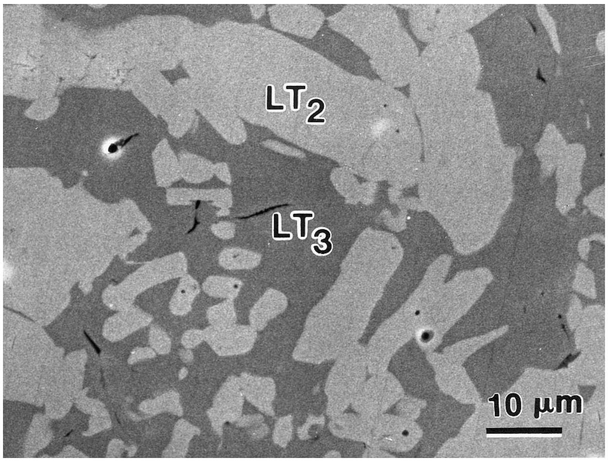


Fig. 7. Backscattered electron SEM image of a quenched sample with 30 mol% La_3O_3 heated at 1500°C. The sample exhibits LT_3 and LT_2 phases.

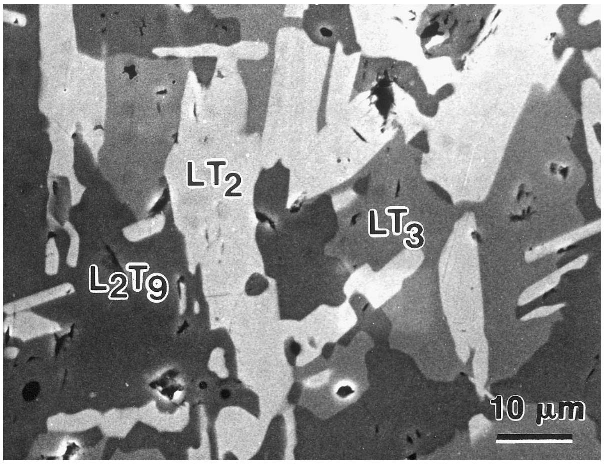


Fig. 8. Backscattered electron SEM image of a quenched sample with the starting composition La_2O_3:$3TiO_2$ equilibrated at 1500°C and annealed at 1300°C for 100 h. The sample is composed of L_2T_9, LT_3 and LT_2.

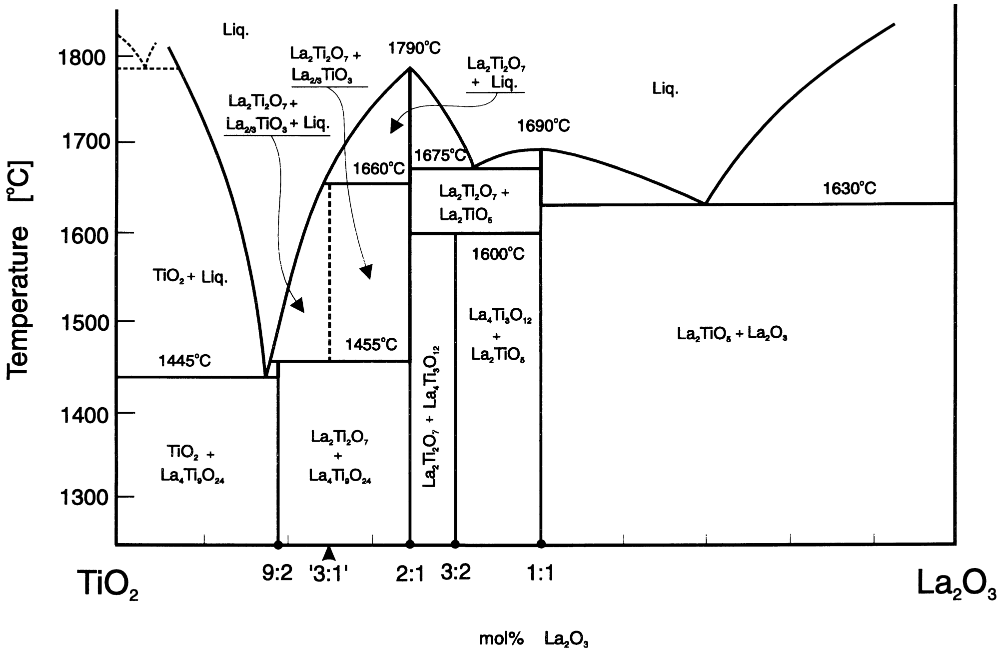


Fig. 9. The pseudo-binary La_2O_3–TiO_2 system.

high temperatures, remains stable. Due to the presence of three stable phases as shown, in Fig. 8, the La_2O_3–TiO_2 system is in the strict sense not a true binary system. Since the oxidation state of Ti^{4+} changes at high temperatures in air to Ti^{3+}, the diagram is to be regarded as a "section" through the complete system at the oxygen pressure in air at 1 atm, compositions being expressed in terms of the oxide components stable at room temperature.

Acknowledgements

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