Effects of Pb\textsuperscript{2+} doping on La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} ceramics

Yuan-Wen Liu · Pang Lin · Ming-Wen Chu

Abstract The kinetic structural evolution of the Pb\textsuperscript{2+}-doped La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} ceramics was investigated. Using electron diffraction and Rietveld analysis of the X-ray powder diffraction patterns, we show that the increase in Pb\textsuperscript{2+} doping results in the structural transition from La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} to a La\textsubscript{2/3}TiO\textsubscript{3}-type phase (Ibmm, No. 74). Further kinetic studies of Pb\textsuperscript{2+} diffusion into La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} ceramics suggest that the La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24}–La\textsubscript{2/3}TiO\textsubscript{3} phase transition requires an activation energy of 607 ± 60 kJ/mol.

Introduction

The La\textsubscript{2}O\textsubscript{3}–TiO\textsubscript{2} system exhibits interesting dielectric properties. In the study of MacChesney et al. [1], there exists three dielectric binary compounds, La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24}, La\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, and La\textsubscript{2}TiO\textsubscript{5}, in this class. More recently, Škapin et al. [2] suggested that the two new phases, La\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} and La\textsubscript{2/3}TiO\textsubscript{3}, should be incorporated into this material system.

The crystal structure of La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} has been resolved by Morris et al. [3] using the orthorhombic space group F\textit{ddd} (No. 70) with the lattice parameters \(a = 1.41458(1)\) nm, \(b = 3.55267(4)\) nm, and \(c = 1.45794(1)\) nm. The La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} lattice consists of a complex network of distorted titanium octahedra, showing corner- and edge-shared characteristics with one 8-fold and two crystallographically distinct 6-fold lanthanum ions in the structure. Figure 1a shows the unit cell of La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} in [001] direction. The La\textsubscript{3}-centered polyhedra form flat layers parallel to the ac plane (see the arrows in Fig. 1a), and the sandwiched region between two consecutive La(3)-centered polyhedra is composed of distorted TiO\textsubscript{6} octahedra that exhibit corner- and edge-shared features (see Fig. 1b, c). Furthermore, Ti(3)O\textsubscript{6} shows less distorted characteristics compared to the other four crystallographically distinct TiO\textsubscript{6} octahedra [3]. In a separate work [4], La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} was reported to possess good microwave dielectric properties, the relative dielectric constant (\(\varepsilon_r\)) ~37, the quality factor (\(Q\)) ~3060 at 8.1 GHz, and the temperature coefficient of the resonant frequency (TCF) ~15 ppm/°C.

The La\textsubscript{2/3}TiO\textsubscript{3}-type perovskite recently attracts significant attention due to its remarkable optical [5, 6], electrical [7–12], and microwave dielectric properties [13–18]. The structure of this A-site deficient phase is, however, unstable considering the associated high vacancy concentration. A careful experimental control is thus essential for synthesizing pure La\textsubscript{2/3}TiO\textsubscript{3} [1]. The slightly oxygen-deficient La\textsubscript{2/3}TiO\textsubscript{3–i} with a non-negligible contribution of Ti\textsuperscript{3+} was prepared using conventional solid-state reaction in a reduced CO\textsubscript{2}–H\textsubscript{2} atmosphere at 1,350 °C [19], using flux growth in air [20], and using hydrothermal method [21]. It was reported that a finite amount of Na\textsuperscript{+}, K\textsuperscript{+}, and/or Li\textsuperscript{+} doping on the A-site is also favorable to stabilize the La\textsubscript{2/3}TiO\textsubscript{3}-type phase [12, 22]. Škapin et al. further indicated that firing stoichiometric La\textsubscript{2}O\textsubscript{3}/3TiO\textsubscript{2} at a temperature above the melting point of La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} ~1455 °C in air results in the presence of Ti\textsuperscript{3+}, dramatically stabilizing the La\textsubscript{2/3}TiO\textsubscript{3}-type perovskite [2]. Other studies also pointed out that the La\textsubscript{2/3}TiO\textsubscript{3}-type phase...
can co-exist with ferroelectric perovskites \cite{14, 23–26} and LaNO$_3$ (N = Al$^{3+}$, Ga$^{3+}$ and Fe$^{3+}$, Refs. \cite{8, 13, 26–29}). More importantly, the crystal structure of the La$_{2/3}$TiO$_3$-type phase is characterized by a long-range cation/vacancy ordering on the perovskite A-site \cite{7, 12, 22, 28, 29}.

