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Synthesis and structural characterization of solid solutions: $Li_{3x}La_{(1-x)}VO_4$ ($0 \leqslant x \leqslant 0.3$), Monazite-type

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$Li_{3x}La_{(1-x)}VO_4$($0 \leqslant x \leqslant 0.3$) solid solutions have been obtained by thermal treatment of lanthanum and lithium nitrates with V_2O_5 in the temperature range 700–980 K. The crystal structure of these single phases has been refined by the Rietveld analysis of powder X-ray diffraction data. The structure refinement of $Li_{0.15}La_{0.95}VO_4$ by neutron diffraction has been also achieved at 295 K. This compound adopts a distorted monazite-type structure: space group $P2_1/n$, $a = 0.7047(1)$ nm $b = 0.7283(6)$ nm $c = 0.6726(8)$ nm, $\beta = 104.86(1)°$, $Z = 4$.

1. Introduction

Lanthanide vanadates and related compounds are of interest owing to their unusual magnetic characteristics and useful luminescent properties. These materials have been employed as model systems for the investigation of polymorphism among the ABO_4-type compounds, because it has been found that zircon-type vanadates transform reconstructively into the denser scheelite structure. Only $LaVO_4$ crystallizes in the monazite-type isomorphous with monoclinic $LaPO_4$ and $CePO_4$ [1, 2]. This ABO_4-type is a somewhat flexible structure containing approximately tetrahedral BO_4 units and a very irregular coordination of the polyhedron about A. The coordination number of A varies from structure to structure and there are wide variations in the A–O distances within a given polyhedron [3].

The lithium addition to mixed oxides of rare-earth-orthophosphates is of great interest, because it allows their use as solid electrolytes as well as for some electrical properties [4–9].

This paper reports the synthesis and structural characterization of the solid solutions $Li_{3x}La_{(1-x)}VO_4$ ($0 \leqslant x \leqslant 0.3$). A neutron diffraction study of the $Li_{0.15}La_{0.95}VO_4$ compound has allowed the position of the lithium in the monazite structure to be determined.

2. Experimental procedure

A mixture, in stoichiometric ratio, of $La(NO_3)_3 \cdot 6H_2O$ (Merck, Germany), V_2O_5 (as described elsewhere [10]) and $LiNO_3$ (Merck) was heated at 700 K for 3 h and subjected to further thermal treatment at 980 K, in air, for 6 h (the duration was determined by preliminary experiments).

Chemical analysis by atomic absorption spectroscopy was in good agreement with the proposed stoichiometry.

Powder X-ray diffraction patterns were registered at the rate of 0.1° (2θ) min^{-1} by means of a Siemens Kristalloflex diffractometer, powered by a D500 generator using nickel-filtered CuK_α radiation. A 2θ step size of 0.04° was used. Rietveld's profile analysis method [11], using the Fullprof program [12], was employed for refinement of X-ray diffraction results in the solid solutions $Li_{3x}La_{(1-x)}VO_4$ ($0 \leqslant x \leqslant 0.3$). The following R factors were calculated
The profile

$$R_p = 100 \Sigma_i [Y_i - Y_{ci}] / \Sigma_i [Y_i] \qquad (1)$$

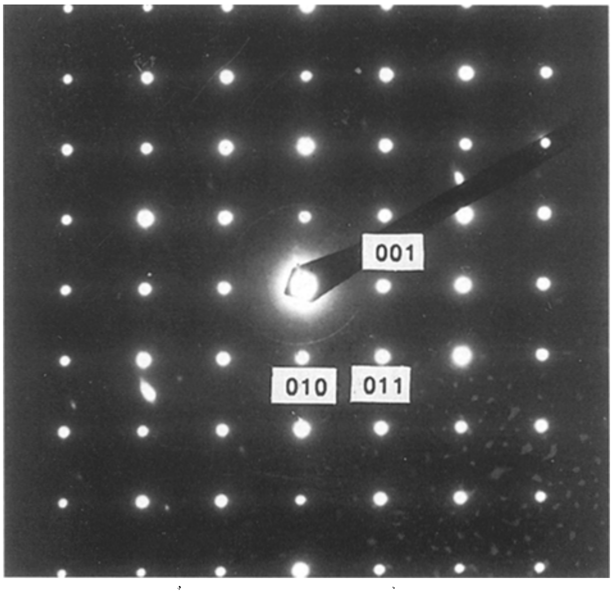

Figure 1 Electron diffraction pattern of $Li_{0.90}La_{0.70}VO_4$. Zone axis $[\bar{1}00]$.

