

Crystal Chemistry and Conductivity Studies in the System $\text{La}_{0.5+x+y}\text{Li}_{0.5-3x}\text{Ti}_{1-3y}\text{Cr}_{3y}\text{O}_3$

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The stoichiometry polymorphism and electrical behavior of solid solutions $\text{La}_{0.5+x+y}\text{Li}_{0.5-3x}\text{Ti}_{1-3y}\text{Cr}_{3y}\text{O}_3$ with perovskite-type structure were studied. Data are given in the form of a solid solutions triangle, phase diagrams, XRD patterns for the three polymorphs, A, β , and C, composition dependence of their lattice parameters, and ionic and electronic conductivity plots. Microstructure and composition were studied by SEM/EDS and electron probe microanalysis. These compounds are mixed conductors. Ionic conductivity decreased when the amount of lithium diminished and electronic conductivity increased with chromium content. © 2000 Academic Press

Key Words: mixed conductors; crystal chemistry; phase diagram.

INTRODUCTION

Research into solid ionic conductors and lithium cathodes is important for the development of solid state lithium batteries. For some time, research focused on doping compounds such as Li_4XO_4 and Li_3YO_4 [$X = \text{Si, Ge, Ti; Y = P, As, V}$] (1–4), and then a few years ago, fast ion conductors with the general formula $\text{Li}_{0.5-3x}\text{RE}_{0.5+x}\text{TiO}_3$, where $\text{RE} = \text{La, Pr, Nd, and Sm}$, were reported (5–7). The maximum bulk conductivity was found in the lanthanum system, with a value of $1.1 \times 10^{-3} \text{ S cm}^{-1}$ for $x = 0.07$, although the total conductivity was less than $10^{-6} \text{ S cm}^{-1}$. More recently, the phase diagram, crystal chemistry, and ion conductivity of the systems $\text{Li}_{0.5-3x}\text{RE}_{0.5+x}\text{TiO}_3$ [$\text{RE} = \text{La, Pr, Nd}$] and $\text{Li}_{0.5-3x}\text{La}_{0.5+x+y}\text{Ti}_{1-3y}\text{Mn}_{3y}\text{O}_3$, which show a similar total conductivity, have been reported (8–12).

The aim of the present work is to investigate the stoichiometry range, thermal stability, crystal chemistry, and electrical behavior of materials of the general formula $\text{Li}_{0.5-3x}\text{La}_{0.5+x+y}\text{Ti}_{1-3y}\text{Cr}_{3y}\text{O}_3$. Since $\text{Li}_{0.5-3x}\text{La}_{0.5+x}\text{TiO}_3$

compounds are the best Li^+ ion conductors and chromium oxides with perovskite structure show electronic conductivity (13), the partial substitution of titanium by chromium in these compounds could lead to mixed conductors.

EXPERIMENTAL

La_2O_3 (99.9% Fluka), TiO_2 (Aldrich 99 + %), Cr_2O_3 (> 99% Fluka), and Li_2CO_3 (Aldrich > 99%) were used as starting materials. 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 with powder of the same composition to avoid losing lithium during thermal treatment. The pellets were fired at 1100°C for 8 h, giving green products which were reground, repelleted, and fired at 1250°C for 12 h.

Phase diagram studies vs temperature were carried out for certain compounds. 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.

Solid solution range, crystalline phase identification, and lattice parameters were determined by powder X-ray diffraction with a Siemens D-500 diffractometer in the reflection mode and an INEL Enraf Nonius FR590 diffractometer in the transmission mode with a psd-120° detector and graphite monochromator, using $\text{CuK}\alpha$. Lattice parameters were obtained using silicon internal standard.