There have been numerous studies concerning influences of Pb$^{2+}$ doping on the La$_2$O$_3$–TiO$_2$ system \cite{30, 31}, whereas a detailed report particularly on the Pb$^{2+}$–La$_4$Ti$_9$O$_{24}$ system remains lacking. We thus performed a systematic investigation of La$_4$Ti$_9$O$_{24}$ ceramics with various Pb$^{2+}$ doping and further discussed the correlation with the La$_{2/3}$TiO$_3$-type phase.

### Experiments

The La$_4$Ti$_9$O$_{24}$ compounds with various Pb$^{2+}$-doping degrees were prepared by the chemical co-precipitation method as shown in Fig. 2. La(NO$_3$)$_3$ · 6H$_2$O (Strem chemicals, 99.9%), TiCl$_4$ (Merck, 99%), Pb(NO$_3$)$_2$ (Showa chemical, 99.5%), and NH$_4$OH (TEDIA company, ACS grade) were exploited as the starting chemicals. The concentration of the mixture solution was kept at ~0.1 M for all syntheses with D.I. water as the solvent. The co-precipitated powders were then calcined at 900 °C for 1 h in air.

The La$_4$Ti$_9$O$_{24}$ ceramic bulks for performing Pb$^{2+}$/La$_4$Ti$_9$O$_{24}$ interaction investigations were prepared by conventional solid-state reaction. After mixing and calcination at 1,000 °C for 1 h in air, the powders were then ground, sieved, and pressed into pellets (9 mm in diameter and 2 mm in thickness) for further sintering at 1,350 °C for 4 h in air. Subsequently, the sintered pellets were polished and coated...
with the PbO slurry, to prevent the PbO coated on the samples escaping when heating, the samples were put into closed platinum crucible with extra PbO powders around the samples. Followed by annealing at 750, 775, 800, 825, 850, 875, and 900 °C for 0.5–14 h using a pre-heated vertical furnace with an air-atmosphere quenching after the heat treatment. The cross-sectional Pb\textsuperscript{2+}/La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} ceramic specimens was then polished and studied by SEM (HITACHI S2500) equipped with EDX and WDX.

The X-ray diffraction (XRD) patterns were recorded at room temperature using a MACScience M18XHF diffractometer with Cu-K\textalpha\textsubscript{1} radiation. The transmission electron microscopy (TEM) study was performed on JEOL 2000FX operating at 200 kV.

**Results and discussion**

The interaction between Pb\textsuperscript{2+} and sintered La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24}

In order to understand the interaction between Pb\textsuperscript{2+} and La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24}, the PbO coated ceramic bulk was annealed at 900 °C for 4 h. Figure 3 shows the SEM/EDS analysis of thus-prepared sample, revealing a significant Pb\textsuperscript{2+} diffusion into La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24}. Further XRD studies were thus performed to investigate the crystallization of each layer indicated in Fig. 3. Figure 4 shows the corresponding XRD pattern and a significant crystallization of the La\textsubscript{2/3}TiO\textsubscript{3}-type phase is clearly observed in Layer I.

The Pb\textsuperscript{2+} diffusion into crystalline La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} results in an increase in the internal stress of La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} due to the relatively large size of Pb\textsuperscript{2+} \((r = 0.129 \text{ nm}, \text{CN} = 8)\) compared to La\textsuperscript{3+} \((r = 0.118 \text{ nm}, \text{CN} = 8)\) and the stereochemical activity of 6s\textsuperscript{2} lone-pair electrons of Pb\textsuperscript{2+} [32]. The formation of the corner-sheared TiO\textsubscript{6} configuration could be a feasible approach to relax this internal stress, thus leading to the modification of the La\textsubscript{2/3}TiO\textsubscript{3} lattice (see Fig. 1) further favoring the distorted La\textsubscript{2/3}TiO\textsubscript{3}-type perovskite [33]. In another view of the influence of impurities on the stability of La\textsubscript{2/3}TiO\textsubscript{3} [12–15, 22–29], the La\textsubscript{2/3}TiO\textsubscript{3}-type perovskite structure could be stabilized by the partial filling of the A-site vacancies with Pb\textsuperscript{2+} ions.

The TEM micrograph of the cross-sectional Pb\textsuperscript{2+} diffused area /La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} interface is shown in Fig. 5a, and the corresponding selected-area electron diffraction (SAED) pattern of the Pb\textsuperscript{2+} diffused area is depicted in Fig. 5b. The estimation of the real-space distance between the first intense ring and the transmitted beam leads to \(-0.28 \text{ nm}\) (see Fig. 5b), suggesting the possible crystallization of a perovskite-related phase at the interface with \(a_p \approx 0.38 \text{ nm}\) \(\left( a_p, \text{the prototypical lattice parameter of cubic perovskites} \right)\) in consistency with the XRD study shown in Fig. 4. Further measuring the composition in the vicinity of the interface by WDX gives rise to (La\textsubscript{4}Pb\textsubscript{3})TiO\textsubscript{3} that is close to the intersection of the PbO–La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} Alkemade line and the PbTiO\textsubscript{3}–La\textsubscript{2/3}TiO\textsubscript{3} tie line (see Fig. 6), the nominal composition of (La\textsubscript{4}Pb\textsubscript{3})TiO\textsubscript{3}. Taking above characteristics into account, we thus proceeded to synthesize the La\textsubscript{2/3}TiO\textsubscript{3}-type phase by Pb\textsuperscript{2+}-doping into La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24}.

