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Rapid communication

La(Li_{1/3}Ti_{2/3})O₃: a new 1:2 ordered perovskite

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Abstract

A new 1:2 ordered perovskite La(Li_{1/3}Ti_{2/3})O₃ has been synthesized via solid-state techniques. At temperature >1185°C, Li and Ti are randomly distributed on the *B*-sites and the X-ray powder patterns can be indexed in a tilted (*b*⁻*b*⁻*c*⁺) *Pbnm* orthorhombic cell (*a* = *a_c*√2 = 5.545 Å, *b* = *a_c*√2 = 5.561 Å, *c* = 2*a_c* = 7.835 Å). However, for *T* ≤ 1175°C, a 1:2 layered ordering of Li and Ti along <111>_{*c*} yields a structure with a *P2₁/c* monoclinic cell with *a* = *a_c*√6 = 9.604 Å, *b* = *a_c*√2 = 5.552 Å, *c* = *a_c*3√2 = 16.661 Å, β = 125.12°. While this type of order is well known in the *A*²⁺(*B*_{1/3}²⁺*B*_{2/3}⁵⁺)O₃ family of niobates and tantalates, La(Li_{1/3}Ti_{2/3})O₃ is the first example of a titanate perovskite with a 1:2 ordering of cations on the *B*-sites.

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Over the last 40 years numerous examples of *B*-site ordered mixed-metal perovskites have been reported in the literature. Compared to the many *A*(*B*_{*x*}^I*B*_{*y*}^{II})O₃ compounds with *x* : *y* = 1 : 1 that form a 1:1 ordered, “doubled” perovskite structure (*a*_{ord} = 2*a_c*, where *a_c* represents the cell parameter of the ideal cubic sub-cell), there are relatively few examples of systems with 1:2 or 1:3 cation order. The first observation of 1:2 order in a perovskite was reported in Ba(Sr_{1/3}Ta_{2/3})O₃ by Galasso et al. [1], where a 1:2 layering of Sr and Ta (...SrTaTa...) along <111> yields a hexagonal superstructure with *a*_{ord} = *a_c*√2 and *c*_{ord} = *a_c*√3 (Fig. 1). This type of arrangement was subsequently observed in other niobate and tantalate members of the *A*²⁺(*B*_{1/3}²⁺*B*_{2/3}⁵⁺)O₃ family of perovskites with *A*²⁺ = Ca, Sr, Ba; *B*²⁺ = Mg, Ca, Sr, Mn, Fe, Co, Ni, Cu, Zn; and *B*⁵⁺ = Nb, Ta [2–4]. These compounds include BaZn_{1/3}Ta_{2/3}O₃, which due to its unique dielectric properties has become one of the most important materials for the microwave ceramics industry. As some investigations have suggested that the best dielectric properties, in particular the lowest microwave losses, are associated with the 1:2 ordered state [5], there is considerable interest in preparing new materials with this structure type. However, aside from the recently reported ordering in BaBi_{2/3}³⁺Te_{1/3}⁶⁺O₃ [6], all of the known 1:2 ordered perovskites are restricted to the *A*²⁺(*B*_{1/3}²⁺*B*_{2/3}⁵⁺)O₃ family. In this rapid communication, we report the synthesis of La(Li_{1/3}Ti_{2/3})O₃, the first

example of a perovskite with 1:2 ordering of *B*¹⁺ and *B*⁴⁺ cations on the octahedral sites.

Previous investigations of the La₂O₃–TiO₂–Li₂O ternary system found a range of mixed *A*-site perovskite solid solutions exist along the pseudo-binary “La_{2/3}TiO₃”–(La_{1/2}Li_{1/2})TiO₃ join [7,8]. Although one of those papers also alluded to a preliminary study of a perovskite compound “LaLi_{1/3}Ti_{2/3}O₃”, no data were included for its preparation and its structure was not investigated [7]. In our work the title compound was initially prepared by mixing stoichiometric amounts of Li₂CO₃ (Baker, 99.0%), TiO₂ (Cerac, 99.9%), and La₂O₃ (Cerac, 99.99%) under acetone in an agate mortar, pre-firing at 700°C to expel CO₂ and calcining at 1050°C. After ball-milling the resultant powder was isostatically pressed into pellets at 80,000 psi. In an attempt to avoid the loss of Li during sintering, the pellets were wrapped in Pt envelopes together with a sacrificial powder of the same composition, annealed at 1300–1350°C for 10 h, and cooled (≤1°C/min) to 900°C. In addition to a perovskite product the powder diffraction patterns of the pellets, and to a greater extent of the sacrificial powder, contained peaks from a La₂Ti₂O₇ impurity phase indicating significant Li loss. Weight measurement revealed that ~8% of the stoichiometric Li content was lost (in the form of Li₂O) during this synthesis procedure. Deliberate introduction of a 10% excess of Li into the initial mixture did eliminate the impurity peaks in the XRD pattern but this effect was lost on prolonged annealing. A more effective method for inhibiting the loss of Li was

