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Crystal structure of the mixed conductors phases, $Li_{0.5-3x}La_{0.5+x+y}Ti_{1-3y}M_{3y}O_3$ (M = Mn, Cr) with $x = 0.133$ and $y = 0.20$

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Perovskite-like solid solutions of general formula $Li_{0.5-3x}La_{0.5+x+y}Ti_{1-3y}M_{3y}O_3$ (M = Mn, Cr) show three polymorphs; A, β and C. The crystal structure of the C polymorphs in manganese– and chromium–lanthanum systems, determined from powder neutron diffraction using Rietveld refinement, are of the ordered perovskite type. The structures of both phases are similar, containing a three dimensional framework of corner-sharing MO_6 (M = Ti or Mn/Cr) octahedra in which the structures are partially collapsed as a result of a cooperative tilting and rotation of octahedra. Orthorhombic unit cell, M = Mn: $a = 5.5411(11)$ Å, $b = 7.8120(14)$ Å, $c = 5.4924(10)$ Å; M = Cr: $a = 5.5014(9)$ Å, $b = 7.7735(15)$ Å, $c = 5.4729(9)$ Å; space group *Pnma* (no. 62). Ionic conductivity takes place by a hopping mechanism between Li^+-occupied and empty A-sites, while electronic conductivity is along octahedra.

The family of Li^+ ion-conductors with perovskite-like structure of general formula $Li_{0.5-3x}RE_{0.5+x}TiO_3$ (RE = La, Pr, Nd, Sm) has been extensively studied because of their high Li-ion conductivity. The maximum bulk ionic conductivity is found in the lanthanum system with a value of 1.1×10^{-3} S cm^{-1} for $x = 0.07$.[1–4]

A few years ago, phase diagrams of La, Pr and Nd systems were reported,[5,6] which show two polymorphs in the lanthanum system, labelled A and β, and three polymorphs, A, β and C, in the praseodymium and neodymium systems. All of these have a perovskite-related structure. Polymorph A is a simple cubic perovskite, while β is a tetragonal perovskite with $a_o = b_o \approx a_c$ and $c_o \approx 2a_c$, and C is an orthorhombic distortion of A with $a_o = \sqrt{2}a_c + \delta$, $b_o \approx 2a_c$ and $c_o = \sqrt{2}a_c - \delta$, where a_c is the parameter of a cubic perovskite.

Recently, the study of titanium substitution by manganese and chromium in lanthanum and praseodymium systems have led to compounds of general formula $RE_{0.5+x+y}Li_{0.5-3x}Ti_{1-3y}Mn_{3y}O_3$ (RE = La, Pr and M = Mn, Cr)[7,8] with large regions of perovskite-like solid solutions. These compounds showed both electronic and Li-ion conductivity. The ionic conductivity was similar in manganese and chromium systems while the electronic conductivity was much higher in the manganese system.

Polymorph C appeared for the first time in lanthanum systems when titanium was substituted by manganese or chromium. The aim of the present work was to obtain the crystal structure of this polymorph in lanthanum systems.

Experimental

Samples were prepared in 10 g quantities from La_2O_3 (99.9% Fluka), TiO_2 (Aldrich 99+%), MnO_2 (>99% Fluka) or Cr_2O_3 (>99% Fluka) and Li_2CO_3 (Aldrich >99%). La_2O_3 and TiO_2 were dried overnight at 900 °C prior to weighing. These chemicals were weighed, mixed in an agate mortar with acetone, dried and heated at 650 °C for 2 h to drive off CO_2. After grinding, samples were pressed into pellets and covered