**Fig. 3** SEM micrograph and EDX line scan of the cross-sectional Pb\textsuperscript{2+}/La\textsubscript{4}Ti\textsubscript{9}O\textsubscript{24} ceramics. S denotes the free surface

**Fig. 4** The corresponding XRD patterns of the sample in Fig. 3
The nominal compositions exploited in the synthesis are given in Table 1, and the specimen indices are also shown in Fig. 6. Note that specimen No. 10 is the intersection composition of the PbO–La$_4$Ti$_9$O$_{24}$ Alkemade line and the PbTiO$_3$–La$_{2/3}$TiO$_3$ tie line. The XRD patterns of the co-precipitation powders calcined at 900 °C are shown in Fig. 7, revealing the increase in the La$_{2/3}$TiO$_3$-type phase with the increase in the Pb$^{2+}$ doping. When the Pb$^{2+}$ doping approaches 3 moles, the La$_{2/3}$TiO$_3$-type structure becomes the dominant phase.

![Fig. 5](image1.png)  
Fig. 5 (a) TEM image of the Pb$^{2+}$ diffused area/La$_4$Ti$_9$O$_{24}$ interface and (b) the corresponding SAED pattern of the Pb$^{2+}$ diffused area

Study of co-precipitated Pb$^{2+}$-doped La$_4$Ti$_9$O$_{24}$

The nominal compositions exploited in the synthesis are given in Table 1, and the specimen indices are also shown in Fig. 6. Note that specimen No. 10 is the intersection composition of the PbO–La$_4$Ti$_9$O$_{24}$ Alkemade line and the PbTiO$_3$–La$_{2/3}$TiO$_3$ tie line. The XRD patterns of the co-precipitation powders calcined at 900 °C are shown in Fig. 7, revealing the increase in the La$_{2/3}$TiO$_3$-type phase with the increase in the Pb$^{2+}$ doping. When the Pb$^{2+}$ doping approaches 3 moles, the La$_{2/3}$TiO$_3$-type structure becomes the dominant phase.

![Table 1](image2.png)  
Table 1 The nominal compositions of the co-precipitated powders

<table>
<thead>
<tr>
<th>Specimen no.</th>
<th>Nominal composition</th>
<th>Composition (mole)</th>
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<tr>
<td></td>
<td>La$^{3+}$ Ti$^{4+}$ Pb$^{2+}$</td>
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</tr>
<tr>
<td>1</td>
<td>(La$<em>{0.44}$ Pb$</em>{0.03}$)TiO$_3$</td>
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<tr>
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<tr>
<td>9</td>
<td>(La$<em>{0.44}$ Pb$</em>{0.28}$)TiO$_3$</td>
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<tr>
<td>10</td>
<td>(La$<em>{0.44}$ Pb$</em>{0.33}$)TiO$_3$</td>
<td>4.00 9.00 3.00</td>
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</table>

![Fig. 7](image3.png)  
Fig. 7 XRD patterns of co-precipitated (La$_{0.44}$Pb$_x$)TiO$_3$ powders calcined at 900 °C for 1 h in air with different Pb$^{2+}$ concentration
The \([-110\) \(p\)-zone SAED pattern of specimen No.10 is shown in Fig. 8 (the subscript ‘p’ denoting cubic perovskites). Note that this pattern shows extra weak reflections, (001) \(O\) and (101) \(O\), indicating an orthorhombic superlattice with \(a \sim b \sim 0.55 \text{ nm} \sim 2a_p\) and \(c \sim 0.77 \text{ nm} \sim 2a_p\). Furthermore, the indices of the weak reflections are compatible with the space group \(Ibmm\) (No. 74). In the study of \(La_{1-x}TiO_3\) (0 \(\leq x \leq 0.33\)) \([7]\), it has been suggested that the crystal structure of the material is a function of the corresponding composition, \(Pbnm\) (No. 62, 0 \(\leq x \leq 0.2\)), \(Ibmm\) (No. 74, 0.2 \(\leq x \leq 0.25\)), and \(Pban\) (No. 50, 0.25 \(\leq x \leq 0.33\)). Moreover, the three orthorhombic cells all possess similar lattice parameters of \(a \sim b \sim \sqrt{2} a_p\) and \(c \sim 2a_p\). Considering the above features, specimen No. 10 with nominal \((La_{0.44}Pb_{0.33})TiO_3\) should thus exhibit the space group \(Ibmm\) (No. 74), which is indeed observed in the SAED study (see Fig. 8).

