

Preparation and Characterization of $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$ with K_2NiF_4 Structure*

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The A_2BX_4 ($\text{X} = \text{F}, \text{O}$) compounds with K_2NiF_4 -type structure are characterized by alternate perovskite (ABX_3) and rocksalt (AX) layers along the c axis. In such a structure the perovskitic octahedron around a B ion can undergo quite large distortions without compromising the lattice stability. This allows the transition metal B ions to assume different electronic configurations (low spin or high spin), thus showing a more or less marked elongation of BX_6 octahedra ($c/a > 1$).

Besides the B ion spin-state, the bond strengths between the X anion and the various metal ions with different electronegativity, that appear to enter A or B sites, also contribute to the distortion of the perovskitic octahedra on the grounds of their size and charge. This condition mainly occurs in compounds belonging to the series $\text{La}_2\text{Li}_{0.5}\text{Me}_{0.5}^{3+}\text{O}_4$ ($\text{Me}^{3+} = \text{Ni}, \text{Co}, \text{Mn}, \text{Cu}$) and $\text{La}_{1.5}\text{Me}_{0.5}^{2+}\text{Li}_{0.5}\text{Me}_{0.5}^{4+}\text{O}_4$ ($\text{Me}^{2+} = \text{Ca}, \text{Sr}, \text{Ba}$; $\text{Me}^{4+} = \text{Mn}, \text{Fe}$) with ordered distribution of Li and Me^{m} ions in BO_6 octahedra. In these compounds the ionic character of the $(\text{Li}-\text{O})_{\text{eq}}$ bonds increases the covalency of the competing $(\text{Me}-\text{O})_{\text{eq}}$ bonds, bringing about their shortening and enhancing the elongation of the Me^{m} octahedral environment ($c/a > 1$).

The possibility of establishing the degree of octahedron distortion caused by competition between $\text{Li}-\text{O}-\text{Me}$ bond strengths has been hitherto blocked by the lack of compounds of this type containing Me^{3+} with electronic configuration n^2np^6 (i.e. $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$), where it must necessarily exclude any effect on the electronic configuration in deforming the octahedron.

The synthesis of $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$ has already been tried unsuccessfully by Blasse [1]; nevertheless we re-examined the possibility of its preparation with positive results.

In this note we report the preparation details; the results of structural analysis for this new phase are

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discussed and compared with those of other already known $\text{La}_2\text{Li}_{0.5}\text{Me}_{0.5}\text{O}_4$ and A_2MeO_4 compounds.

Experimental

Mixtures of lanthanum and aluminum nitrates with atomic ratios $\text{La}/\text{Al} = 4$ were thermally decomposed following a procedure we described in previous work [2, 3]. The highly reactive solid so obtained (specific surface $\approx 150 \text{ m}^2/\text{g}$) was added to LiOH in a slight excess (about 5 wt%) as regards the stoichiometry and carefully homogenized by grinding in an agate mortar. The powder was pressed into tablets and heated at 800°C in air for about 10 h in silver vessels.

Results and Discussion

The microcrystalline solid obtained in this way, examined by X-ray powder diffractometry ($\text{Cu K}\alpha$ radiation; $\lambda = 1.5418 \text{ \AA}$), was found to be monophasic. Its XR powder diffractogram characterizes a tetragonal K_2NiF_4 structure with $a_0 = 3.772 \pm 0.001$, $c_0 = 12.757 \pm 0.004 \text{ \AA}$; $c_0/a_0 = 3.38$ (space group = $I4/mmm$). As for other already known terms of the $\text{La}_2\text{Li}_{0.5}\text{Me}_{0.5}\text{O}_4$ series, also for this compound the XR powder diffraction patterns alone do not reveal superlattice reflections that prove an ordering of Li^+ and Al^{3+} ions in octahedral B sites.

Therefore the structural refinement was based on the space group $I4/mmm$, using a starting model characterized by La in A sites (4e), Al and Li statistically distributed in B sites (2a), and oxygen in 4e (O_{II}) and 4c (O_{I}). This model was refined first for atomic coordinates and then for isotropic thermal factor. The minimum reliability factor was $R = 7.0$ percent with the parameter values given in Table I. In Table II are reported the calculated and observed intensities together with the lattice spacings of the reflections.

TABLE I. Crystallographic Parameters for $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$

Atoms in position	x	y	z	Occupancy	B (\AA^2)
Li (4e)	0	0	0.3625	2	0.6
Li (2a)	0	0	0	0.5	0.9
Al (2a)	0	0	0	0.5	1.2
O_{II} (4c)	0.5	0	0	2	0.3
O_{I} (4e)	0	0	0.17	2	0.7

Bond lengths: $\text{Me}-\text{O}_{\text{I}} = 2.169 \text{ \AA}$, $\text{Me}-\text{O}_{\text{II}} = 1.886 \text{ \AA}$. $c/a = 1.15$. Reliability factor $R = 0.070$. Space group = $I4/mmm$.