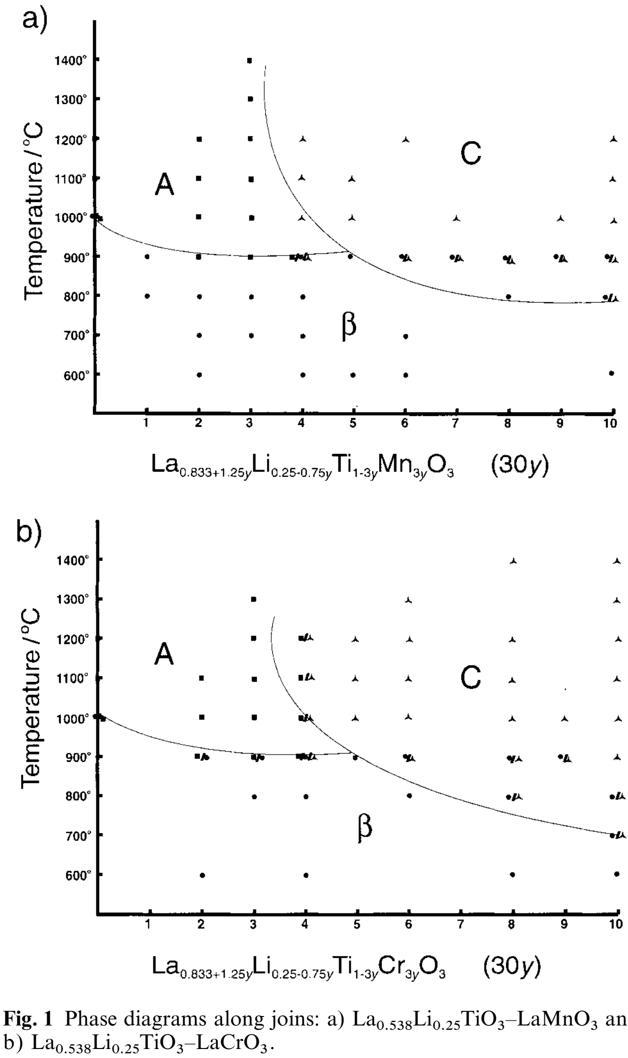

Fig. 1 Phase diagrams along joins: a) $La_{0.538}Li_{0.25}TiO_3$–$LaMnO_3$ and b) $La_{0.538}Li_{0.25}TiO_3$–$LaCrO_3$.

Table 1 Crystallographic data for $La_{0.833}Li_{0.10}Ti_{0.40}Mn_{0.60}O_3$[a]

Atom	Site	x/a	y/b	z/c	$U_{iso}/10^{-2}$ Å^2	Occupancy
La	4c	0.0067(12)	0.25	0.9968(14)	1.2(5)	0.832(5)
Li	4c	0.388(4)	0.25	0.439(5)	2.1(6)	0.11(4)
Ti	4b	0.5	0.0	0.0	1.1(5)	0.395(5)
Mn	4b	0.5	0.0	0.0	1.1(5)	0.605(5)
O(1)	4c	0.5156(9)	0.25	0.0134(8)	—	1.00
O(2)	8d	0.2541(6)	0.0413(6)	0.7374(8)	—	1.00

Anisotropic temperature factors/10^{-2} Å^2

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	9.8(5)	0.8(9)	3.2(8)	0.00	−5.1(9)	0.00
O(2)	0.6(7)	1.4(6)	3.6(8)	−0.25(8)	−0.24(7)	−2.1(7)

Bond lengths and angles

La coordination	
La–O(1)	2.710(7)
La–O(1)	2.604(7)
La–O(2) ×2	2.542(7)
La–O(2) ×2	2.913(8)
La–O(2) ×2	2.616(8)
La–Li	0.699(1)

Li coordination	
Li–O(1)	2.442(8)
Li–O(1)	2.079(7)
Li–O(2) ×2	2.426(7)
O(1)–Li–O(1)	114.1(8)
O(1)–Li–O(2)	67.2(8)
O(1)–Li–O(2)	137.3(9)
O(2)–Li–O(1)	84.4(9)

M coordination	
M–O(1) ×2	1.956(5)
M–O(2) ×2	1.945(4)
M–O(2) ×2	1.987(4)
O(1)–M–O(1)	180
O(1)–M–O(2) ×2	80.1(8)
O(1)–M–O(2) ×2	99.9(8)
O(1)–M–O(2) ×2	95.9(8)
O(1)–M–O(2) ×2	84.1(7)
O(2)–M–O(2) ×2	180
O(2)–M–O(2) ×2	89.0(7)
O(2)–M–O(2) ×2	90.9(7)

[a] Space group: *Pnma* (no. 62); $a_o=5.5411(11)$ Å, $b_o=7.8120(14)$ Å, $c_o=5.4924(10)$ Å; $R_{wp}=8.13\%$, $R_p=6.04\%$.