Some samples were studied by EPMA to verify the homogeneity with a CAMECA SX50 EPMA instrument. Elemental maps were obtained with an AN10000 EDS coupled to a JEOL JSM-840 microscope. Stoichiometry was obtained by ICP with a Jovin Ivon. DC measurements were carried out using a HP 3435A multimeter, and AC measurements with a HP 4192A impedance analyzer over the range $5 \text{ Hz} < f < 1.3 \times 10^7 \text{ Hz}$. Data correction was

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carried out in order to avoid stray inductance, although data above 5×10^6 Hz were discarded.

RESULTS AND DISCUSSION

A. Solid Solutions Diagram

The triangle LaCrO_3 – $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ – $\text{La}_{0.66}\text{TiO}_3$ in the system Li_2O – La_2O_3 – TiO_2 – Cr_2O_3 was chosen for a detailed study since the join $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ – $\text{La}_{0.66}\text{TiO}_3$ has been reported (8) elsewhere and LaCrO_3 has a structure similar to that of the compounds on this join.

This triangle was studied by synthesizing compositions of the general formula $\text{La}_{0.5+x+y}\text{Li}_{0.5-3x}\text{Ti}_{1-3y}\text{Cr}_3\text{yO}_3$ ($y < 0.33$) under the heating conditions described above. The results were used to construct the composition diagram shown in Fig. 1.

Three distinct areas were found on this triangle: a large region of perovskite-like solid solutions and two regions of mixed phases. The region that was within the vertex $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ was a mixture of perovskite-like compound and Li_2TiO_3 , while the region closest to the vertex $\text{La}_{2/3}\text{TiO}_3$ was a mixture of a perovskite-like phase, $\text{La}_2\text{Ti}_2\text{O}_7$, Cr_2O_3 , and TiO_2 .

B. Electron Probe Microanalysis (EPMA) and Scanning Electron Microscopy (SEM/EDS)

A number of samples from the three regions observed in the composition triangle were studied by EPMA and SEM/EDS to obtain element analyses and elemental maps. Element analyses were carried out with a fixed beam of 15 kV and 20 nA over 15 different points of the sample

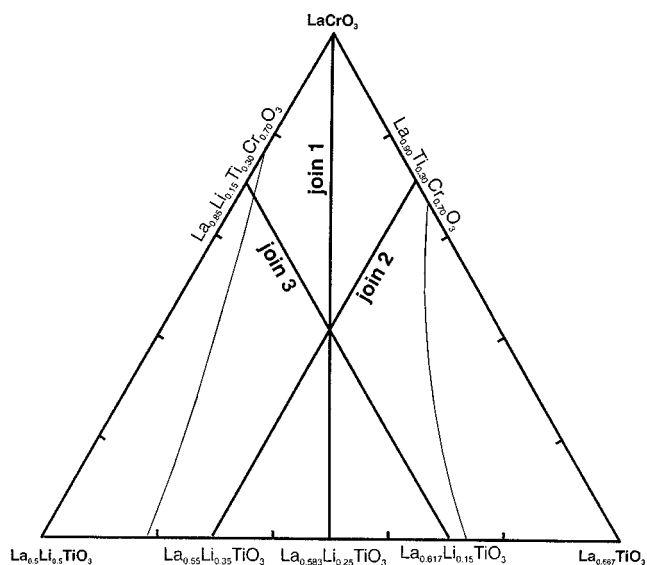


FIG. 1. Composition triangle of the system $\text{La}_{0.5+x+y}\text{Li}_{0.5-3x}\text{Ti}_{1-3y}\text{Cr}_3\text{yO}_3$ and joins studied.

surface, with SrTiO_3 , LaB_6 , and Cr_2O_3 as standards for Ti and O, La, and Cr, respectively. The lithium content could not be obtained directly and so had to be calculated by assuming three oxygen atoms per unit formula and valences 3+ for La and Cr and 4+ for Ti. The elemental maps of Ti, La, and Cr were produced with an electron beam of 15 kV and 20 nA using a Link AN10000 EDS coupled to a Jeol JSM-840 microscope.

Element maps were obtained for three samples from each of the three regions observed in the composition triangle.