TABLE II. X-ray Powder Diffraction Pattern of $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$

hkl	d	I_{obs}	I_{calc}	hkl	d	I_{obs}	I_{calc}
1 0 1	3.6172	89	88.6	2 0 6	1.4109	8	8.6
0 0 4	3.1892	50	38.4	1 2 5	1.4071	9	8.4
1 0 3	2.8218	100	102.6	1 1 8	1.3687	9	7.9
1 1 0	2.6672	76	79.5	2 2 0	1.3336	11	10.8
1 1 2	2.4607	8	9.3	3 0 1	1.2513	3	3.5
0 0 6	2.1262	10	10.0	1 2 7	1.23769	19	17.4
1 0 5	2.1133	25	18.3	2 2 4	1.23037	8	7.7
1 1 4	2.0460	71	71.4	2 0 8	1.21770	9	8.4
2 0 0	1.8860	37	39.9	3 0 3	1.20573	5	6.8
2 1 1	1.6723	18	19.0	1 3 0	1.19281	10	10.6
1 1 6	1.6626	6	8.1	1 1 10	1.15084	4	5.2
1 0 7	1.6409	24	23.3	2 2 6	1.12976	5	5.6
2 0 4	1.6234	18	20.2	3 0 5	1.12782		
0 0 8	1.5946	6	5.6	3 1 4	1.11723	16	16.7
1 2 3	1.5690	29	33.6	1 0 11	1.10852	11	9.4

Tetragonal cell: $a_0 = 3.772 \pm 0.001$, $c_0 = 12.757 \pm 0.004$ Å.
Internal silicon standard: $a_0 = 5.4306$ Å.

In the isomorphous compounds $\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$ [4] and $\text{La}_{1.5}\text{Sr}_{0.5}\text{Li}_{0.5}\text{Fe}_{0.5}\text{O}_4$ [5] an ordering of Li^+ and Me^{n+} cations in octahedral sites was evidenced by electron and neutron diffraction respectively. This argument, together with the closeness of the mean deformation of the octahedron $(\text{Li}_{0.5}\text{Me}_{0.5})\text{O}_6$ ($c/a = 1.15$ for the title compound and 1.147 for the Co-containing isomorphous compound), induced us to suppose an ordered distribution of both ions in B sites for $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$ also.

The possibility to separately estimate the deformations of LiO_6 and AlO_6 octahedra would require a structural analysis based on a pseudo-tetragonal orthorhombic unit cell having $a = a_0\sqrt{2}$ and $c = c_0$, as we did for the ordered compound $\text{La}_2\text{Li}_{0.5}\text{Au}_{0.5}\text{O}_4$

whose XR powder diffraction pattern showed superstructure lines of significant intensities that allowed a structural analysis based on space group $Cmmm$ [6].

The lack of these superstructure reflections compels us to estimate the deformation of AlO_6 octahedra assuming at first approximation the $I4/mmm$ space group (tetragonal K_2NiF_4). Starting from O_{II} atomic coordinates and the relation $(\text{Me}-\text{O})_{\text{eq}} = a_0 - (\text{Li}-\text{O})_{\text{eq}}$ we estimated the c/a ratio for AlO_6 octahedra after previous determination of $(\text{Li}-\text{O})_{\text{eq}}$, using the method of Brown and Wu [7].

The same calculation has been carried out for $\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$ employing the crystallographic data reported in ref. 8. The result obtained with the method we adopted perfectly agrees with that calculated by Demazeau *et al.* [8]. Using the above method we recalculated the c/a ratios for other already known $\text{A}_2\text{Li}_{0.5}\text{Me}_{0.5}\text{O}_4$ compounds and the results are shown in Table III. In the same Table we report other data (crystallographic parameters and electronic configurations of the transition metal ions) for compounds of the K_2NiF_4 -type. Assuming the c/a ratio, in order to estimate the octahedral deformation, it can be shown that this value markedly changes according to the ions entering these compounds, going from 0.98 for K_2NiF_4 to 1.42 for $\text{La}_{1.75}\text{Li}_{0.75}\text{Fe}_{0.5}\text{O}_4$.

Excluding from our considerations K_2NiF_4 , the mixed oxides have been divided into two groups, according as to whether the B sites are occupied by Me^{3+} only or by ordered Li^+ and Me^{n+} ions, assuming as 'model compound' for each group LaSrAlO_4 and $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$ respectively, both characterized by cations with d^0 outer orbitals.