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to use an Li-rich sacrificial powder, namely Li_2TiO_3 , which does not melt within the synthesis temperature range [9] and has considerable tolerance to Li loss without undergoing phase decomposition [10].

The XRD pattern collected from a stoichiometric pellet of $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$, prepared via the Li_2TiO_3 -muffling route using the same calcination temperatures described above, is shown in Fig. 2. Although many of the peaks in the pattern could be indexed in a $Pbnm$ orthorhombic cell ($a = a_c\sqrt{2} = 5.545 \text{ \AA}$, $b = a_c\sqrt{2} = 5.561 \text{ \AA}$, $c = 2a_c = 7.835 \text{ \AA}$) with a tilted structure similar to LaFeO_3 ($b^-b^-c^+$ in Glazer notation [11]), a set of additional reflections (denoted with asterisks) remained unindexed. However, the pattern could be completely indexed using a monoclinic cell (space group $P2_1/c$) recently described for a 1:2 B -site ordered form

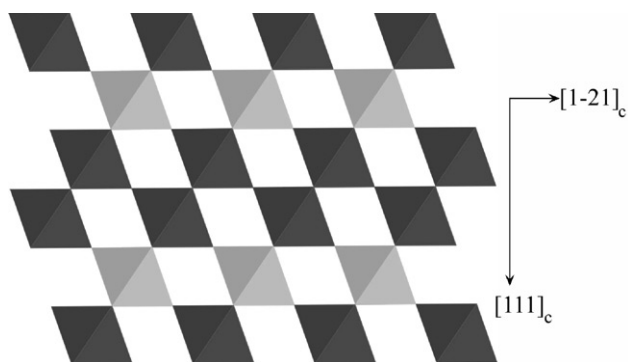


Fig. 1. Polyhedral representation of the 1:2 ordered $A^{2+}(B_{1/3}^{2+}B_{2/3}^{5+})\text{O}_3$ systems. B^{5+} octahedra are shown in black, B^{2+} octahedra in gray; oxygen and Ba ions are omitted for clarity. Crystallographic directions are given for cubic sub-cell.

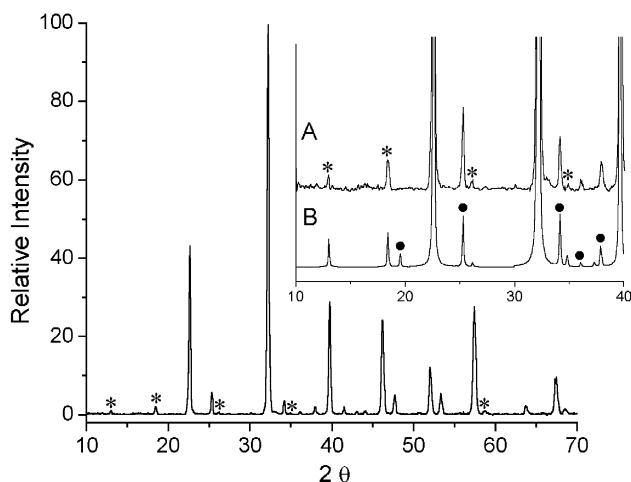


Fig. 2. Powder X-ray diffraction pattern of slow-cooled $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$ (ordering peaks are marked with asterisks). Inset shows the agreement between observed (A) and calculated (B) diffraction patterns in the lower angle region of the patterns; reflections arising from octahedral tilting are dotted.

of $\text{Ca}(\text{Ca}_{1/3}\text{Nb}_{2/3})\text{O}_3$ that exhibits the same type of tilt system [12,13]. Least-squares refinement of the cell parameters using the $P2_1/c$ structure yielded $a = a_c\sqrt{6} = 9.604 \text{ \AA}$, $b = a_c\sqrt{2} = 5.552 \text{ \AA}$, $c = a_c3\sqrt{2} = 16.661 \text{ \AA}$, $\beta = 125.12^\circ$. Electron diffraction studies (conducted using a Philips 420T TEM/STEM operated at 120 kV) confirmed the presence of 1:2 type order with the ordering reflections at $k = 1/3(111)^*_c$ being clearly visible in the patterns collected along $[110]_c$ (see Fig. 3).