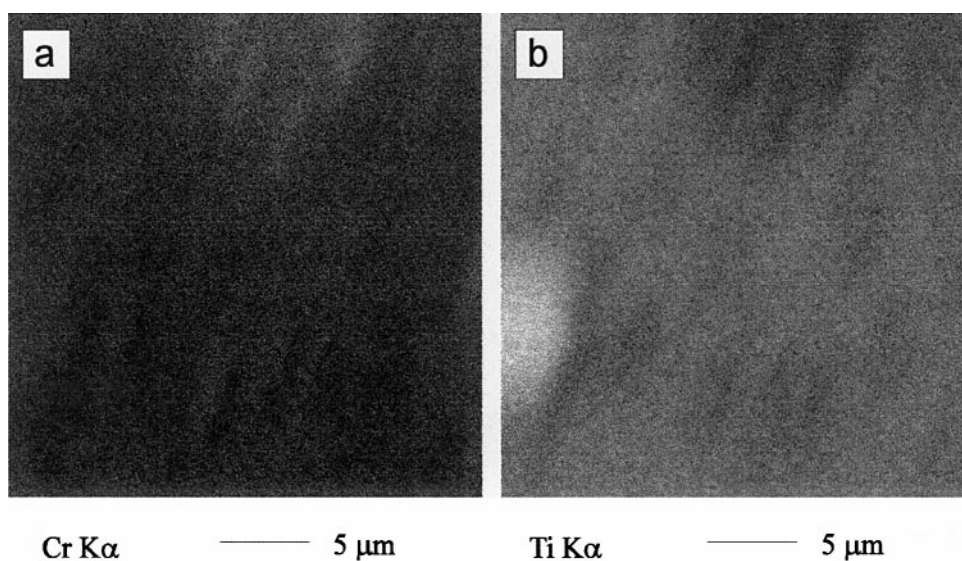


FIG. 2. Elemental maps for $\text{La}_{0.65}\text{Li}_{0.05}\text{Ti}_{0.90}\text{Cr}_{0.10}\text{O}_3$ (multiphase region): (a) map of Cr and (b) map of Ti.

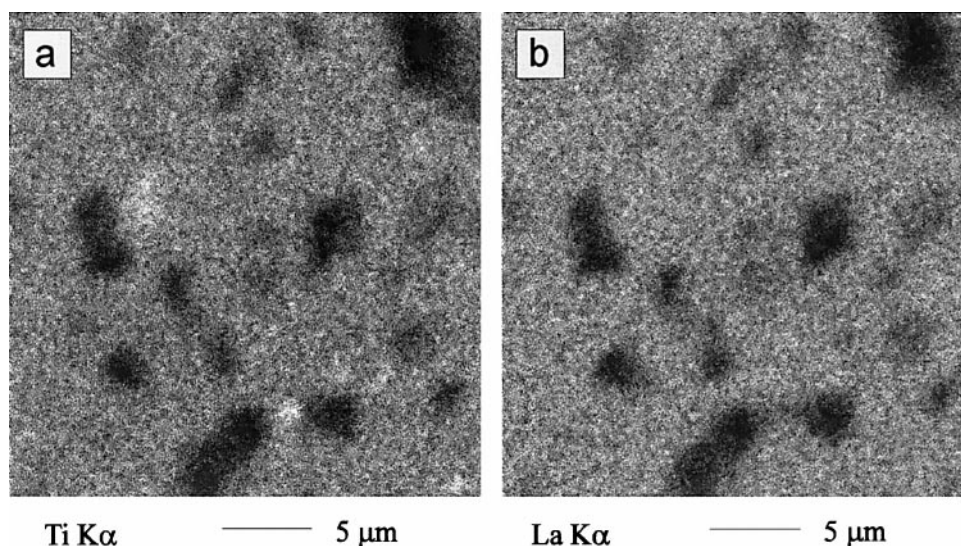


FIG. 3. Elemental maps for $\text{La}_{0.517}\text{Li}_{0.45}\text{Ti}_{0.90}\text{Cr}_{0.10}\text{O}_3$ (multiphase region): (a) map of Ti and (b) map of La.