The AlO_6 octahedral deformation ($c/a = 1.08$) can be construed as due merely to the bond strengths competition associated with 180° (La,Sr)-O-Al linkages along the c -axis. In compounds of this

TABLE III. Crystallographic Parameters and Electronic Configuration of Me^{n+} Ions for some A_2BX_4 Compounds

Compound	a_0	c_0	c_0/a_0	c/a	Elec. conf.	Reference
K_2NiF_4	4.006	13.071	3.26	0.985	d^8	9
La_2NiO_4	3.866	12.65	3.27	1.1	d^8	10
LaSrCuO_4			3.52	1.186	d^8 JT	11
LaSrAlO_4	3.758	12.645	3.36	1.08	d^0	
LaSrCoO_4	3.80	12.50	3.29	1.065	d^6 LS	1
LaSrFeO_4	3.870	12.68	3.28	1.10	d^5 HS	12
LaSrCrO_4	3.84	12.52	3.27	1.085	d^3	1
$\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$	3.772	12.757	3.38	1.35	d^0	
$\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$	3.783	12.61	3.34	1.34	d^6 LS	8
$\text{La}_{1.5}\text{Sr}_{0.5}\text{Li}_{0.5}\text{Mn}_{0.5}\text{O}_4$	3.802	12.665	3.33		d^3	13
$\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$	3.756	12.87	3.43		d^7 JT	14
$\text{La}_2\text{Li}_{0.5}\text{Mn}_{0.5}\text{O}_4$	3.791	12.96	3.42	1.39	d^4 JT	15
$\text{La}_{1.5}\text{Sr}_{0.5}\text{Li}_{0.5}\text{Fe}_{0.5}\text{O}_4$	3.76	13.01	3.46		d^4 JT	16
$\text{La}_{1.75}\text{Li}_{0.75}\text{Fe}_{0.5}\text{O}_4$	3.765	12.918	3.43	1.42	d^4 JT	2
$\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$	3.731	13.20	3.54		d^8 JT	11

group a deformation of this order must be regarded therefore as independent of electronic configuration of Me^{n+} ions in the octahedral B sites. In compounds containing non-Jahn–Teller Me^{n+} ions (Fe^{3+} , Cr^{3+} , Co^{3+} , Ni^{2+}) the c/a ratio is really about 1.08 ± 0.02 . The larger elongation we find for CuO_6 octahedra in LaSrCuO_4 ($c/a = 1.18$) may be explained as the result of the Jahn–Teller (J.T.) effect of the outer 3d electron of the Cu^{3+} ion.

Considerations of the same kind suggest the elongation of AlO_6 octahedra in $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$ ($c/a = 1.34$) as the typical one for MeO_6 in compounds of the second group, due to the competition mainly between Li–O–Me bond strengths in the perovskite layers.

Even if we dispose of structural analysis data for a few compounds of this type, it still clearly appears that in $\text{La}_2\text{Li}_{0.5}\text{Mn}_{0.5}\text{O}_4$ ($c/a = 1.39$) and $\text{La}_{1.75}\text{Li}_{0.75}\text{Fe}_{0.5}\text{O}_4$ ($c/a = 1.42$), the J.T. effect causes an important increase in the elongation in MeO_6 octahedra already strongly deformed owing to Li–O–Me competition. In the presence of non-J.T. Me^{n+} ions, the deformation of MeO_6 octahedra should be of the same order as that of AlO_6 octahedra, as occurs in $\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$ ($c/a = 1.34$). On the contrary, we may suppose that in $\text{La}_{1.5}\text{Sr}_{0.5}\text{Li}_{0.5}\text{Fe}_{0.5}\text{O}_4$, $\text{La}_2\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}_4$ and especially in $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$, which all contain J.T. Me^{n+} ions, the c/a ratio would be higher than 1.34.

In the ternary system La_2O_3 – Li_2O – Al_2O_3 , in the field comprised among La_2O_3 , Li_5AlO_4 and LiLaO_2 , a new phase was also evidenced. Its XR diffraction pattern shows reflections indexable as required for a tetragonal unit cell, still K_2NiF_4 -type, with $a_0 = 3.668$ and $c_0 = 13.257$ Å. It has not been possible until now to achieve any samples pure enough to state exactly the composition of this new phase and study its structure. The starting composition of the La_2O_3 , Al_2O_3 and Li_2O oxide mixture that supplied samples with highest content of this phase correspond to atomic ratios $\text{La}:\text{Al}:\text{Li} = 1:0.15:1$.

The XR powder diffraction pattern shown in Fig. 1 is that yielded by a sample heated at 800°C in air for about 2 h, compared with that of $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$.

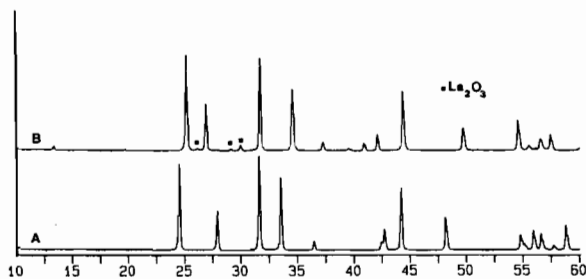


Fig. 1. Diffraction patterns of: (A) $\text{La}_2\text{Li}_{0.5}\text{Al}_{0.5}\text{O}_4$; and (B) sample with starting composition $\text{La}:\text{Al}:\text{Li} = 1:0.15:1$.

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