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TABLE I Lattice parameters variation for $Li_{3x}La_{(1-x)}VO_4$ ($0 \leqslant x \leqslant 0.3$) compounds

Compound	a (nm)	b (nm)	c (nm)	β (deg)	V (10^{-3} nm^3)
$x = 0$	0.704 7(1)	0.728 6(1)	0.672 5(1)	104.85(1)	333.75
$x = 0.05$	0.704 7(1)	0.728 3(6)	0.672 6(8)	104.86(1)	333.65
$x = 0.10$	0.704 2(2)	0.728 0(6)	0.671 7(2)	104.84(3)	332.82
$x = 0.20$	0.703 8(2)	0.727 2(3)	0.671 5(3)	104.84(2)	332.21
$x = 0.30$	0.703 4(4)	0.726 8(3)	0.671 2(3)	104.83(2)	331.70

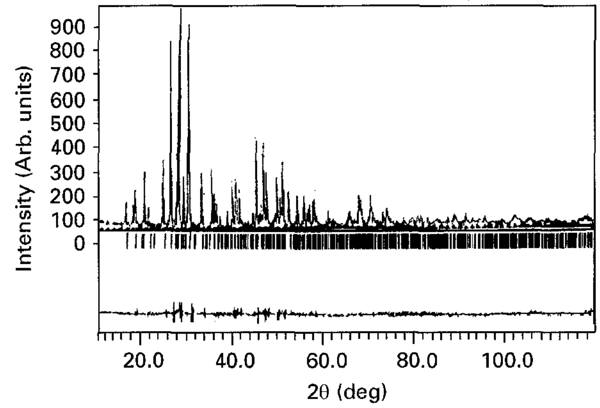

Figure 2 (···) Observed, (—) calculated and difference diffraction profiles for $Li_{0.90}La_{0.70}VO_4$.

The weighted profile

$$R_{WP} = 100\{\Sigma_i[W_i(Y_i - Y_{ci})^2]/\Sigma_i[W_iY_i^2]\}^{1/2} \quad (2)$$

The Bragg

$$R_B = 100\Sigma[I_i - I_{ci}]/\Sigma[I_i] \quad (3)$$

$$R_F = 100\Sigma_i[(I_i)^{1/2} - (I_{ci})^{1/2}]/\Sigma_i(I_i)^{1/2} \quad (4)$$

Electron diffraction was performed with an electron microscope Jeol 2000 FX operating at 100 kV. The sample was crushed and dispersed in acetone.

The neutron powder diffraction data were collected at 295 K on the high-resolution powder diffractometer D2B at the Institut Laue-Langevin in Grenoble (France). The neutron diffraction pattern was analysed by the Rietveld method [11]. A pseudo-voight function was chosen to generate the line shape of the diffraction peaks. The coherent scattering lengths for lanthanum, lithium, vanadium and oxygen were 8.240, − 1.90, − 0.324 and 5.805 fm, respectively [13]. The structure of $LaVO_4$ [3] was used as a trial model: La, 0(1), 0(2), 0(3), 0(4), Li and V at (x, y, z). In this study 47 parameters were refined.

TABLE II Fractional atomic coordinates of $Li_{0.90}La_{0.70}VO_4$

Atom	Position	x	y	z
La	4e	0.276 8(2)	0.157 7(2)	0.104 8(2)
Li	4e	0.193 7(1)	0.246 5(2)	0.213 6(1)
V	4e	0.300 8(1)	0.165 1(1)	0.617 9(1)
O(1)	4e	0.245 8(3)	− 0.002 2(3)	0.428 6(3)
O(2)	4e	0.386 9(1)	0.343 7(1)	0.496 2(1)
O(3)	4e	0.484 8(2)	0.106 9(3)	0.825 6(1)
O(4)	4e	0.108 3(1)	0.220 8(2)	0.730 7(1)

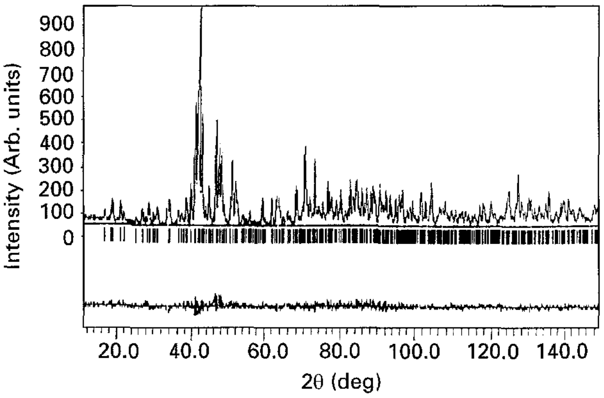

Figure 3 (···) Observed, (—) calculated and difference profiles for $Li_{0.15}La_{0.95}VO_4$.