Only one phase with a homogeneous element distribution was found for $\text{La}_{0.75}\text{Li}_{0.15}\text{Ti}_{0.60}\text{Cr}_{0.40}\text{O}_3$. Elemental maps for $\text{La}_{0.65}\text{Li}_{0.05}\text{Ti}_{0.90}\text{Cr}_{0.10}\text{O}_3$ (Fig. 2) showed the presence of at least three phases: a large region of perovskite-like compound, light spots in Cr maps (Fig. 2a) attributed to CrO_3 , and lighter areas in the Ti map (Fig. 2b) of $\text{La}_2\text{Ti}_2\text{O}_7$.

Elemental maps for $\text{La}_{0.517}\text{Li}_{0.45}\text{Ti}_{0.90}\text{Cr}_{0.10}\text{O}_3$ (Fig. 3) showed two regions of composition. The largest region corresponds to a perovskite compound, while light areas on the Ti map correspond to Li_2TiO_3 .

The results of elemental analyses for the single phase region are summarized in Table 1. These values are in good agreement with the expected values for starting compositions. In mixed regions, values of analyses for different spots matched those for the proposed compounds.

C. Phase Diagrams and Crystal Chemistry

Phase diagrams and cell volume were obtained for three joins on the composition triangle (Fig. 1). Along join

1 [$\text{La}_{0.538}\text{Li}_{0.25}\text{TiO}_3$ - LaCrO_3], the lithium and lanthanum composition and the number of vacancies changed, while along join 2 [$\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ - $\text{La}_{0.90}\text{Ti}_{0.30}\text{Cr}_{0.70}\text{O}_3$], the number of vacancies was constant and along the join 3 [$\text{La}_{0.617}\text{Li}_{0.15}\text{TiO}_3$ - $\text{La}_{0.85}\text{Li}_{0.15}\text{Ti}_{0.30}\text{Cr}_{0.70}\text{O}_3$], the amount of lithium was constant.

Three polymorphs, labeled A, C and β , by analogy with similar polymorphs in the $\text{RE}_{0.5+x}\text{Li}_{0.5-3x}\text{TiO}_3$ ($\text{RE} = \text{Pr}$ and Nd) (8, 9) systems, were identified. These three polymorphs have a perovskite-related structure.

The polymorph A is a simple cubic perovskite (Table 2) and the polymorph C (Table 3) is an orthorhombic distortion of A, with a unit cell which is approximately 4 times larger. The cells of a and c are related by $a_o = 2a_c + \delta$, $b_o = 2a_c$, and $c_o = 2a_c - \delta$, where a_c is the cell parameter of the cubic A phase and δ is the degree of orthorhombicity. The polymorph β is a tetragonal perovskite with unit cell $a_o = ac - \delta$ and $c_o = 2a_c + \Delta$ (Table 4).

Polymorph A and C only form at high temperatures, phase C for small number of vacancies in the structure and

TABLE 1

$\text{La}_{0.5+x+y}\text{Li}_{0.5-3x}\text{Ti}_{1-3y}\text{Cr}_{3y}\text{O}_3$		Starting compositions				Experimental compositions			
x	y	La	Ti	Cr	Li	La	Ti	Cr	O
0.080	0.000	0.580	1.000	0.000	0.250	0.581(8)	1.00(1)	0.000	2.98(3)
0.100	0.067	0.667	0.800	0.200	0.200	0.660(6)	0.790(7)	0.210(7)	2.91(5)
0.142	0.233	0.875	0.300	0.700	0.075	0.86(1)	0.291(8)	0.709(7)	2.93(3)
0.167	0.333	1.000	0.000	1.000	0.000	1.015(9)	0.000	1.000(9)	2.99(4)
0.100	0.133	0.733	0.600	0.400	0.200	0.721(8)	0.609(6)	0.391(5)	2.90(4)
0.067	0.067	0.634	0.800	0.200	0.300	0.630(5)	0.810(8)	0.190(5)	3.01(3)

Note. Experimental values of oxygen content carry greater uncertainty than La, Ti, and Cr due to partial absorption of the $\text{OK}\alpha$ signal by the carbon coating.