The formation of a 1:2 ordered structure in $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$ was supported by calculations of the X-ray diffraction pattern of the $P2_1/c$ superstructure. In these calculations the positions of the oxygen atoms were estimated using the same tilt angles observed in LaFeO_3 which has an almost identical tolerance factor (0.961 compared to 0.957 for $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$) [14]. The calculated and experimental patterns are compared in the inset in Fig. 2; complete data for the indexing and intensities are given in Table 1. The excellent agreement between the observed and calculated intensities of the peaks originating from the chemical order provides additional direct support for the 1:2 ordering of Li and Ti on the B -site. As expected some differences were observed in the calculated intensities of the tilting

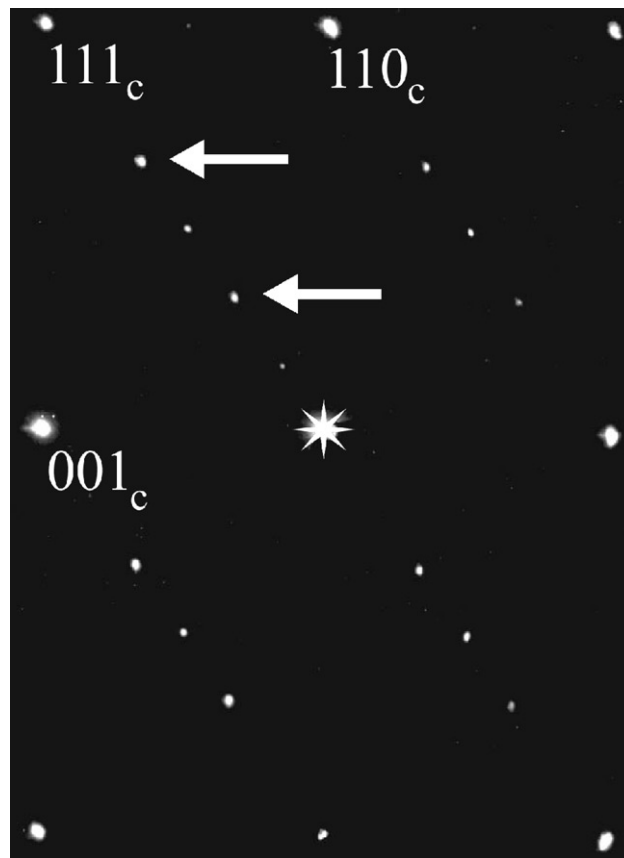


Fig. 3. $(110)_c$ zone axis electron diffraction pattern of ordered $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$; examples of reflections associated with tripling of $(111)_c$ direction are arrowed.

Table 1
Indexed diffraction pattern of 1:2 ordered $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$

$2\theta_{\text{obs}}$	$2\theta_{\text{calc}}^a$	I_{obs}	I_{calc}^a	(hkl)
12.96	12.97	1	2	(002)
18.42	18.44	2	2	(-111), (-202)
22.60	22.61	46	55	(11-3), (200)
25.31	25.32	6	4	(-213), (0-13)
26.11	26.12	1	<1	(004)
32.19	32.20	100	100	(20-6), (31-3), (1-13), (020)
34.16	34.21	4	4	(30-6), (10-6), (120)
34.89	34.87	<1	1	(-315), (-311), (0-22)
36.10	36.12	1	1	(21-6)
37.95	37.95	2	2	(3-10), (-223), (02-3)
39.70	39.71	32	31	(40-6), (-406), (-220)
41.47	41.38	2	1	(-413), (2-13)
43.04	43.04	1	1	(-416), (016), (-323), (1-23)
46.18	46.18	28	49	(400), (-226)
47.67	47.69	5	3	(32-6), (12-6)
50.68	50.60	2	1	(-423), (2-23)
52.03	52.02	13	15	(31-9), (-513), (3-13), (-426), (0-26), (13-3)
53.33	53.40	6	3	(41-9), (21-9)
57.43	57.42	32	35	(-519), (11-9), (206), (4-20), (-333), (1-33)
58.72	58.71	1	1	(12-8), (-524)

^a $2\theta_{\text{calc}}$ and I_{calc} values are weighed averages over corresponding (hkl).

reflections, which depend strongly on the exact positions of the oxygen atoms. A complete refinement of the structure, using data collected using neutron and synchrotron X-ray diffraction, is currently in progress.