3. Results

Fig. 1 gives the electron diffraction pattern in the zone axis [1 0 0], which is consistent with a monoclinic symmetry.

The X-ray powder diffraction patterns show systematic absences of reflections $h0l$, with $h + l = 2n + 1$,

TABLE III Bond lengths for $Li_{0.90}La_{0.70}VO_4$

La–O(1)	0.252 2(3) nm	Li–O(1)	0.228 3(3) nm	V–O(1)	0.172 9(5) nm
	0.248 3(3) nm		0.215 3(3) nm	V–O(2)	0.172 4(5) nm
La–O(2)	0.287 8(3) nm	Li–O(2)	0.215 0(2) nm	V–O(3)	0.169 5(4) nm
	0.265 1(3) nm		0.236 4(2) nm	V–O(4)	0.169 7(4) nm
	0.256 7(4) nm	Li–O(3)	0.210 3(3) nm	Shannon	0.175 nm
La–O(3)	0.251 5(3) nm	Shannon	0.208 nm		
	0.268 2(3) nm				
La–O(4)	0.251 5(3) nm				
	0.249 5(4) nm				
Shannon	0.261 nm				

and $0k0$, with $k = 2n + 1$. Both are compatible with the space group $P2_1/n$. The unit-cell parameters were refined for five compositions and were indexed in monoclinic cells with similar parameters (Table I).

TABLE IV Crystallographic parameters for $Li_{0.15}La_{0.95}VO_4$ from Rietveld refinement of neutron diffraction data

Space group	$P2_1/n$ (no. 14)	No. steps (2θ)	0.05
Z	4	No. variables	47
a (nm)	0.704 7(1)	No. reflections	676
b (nm)	0.728 3(6)	No. atoms/asymmetric unit	7
c (nm)	0.672 6(8)		
β (deg)	104.86(1)	Limits of 2θ (deg)	10–153
V (10^{-3}) nm	333.65		

$R_B = 4.8$, $R_{WP} = 7.50$, $R_P = 7.01$, $R_F = 2.9$, $R_E = 6.02$

X-ray powder diffraction and electron microscopy show that the products were single phases, and they could be adequately described as related with the monazite-type structure.

The atomic coordinates are given in Table II and bond distances are listed in Table III for $Li_{0.90}La_{0.70}VO_4$. The agreement between the observed and calculated diffraction profiles is shown in Fig. 2. The profile R factors ($R_B = 5.1$; $R_{WP} = 16.7$; $R_P = 12.1$ $R_F = 4.3$ and $R_E = 7.1$) are indicative of a reliable structural model.

The mean Li–O, V–O and La–O distances are in agreement with the ionic radii as given by Shannon [14]. In spite of the above R factor values, it must be pointed out that these structural results deduced from X-ray diffraction data, are somewhat rough as far as

TABLE V Fractional atomic coordinates and thermal parameters of $Li_{0.15}La_{0.95}VO_4$ at 295 K

Atom	Position	x	y	z	B (10^{-2} nm^2)
La	4e	0.2764(1)	0.1575(3)	0.1044(13)	0.46
Li	4e	0.1939(1)	0.2467(1)	0.2139(1)	2.15
V	4e	0.3006(1)	0.1649(2)	0.6169(1)	0.04
O(1)	4e	0.2450(2)	− 0.0020(8)	0.4281(5)	0.83
O(2)	4e	0.3866(2)	0.3444(5)	0.4959(1)	1.07
O(3)	4e	0.4836(4)	0.1058(2)	0.8245(2)	1.15
O(4)	4e	0.1180(8)	0.2207(2)	0.7283(2)	1.01

TABLE VI Bond lengths for $Li_{0.15}La_{0.95}VO_4$

La–O(1)	0.2527(6) nm	Li–O(1)	0.2285(5) nm	V–O(1)	0.1729(4) nm
	0.2490(1) nm		0.2157(9) nm	V–O(2)	0.1729(8) nm
La–O(2)	0.2888(3) nm	Li–O(2)	0.2151(1) nm	V–O(3)	0.1695(5) nm
	0.2655(2) nm		0.2377(2) nm	V–O(4)	0.1695(6) nm
	0.2564(7) nm	Li–O(3)	0.2117(1) nm	Shannon	0.175 nm
La–O(3)	0.2520(3) nm	Shannon	0.208 nm		
	0.2688(7) nm				
La–O(4)	0.2531(6) nm				
	0.2500(1) nm				
Shannon	0.261 nm				