TABLE 2

h	k	l	d_{obs}	d_{calc}	I/I_0
1	0	0	3.8783	3.8775	6
1	1	0	2.7412	2.7418	100
1	1	1	2.2380	2.2387	18
2	0	0	1.9384	1.9388	40
2	1	0	1.7338	1.7341	3
2	1	1	1.5828	1.5830	30
2	2	0	1.3708	1.3709	13
3	0	0	1.2929	1.2925	2
3	1	0	1.2262	1.2262	10

Note. Cubic system: $a_0 = 3.8775(7) \text{ \AA}$, $V = 58.298(2) \text{ \AA}^3$, $Z = 1$.

phase A for a large number. Although these phases are stable at high temperatures, they can, nevertheless, be preserved at room temperature by quenching. The polymorph C, which is absent in the system $\text{La}_{0.5+x}\text{Li}_{0.5-3x}\text{TiO}_3$, appears when titanium is partially substituted by chromium. The polymorph β extends along the whole range of compositions on the three joins at low temperatures (Fig. 4).

Cell volume was measured against the amount of lanthanum along these three joins (Fig. 5) and was found to increase whenever the lanthanum content increases, while for the same amount of lanthanum, it decreased as the lithium content increased. Since both lithium and lanthanum should be in 12-coordinated sites, steric effects are predominant in lanthanum substitution, making cells larger, while electrostatic interaction between lithium and

TABLE 3

h	k	l	d_{obs}	d_{calc}	I/I_0
0	0	2	3.8832	3.8788	16
2	0	0	2.7461	2.7483	100
1	1	2	2.7387	2.7429	74
1	0	3	2.3391	2.3399	2
2	0	2	2.2411	2.2425	26
0	2	2	2.2332	2.2368	13
0	0	4	1.9390	1.9394	64
2	2	2	1.7363	1.7348	4
1	3	0	1.7330	1.7322	4
2	0	4	1.5844	1.5846	52
1	3	2	1.5798	1.5816	28
2	2	4	1.3731	1.3715	14
0	4	0	1.3696	1.3689	20
3	1	4	1.2945	1.2941	2
0	0	6	1.2928	1.2929	1
0	4	2	1.2901	1.2909	1
4	2	0	1.2278	1.2282	11
2	4	0	1.2259	1.2253	18

Note. Orthorhombic system: $a_0 = 5.497(6) \text{ \AA}$, $b_0 = 5.476(3) \text{ \AA}$, $c_0 = 7.758(8) \text{ \AA}$, $V = 233.53(2) \text{ \AA}^3$, $Z = 4$.

octahedrons is more important in lithium substitution, with the reverse effect on the cells.

D. Electrical Measurements (AC/DC)

An HP 4192A analyzer was used for AC measurements, and an HP 3435A multimeter was for DC measurements. These measurements were carried out from 25°C to 100°C for compounds on join 1, $\text{La}_{0.583+1.25y}\text{Li}_{0.25-0.75y}\text{Ti}_{1-3y}\text{Cr}_{3y}\text{O}_3$. Along this join, three types of behavior were shown. For $y = 0.0$, only ionic conductivity and two semicircles and a spike were observed. The center of these semicircles was depressed below the baseline, indicating a non-Debye response, which is usual in ionic conductors (14, 15). For $0 < y \leq 0.133$, compounds were mixed conductors with greater ionic than electronic conductivity and three semicircles were observed. The third semicircle became smaller as the electronic conductivity was increased. Finally, for $y > 0.133$, electronic conductivity was greater than ionic conductivity, and only two semicircles were observed.