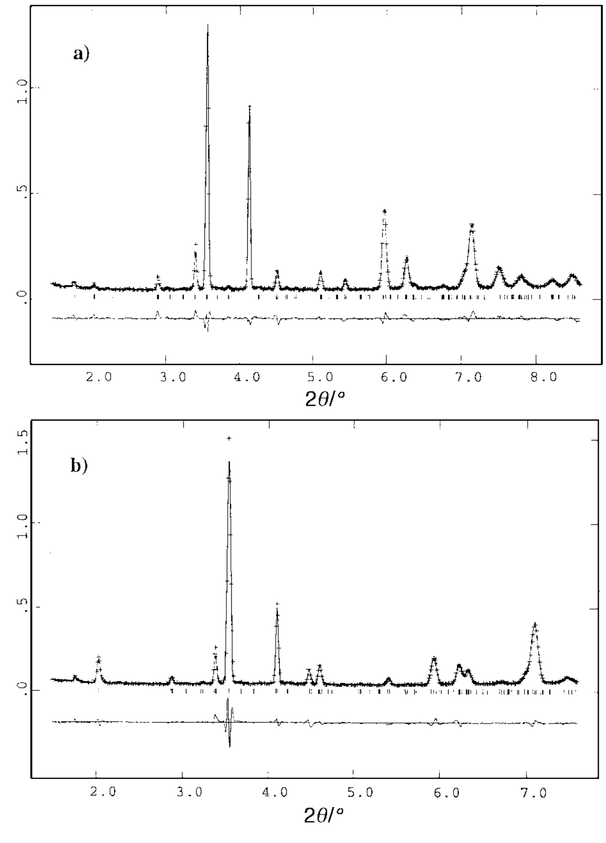

Fig. 2 Observed, calculated (upper curve) and difference (lower curve) neutron profiles for a) $La_{0.833}Li_{0.10}Ti_{0.40}Mn_{0.60}O_3$ and b) $La_{0.833}Li_{0.10}Ti_{0.40}Cr_{0.60}O_3$.

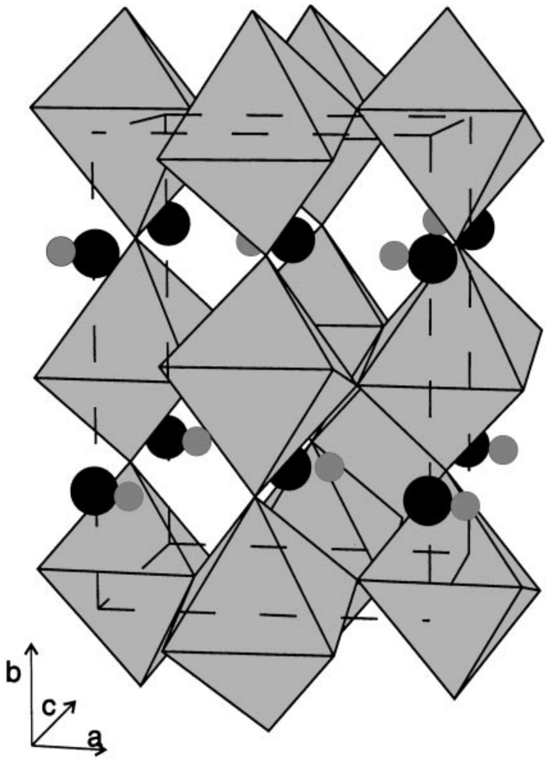

Fig. 3 Polymorph C structure of $La_{0.833}Li_{0.10}Ti_{0.40}Mn_{0.60}O_3$; octahedra, MO_6 (M=Ti/Mn); black balls, La; and gray balls, Li.

Table 2 Crystallographic data for $La_{0.833}Li_{0.10}Ti_{0.40}Cr_{0.60}O_3$[a]

Atom	Site	x/a	y/b	z/c	$U_{iso}/10^{-2}$Å^2	Occupancy
La	4c	0.0067(16)	0.25	0.9910(12)	0.63(10)	0.830(5)
Li	4c	0.355(8)	0.25	0.433(7)	1.8(8)	0.10(4)
Ti	4b	0.5	0.0	0.0	0.88(17)	0.402(5)
Cr	4b	0.5	0.0	0.0	0.88(17)	0.588(5)
O(1)	4c	0.5043(8)	0.25	0.0124(8)	—	1.00
O(2)	8d	0.2593(7)	0.0378(6)	0.7424(8)	—	1.00

Anisotropic temperature factors/10^{-2} Å^2

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	8.9(9)	1.0(5)	3.2(7)	0.00	−1.2(8)	0.00
O(2)	1.2(7)	1.4(4)	2.3(6)	−0.46(5)	0.72(7)	−1.8(8)

Bond lengths and angles

La coordination	
La–O(1)	2.588(6)
La–O(1)	2.815(6)
La–O(2) ×2	2.555(6)
La–O(2) ×2	2.883(8)
La–O(2) ×2	2.625(8)
La–Li	0.866(11)

Li coordination	
Li–O(1)	2.447(7)
Li–O(1)	2.001(6)
Li–O(2) ×2	2.444(6)
O(1)–Li–O(1)	120.5(8)
O(1)–Li–O(2)	70.8(8)
O(1)–Li–O(2)	137.4(9)
O(2)–Li–O(1)	84.9(9)

M coordination	
M–O(1) ×2	1.946(5)
M–O(2) ×2	1.942(4)
M–O(2) ×2	1.984(4)
O(1)–M–O(1)	180
O(1)–M–O(2) ×2	81.2(9)
O(1)–M–O(2) ×2	98.8(9)
O(1)–M–O(2) ×2	95.7(9)
O(1)–M–O(2) ×2	84.3(8)
O(2)–M–O(2) ×2	180
O(2)–M–O(2) ×2	89.1(8)
O(2)–M–O(2) ×2	90.8(8)

[a]Space group: *Pnma* (no. 62); $a_o = 5.5014(9)$ Å, $b_o = 7.7735(15)$ Å, $c_o = 5.4729(9)$ Å; $R_{wp} = 7.32\%$, $R_p = 5.18\%$.

with powder of the same composition to avoid loss of lithium during thermal treatment. The pellets were fired at 1100 °C for 8 h giving green products which were reground, repelleted and fired at 1200 and 1250 °C for 12 h.