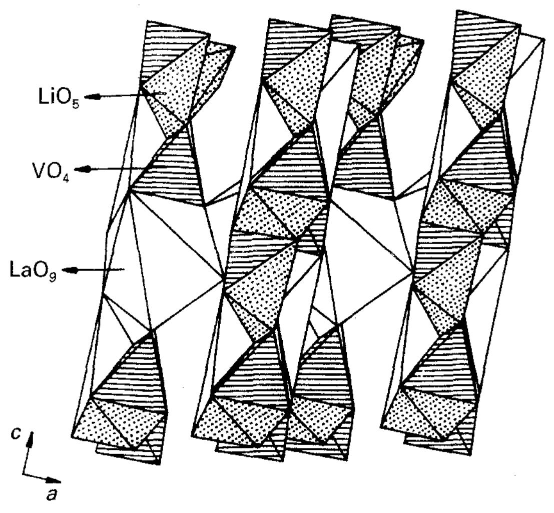

Figure 4 $Li_{3x}La_{(1-x)}VO_4$ ($0 \leqslant x \leqslant 0.3$) structure viewed along the (0 1 0) direction.

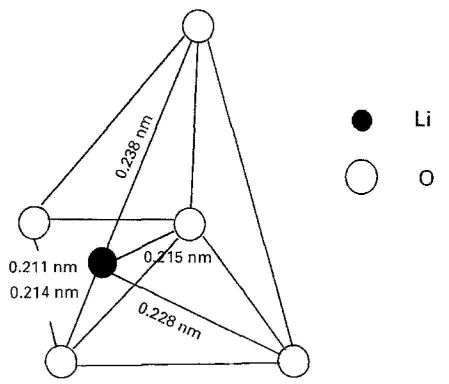

Figure 5 The five-coordinate lithium–oxygen square pyramid in $Li_{3x}La_{(1-x)}VO_4$ ($0 \leqslant x \leqslant 0.3$).

the interatomic distances are concerned, owing to the low scattering factors of lithium and oxygen atoms.

The structure determination of $Li_{0.90}La_{0.70}VO_4$ from X-ray diffraction analysis and the space group assignment by means of electron diffraction data, suggest that this compound is defined by LaO_9, LiO_5 and VO_4 with the monoclinic space group $P2_1/n$.

Therefore, more precise information was obtained by means of a neutron diffraction study on a polycrystalline sample of $Li_{0.15}La_{0.95}VO_4$. Crystallographic data for $Li_{0.15}La_{0.95}VO_4$ obtained from the Fullprof program are reported in Table IV. The profile R factors are compatible with our previous structural model and the atomic coordinates are given in Table V. This model provides good agreement between observed and calculated neutron diffraction profiles, as shown in Fig. 3.

Because virtually analogous unit-cell parameters were obtained from X-ray and neutron diffraction data, it may be concluded that these $Li_{3x}La_{(1-x)}VO_4$ $(0 \leqslant x \leqslant 0.3)$ derivatives adopt a common structure which is in proper accord with the parent monazite type. Both the main bond distances around lanthanum, lithium and vanadium atoms, and the mean metal–oxygen distances as well as those calculated from the ionic radii [15], are given in Table VI. This refinement provides more reliable values for metal–oxygen bond distances that those previously obtained by X-ray diffraction.

The overall structure could then be described by means of (VO_4) tetrahedra, (LaO_9) polyhedra and (LiO_5) units. Fig. 4 shows a view of this structural model. The lithium atoms are coordinated to five oxygens, in a polyhedron which is related to a distorted square pyramid (Table VII) as is shown in detail in Fig. 5. Such an irregular polyhedron is rather unusual for lithium, but in this structure it apparently favours the most efficient packing of atoms [16].

From these results, it can be observed that around the lithium occupied positions there are other vacant sites towards which this cation could migrate and, therefore, these materials are to be good ionic conductors. Such properties are being investigated and results to data are extremely interesting.

TABLE VII Angles 0–Li–0 in $Li_{0.15}La_{0.95}VO_4$

O(1)–Li–O(2)	97.9 (8)°	O(1)–Li–O(3)	101.0 (9)°
O(1)–Li–O(2)	87.5 (5)°	O(2)–Li–O(3)	75.4 (6)°
O(1)–Li–O(3)	87.8 (4)°		

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