An equivalent circuit (Fig. 6) with two parallel branches, one of them related to ionic conductivity and the other one to electronic conductivity, has been used to fit experimental measurements. The electronic part was comprised of two RC elements associated with grain and grain boundary responses, while the ionic part was made of two RC

TABLE 4

h	k	l	d_{obs}	d_{calc}	I/I_0
0	0	2	3.8817	3.8804	13
1	0	0	3.8704	3.8730	2
0	1	1	3.4636	3.4654	2
1	0	2	2.7449	2.7412	100
1	1	0	2.7390	2.7386	54
0	0	3	2.5849	2.5869	1
1	1	2	2.2377	2.2375	33
0	0	4	1.9388	1.9402	59
2	0	0	1.9345	1.9365	36
1	0	4	1.7348	1.7347	6
2	0	2	1.7330	1.7327	2
2	1	1	1.6907	1.6905	6
1	1	4	1.5837	1.5832	60
1	2	2	1.5817	1.5816	15
2	0	3	1.5513	1.5503	1
0	2	4	1.3712	1.3706	29
2	2	0	1.3693	1.3693	4
0	0	6	1.2930	1.2935	5
1	0	6	1.2265	1.2269	24
3	0	2	1.2251	1.2250	2
2	0	5	1.2118	1.2111	1
3	1	1	1.2091	1.2098	< 1

Note. Tetragonal system: $a_0 = 3.873(1) \text{ \AA}$, $c_0 = 7.761(2) \text{ \AA}$, $V = 116.413(3) \text{ \AA}^3$, $Z = 2$.