In an attempt to locate any transitions in the ordering at elevated temperature, samples (pellets or pellet fragments) of ordered $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$ were placed in Pt envelopes with a sacrificial powder of the same composition, annealed for 1 h (to avoid any loss of Li), and air-quenched. The 1:2 ordered structure was found to transform directly to a disordered perovskite (with a *Pbnm* orthorhombic cell) between 1175°C and 1185°C (Fig. 4). The order–disorder transition temperature is quite low compared to those observed in the $A^{2+}(\text{B}_{1/3}^{2+}\text{B}_{2/3}^{5+})\text{O}_3$ family of 1:2 ordered perovskites which retain an ordered arrangement to $T^{\text{s}} > 1350^\circ\text{C}$. The ordered form of $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$ was readily recovered by annealing at 1100–1150°C.

It is noteworthy that the cation order in this compound seems to be very sensitive to an excess of Li. For example, if a pellet with 10% excess Li is used to prepare $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$ via the Li_2TiO_3 –“muffling” route, the resultant perovskite product is disordered. This behavior probably arises from the partial substitution of Li onto the *A*-site and suggests that a series of solid solutions might exist along the $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$ – $(\text{La}_{1/2}\text{Li}_{1/2})\text{TiO}_3$ join in the Li_2O – La_2O_3 – TiO_2 ternary system.

The addition of $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$ to the relatively short list of perovskites with 1:2 *B*-site order is consistent with the criteria previously identified for the stabilization of this structure type [6,15–17]. In the 1:2 ordered

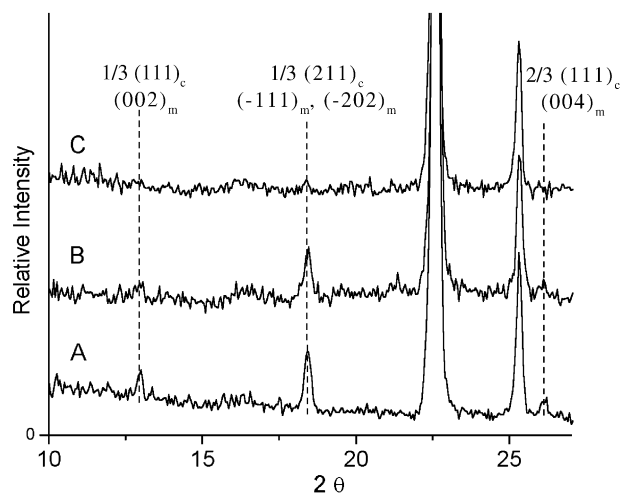


Fig. 4. Low-angle region of the diffraction pattern of $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$: (A) slow-cooled, (B) quenched from 1175°C, (C) quenched from 1185°C. 1:2 ordering peaks are indexed in terms of the cubic sub-cell and the monoclinic supercell.

$A(\text{B}_{1/3}^I\text{B}_{2/3}^{II})\text{O}_3$ systems, the different size and charge of the $\langle 111 \rangle_c$ ordered B^I/B^{II} cations is accommodated via a concerted displacement of the intermediate anion layers toward the smaller, more highly charged *B*-site ion (typically B^{II}). However, because the anions lying between two B^{II} layers are over-bonded, the structure only forms when the B^{II} cations can undergo a displacement away from the center of their octahedra to lengthen the three B^{II} – O – B^{II} bonds and shorten the three B^{II} – O – B^I bonds. (e.g. Refs. [6,18]). This off-centered coordination is usually observed only for small

highly charged cations such as Nb^{5+} , Ta^{5+} , and Ti^{4+} or cations with a lone pair of electrons (e.g. Bi^{3+}). Therefore, while 1:2 order is observed in the $A^{2+}(B_{1/3}^{2+}B_{2/3}^{5+})\text{O}_3$ niobates and tantalates, in $\text{Ba}(\text{Te}_{1/3}^{6+}\text{Bi}_{2/3}^{3+})\text{O}_3$ [6], and the new $\text{La}(\text{Li}_{1/3}\text{Ti}_{2/3})\text{O}_3$ perovskite reported here, it is not adopted by compounds such as $\text{Ba}(\text{W}_{1/3}\text{Sc}_{2/3}^{3+})\text{O}_3$ or $\text{La}(\text{Ta}_{1/3}\text{M}_{2/3}^{2+})\text{O}_3$, where a distorted octahedral environment for the majority *B*-site ion (Sc and M^{2+} (Zn, Mg), in the examples cited) is not stable [16,17].

Acknowledgments

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