Phase purity was checked by X-ray powder diffraction using a Siemens D-500 diffractometer. Stoichiometries were obtained by ICP with a JOVIN IVON apparatus.

Phase diagram studies *vs.* temperature were carried out for joins $La_{0.583}Li_{0.25}TiO_3$–$LaMO_3$ where M = Cr or Mn. Small pelleted samples were wrapped in platinum foil envelopes, placed in a furnace and annealed isothermally for 15 min in order to reach equilibrium. Finally they were dropped in liquid nitrogen to quench the phase. Samples for neutron diffraction were pressed in several pellets, annealed at 1000 °C for 15 min and quenched in liquid nitrogen. Powder neutron diffraction data were collected on the KSN-2 diffractometer located at the LVR-15 research reactor near Prague. The crystal structures were refined by the Rietveld method with the program GSAS,[9] using data collected at $\lambda = 0.1362$ nm, between 10 and 85° in 2θ and taking into consideration the absorption correction for the natural mixture of the lithium isotopes.

Results

Phase diagrams

Polymorphs A, β and C were identified along both joins [Fig. 1(a) and (b)]. Polymorphs A and C only form at high temperatures ($T \geqslant 800$ °C), although they can be preserved at room temperature by quenching. Polymorph C spreads over a large region for $y \geqslant 0.133$ while polymorph β extends along the whole range of composition at low temperatures.

Samples of composition $La_{0.833}Li_{0.10}Ti_{0.40}M_{0.60}O_3$ (M = Cr or Mn) were synthesized and annealed at 1000 °C and were studied by powder neutron diffraction, since they were clearly located in the polymorph C region for this temperature and composition.

Crystal structure

The structures were refined initially using the parameters of the polymorph C in the system $Pr_{0.5+x}Li_{0.5-3x}TiO_3$[10] with La and Li placed on the larger A sites of the perovskite structure (ABO_3) and Ti and Mn or Cr on the octahedral B sites. Occupancies for La/Li and Ti/Mn or Cr were constrained at the values 0.83/0.10 and 0.40/0.60 respectively, which were obtained by ICP. In the first stage, lithium coordinates were fixed and lanthanum, titanium and manganese or chromium coordinates and temperature factors were refined. Finally lithium coordinates, isotropic thermal parameters and occupancies were refined.

Final refined atomic coordinates, temperature factors, bond angles and lengths for $La_{0.833}Li_{0.10}Ti_{0.40}Mn_{0.60}O_3$ and $La_{0.833}Li_{0.10}Ti_{0.40}Cr_{0.60}O_3$ are given in Tables 1 and 2, respectively, with fitted neutron diffraction profiles for manganese– and chromium–lanthanum compounds [Fig. 2(a) and 2(b)].

The structure (Fig. 3) contains a three dimensional framework of corner-sharing MO_6 (M = Ti or Mn/Cr) octahedra in which the structure is partially collapsed in all three directions as a result of a cooperative tilting and rotating of octahedra.

Although polymorphs C in the manganese– and chromium–lanthanum systems show similar features to those in praseodymium and neodymium systems, there are some differences.

For instance, rare earth elements are placed close to the theoretical A-site in all of these systems, however, Pr and Nd[10,11] are clearly displaced from this site by 0.098 and 0.141 Å, respectively, which allows them to adopt a distorted eight-coordination for RE–O, while La is closer to theoretical A-site with distances of 0.041 and 0.061 Å for manganese and chromium systems, giving a distorted 12-coordination with La–O distances in the range 2.555–2.883 Å in the lanthanum–chromium system. This behaviour could be associated to rare earth size, since it is more difficult for a large element to move off the cell centre.

On the other hand, Li^+ in manganese– and chromium–lanthanum systems is clearly off-centre with a displacement of 0.7053 and 0.8382 Å, respectively, *cf.* 0.5260 Å in the praseodymium system. This displacement allows lithium to adopt a distorted tetrahedral coordination.

MO_6 (M = Ti or Cr/Mn) octahedra are more distorted than in Pr and Nd systems with M–O distances between 1.945 and 1.987 Å in the manganese system and 1.942–1.984 Å in the chromium system. The distance M–O(1) is slightly larger in the manganese than in the chromium system probably due to electronic effects.

These phases show both Li^+-ion and electronic conductivity. From the structure, it is presumed that ionic conductivity takes place by a hopping mechanism among Li^+-occupied and empty A-sites, while electronic conductivity is along octahedra.

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