We then performed Rietveld analysis (RIETICA software \([34]\)) on the XRD pattern of specimen No.10 using space group \(Ibmm\) (No. 74) with the nominal composition \((La_{0.44}Pb_{0.33})TiO_3\). The refined lattice parameters are shown in Table 2, and the presence of heavy Pb limits the determination of the respective atomic position with enough precisions \([35]\).

**Kinetic studies of Pb\(^{2+}\) diffusion into \(La_4Ti_9O_{24}\)**

The kinetics of Pb\(^{2+}\) diffusion into \(La_4Ti_9O_{24}\) ceramics was investigated at various annealing temperatures and the average thickness of the reacted layer was estimated by SEM. Figure 3 represents a typical example of the SEM estimation of the reacted layer. The reacted zone consists of the orthorhombic \(La_{2/3}TiO_3\)-type phase with the nominal composition \((La_{0.44}Pb_{0.33})TiO_3\). Figure 9 exhibits the linear dependence of the square of the thickness of the reacted layer, \(x\), on the heat-treated time, \(t\), in excellent agreement with the parabolic law \(x^2 = kt\), where \(k\) is the growth rate coefficient. The kinetic study thus indicates that the Pb\(^{2+}\)/\(La_4Ti_9O_{24}\) interaction strictly obeys the theory of the reactive diffusion \([36, 37]\). Calculating the gradient of each line in Fig. 9 leads to the growth rate coefficient, \(k\), at different annealing temperatures, tabulated in Table 3. Furthermore, the experimental \(k\) values were used to determine the associated activation energy, \(E_a\), for the formation of orthorhombic \((La_{0.44}Pb_{0.33})TiO_3\) using the Arrhenius plot (Fig. 10) and the following least-square equation,

\[
\ln(k) = -\frac{E_a}{RT} + A,
\]

where \(T\) is the annealing temperature; \(R\) is the universal gas constant, and \(A\) is a constant, resulting in \(E_a \sim 607 \pm 60 \text{ kJ/mol}\). Similar \(E_a\) value of Pb\(^{2+}\) diffusion could be compared in the study of Cherniak et al. \([38]\).

The good correlation between the parabolic rate constant for Pb\(^{2+}\) and that for the activation energy provides

![Fig. 8 The \([-110\) \(p\)-zone SAED pattern of \((La_{0.44}Pb_{0.33})TiO_3\). The subscript ‘o’ represents the orthorhombic superstructure](image)

![Fig. 9 The thickness square of the reacted layer at different temperatures as a function of on different annealing times](image)

<table>
<thead>
<tr>
<th>2 Theta range (°)</th>
<th>Step size (°)</th>
<th>Step time (s)</th>
<th>Crystal class</th>
<th>Space group</th>
<th>(A) (nm)</th>
<th>(B) (nm)</th>
<th>(C) (nm)</th>
<th>(V) (nm(^3))</th>
<th>Calculated density (g/cm(^3))</th>
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<td>20–80°</td>
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<td>0.5 s</td>
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<td>(Ibmm) (No. 74)</td>
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<td>0.55064</td>
<td>0.77825</td>
<td>0.23728</td>
<td>6.018</td>
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</table>

**Table 2 The Rietveld refinement results of \(La_{0.44}Pb_{0.33}TiO_3\)**
evidence to the assumption that the reaction kinetics of (La0.44Pb0.33)TiO3 phase formation is controlled by Pb2+ diffusion in the (La0.44Pb0.33)TiO3 ceramics, not the Pb2+/La4Ti9O24 interface reaction rate controlling process.

Conclusions

The structure of La4Ti9O24 ceramics with different Pb2+ doping additions was investigated. When 1 mole of La4Ti9O24 ceramics is reacted with 3 moles of PbO, the ‘parent’ La4Ti9O24 phase transforms to the La2/3TiO3-type phase with a composition of (La0.44Pb0.33)TiO3. Further electron diffraction and XRD refinements indicated that (La0.44Pb0.33)TiO3 crystallizes in the orthorhombic space group Ibmm (No. 74) with a = 0.55371 nm, b = 0.55064 nm, and c = 0.77825 nm. The activation energy of this Pb2+-induced phase transition is 607 ± 60 kJ/mol.

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References