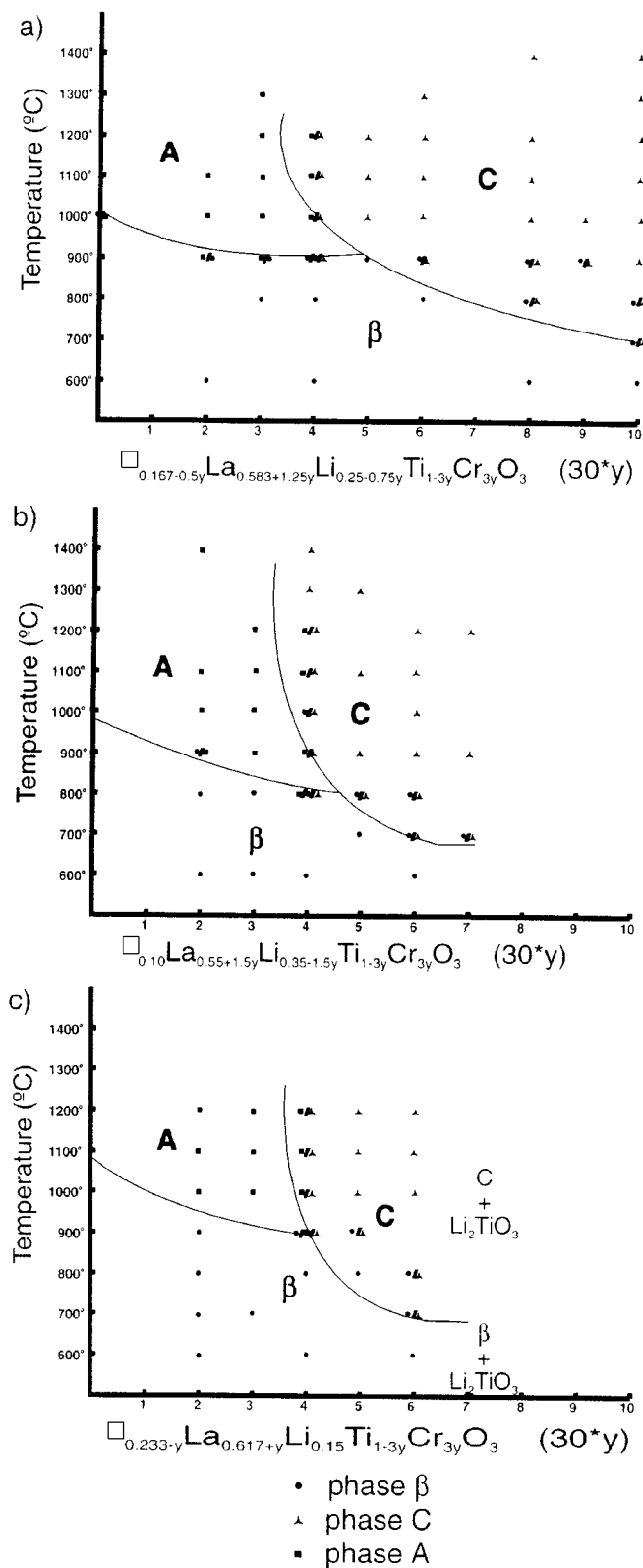


FIG. 4. Phase diagram along each join: (a) $\text{La}_{0.538}\text{Li}_{0.25}\text{TiO}_3\text{-LaCrO}_3$, (b) $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3\text{-La}_{0.90}\text{Ti}_{0.30}\text{Cr}_{0.70}\text{O}_3$, and (c) $\text{La}_{0.617}\text{Li}_{0.30}\text{TiO}_3\text{-La}_{0.85}\text{Li}_{0.15}\text{Ti}_{0.30}\text{Cr}_{0.70}\text{O}_3$.

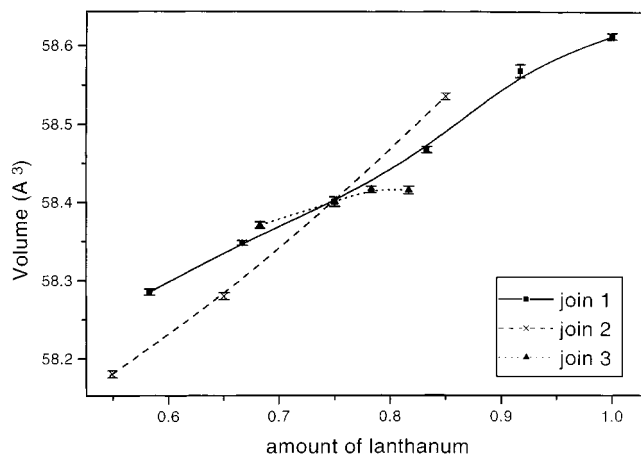


FIG. 5. Cell volume vs composition in lanthanum along the three joins samples quenched from 1000°C.

elements with two CPE (16) (constant phase elements) for grain and grain boundary response and an additional CPE element to model a blocking electrode for lithium ions. All fitting used the Zview software package (17).

Overall electronic conductivity, DC measurements, showed that samples doped with chromium became mixed conductors. Electronic conductivity is dependent on chromium content (Fig. 7). It increased as the amount of chromium increased. The variation in ionic conductivity with the lithium composition at 25°C is quite large; it decreased as the amount of lithium diminished (Fig. 8), although ionic and electronic conductivity remained similar for $y = 0.10$ (close to $10^{-6} \Omega^{-1} \text{cm}^{-1}$). The compounds of general formula $\text{La}_{0.5+x+y}\text{Li}_{0.5-3x}\text{Ti}_{1-3y}\text{Cr}_{3y}\text{O}_3$ show lower conductivity than the similar compounds of general formula $\text{La}_{0.5+x+y}\text{Li}_{0.5-3x}\text{Ti}_{1-3y}\text{Mn}_{3y}\text{O}_3$ (12).

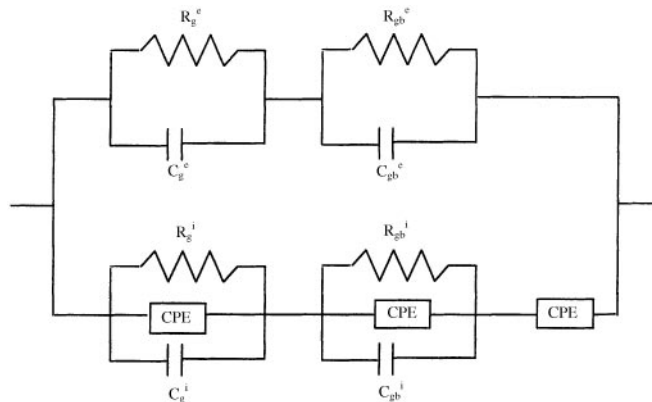


FIG. 6. Equivalent circuit for fitting AC data.

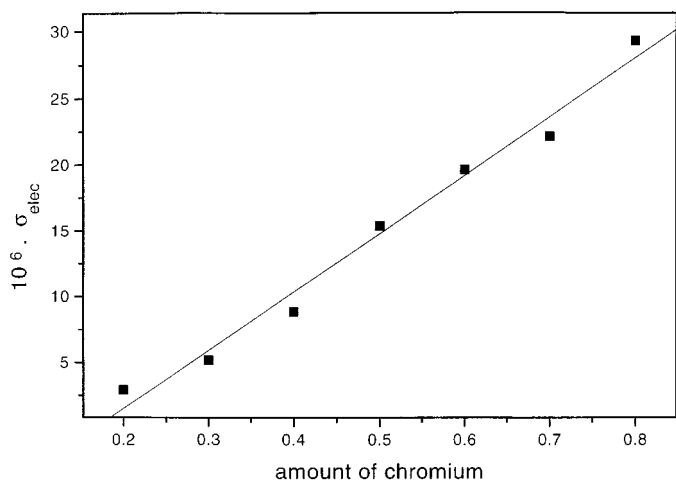


FIG. 7. Plot of σ_{25} (overall electronic conductivity at 25°C) vs composition in chromium.

CONCLUSIONS

A large range of single phase solid solutions have been synthesized in the triangle LaCrO_3 – $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ – $\text{La}_{2/3}\text{TiO}_3$. The phase diagram in the single phase region

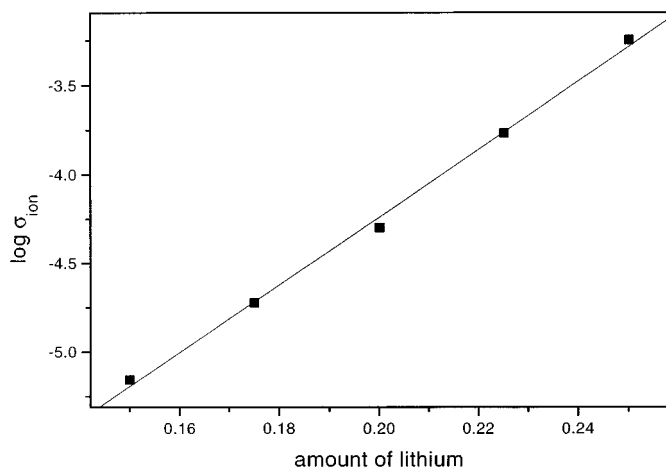


FIG. 8. Plot of $\log \sigma_{25}$ (bulk ionic conductivity at 25°C) vs composition in lithium.

showed the existence of three polymorphs with perovskite-like structure, labeled as A, C, and β . The polymorph A has a cubic perovskite structure, C is an orthorhombic distortion of A with a cell quadruple that of A, and β is a tetragonal phase with a double cell.

Cell volume increased whenever the lanthanum content increased. Nevertheless, it decreased as the lithium content increased for the same amount of lanthanum. This is attributable to an electrostatic interaction between lithium ions and negative octahedrons that shrank the cell.

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