

# Single-crystal synthesis and structure refinement of the $\text{LiCoO}_2$ – $\text{LiAlO}_2$ solid-solution compounds: $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$ and $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$

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## Abstract

Single crystals of the  $\text{LiCoO}_2$ – $\text{LiAlO}_2$  solid solution compounds  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$  were synthesized by a flux method using alumina crucibles. A single-crystal X-ray diffraction study confirmed the trigonal  $R\bar{3}m$  space group and the lattice parameters  $a = 2.8056(11) \text{ \AA}$ ,  $c = 14.1079(15) \text{ \AA}$ , and  $c/a = 5.028$  for  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$ , and  $a = 2.8023(7) \text{ \AA}$ ,  $c = 14.184(4) \text{ \AA}$ , and  $c/a = 5.061$  for  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$ . The crystal structures have been refined to the conventional values  $R = 3.2\%$  and  $wR = 2.4\%$  for  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$ , and  $R = 3.6\%$  and  $wR = 3.5\%$  for  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$ . The evidence of the location of Al atoms in the pseudotetragonal coordination ( $6c$  site), reported previously in  $\text{LiAl}_{0.2}\text{Co}_{0.8}\text{O}_2$ , could not be observed in the present electron density distribution maps in both  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$ . The octahedral distortion analysis indicated that the Al-substitution strongly affected the distortion of the  $\text{LiO}_6$  octahedron in this solid-solution compound system, but hardly affected that of the  $(\text{Al,Co})\text{O}_6$  octahedron.

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**Keywords:** Crystal growth; Crystal structure;  $\text{LiCoO}_2$ ;  $\text{LiAlO}_2$ ; Layered cobalt oxide; Single-crystal X-ray diffraction; Electron density analysis; MEM

## 1. Introduction

Lithium cobalt dioxide,  $\text{LiCoO}_2$ , has a trigonal  $\alpha$ - $\text{NaFeO}_2$  structure and is the most widely used cathode material of commercial secondary lithium-ion batteries due to its advantages, including easy preparation and a high theoretical specific capacity. In order to improve its electrode performance, the substitution of Co with metal ions has been reported. Recently, Ceder et al. have shown that the  $\text{LiCoO}_2$ – $\text{LiAlO}_2$  solid-solution compound,  $\text{LiAl}_y\text{Co}_{1-y}\text{O}_2$ , is potentially attractive for electrochemical applications because of the higher intercalation voltage, higher energy density, and lower cost, although it shows large capacity fading during cycling [1,2]. The local structural properties of these  $\text{LiAl}_y\text{Co}_{1-y}\text{O}_2$  solid solution compounds with  $0 < y < 1$  have been reported by powder XRD, NMR and XAFS analyses using polycrystalline samples [3–5]. Alcántara et al. [3] reported additional partial occupancy of the  $6c$  sites by the Al atoms in the Rietveld refinement, although they have never reported the

atomic displacement parameters. However, Gaudin et al. [5] recently reported a simple solid-solution model of the octahedral sites randomly occupied by Co and Al.

We have recently synthesized single crystals of the end member compound,  $\text{LiCoO}_2$  by a flux method, and revealed the precise structural and physical properties [6,7]. To clarify the true crystal symmetry and precise structural properties of the  $\text{LiAl}_y\text{Co}_{1-y}\text{O}_2$  compounds, well-characterized single-crystal specimens are highly desirable; however, the corresponding single crystals have not yet been synthesized. In the present study, we report the synthesis of single crystals by a flux method using alumina crucibles, and the structure refinements of two solid-solution compounds,  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$ , by single-crystal X-ray structure analysis.

## 2. Experimental

The single-crystal synthesis was performed by a flux method, which was similar to that described in previous reports [6,7] but using alumina crucibles. The as-prepared  $\text{LiCoO}_2$  powder for a battery use (Cell Seed C, Nippon

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Chemical Industrial Co., Ltd., Japan) was mixed with  $\text{Li}_2\text{O}$  (99.9%) and  $\text{LiCl}$  (99.9%) to form flux material in the nominal weight ratio of  $\text{LiCoO}_2:\text{Li}_2\text{O}:\text{LiCl} = 1:4:4$ . The mixture was heated at 1173–1373 K for 10 h in alumina crucibles, gradually cooled to 973 K at a rate of 2 K/h, and then cooled naturally. The products were easily separated from the frozen flux by rinsing the crucible in water for several hours. The crystals thus obtained were investigated by SEM–EDX (JEOL JSM-5400) and inductive coupled plasma spectroscopy (ICP). The crystal symmetry and intensity data were examined by the single-crystal X-ray diffraction method.

### 3. Results and discussion

#### 3.1. Single-crystal synthesis

In the present experimental conditions using  $\text{Al}_2\text{O}_3$  crucibles, considerable aluminum contamination from the container material was observed. Black platelet crystals of about  $0.5 \times 0.5 \times 0.2 \text{ mm}^3$  (maximum) were obtained, as shown in Fig. 1. The chemical composition of the grown crystals was analyzed by ICP and SEM–EDX. Both measurements for the molar ratio of  $\text{Co}/\text{Al}$  showed almost the same results. We performed flux growth experiments with different maximum temperatures between 1173 and 1373 K. When the maximum temperature was increased, the resultant Al-content in the produced crystals increased. However, above 1273 K, single crystals of  $\gamma\text{-LiAlO}_2$  were also synthesized. These results are in good agreement with the previous reports for polycrystalline samples [5] and for a computed phase diagram [8]. Furthermore, the obtained  $\text{Li}(\text{Al}_y\text{Co}_{1-y})\text{O}_2$  crystals changed from opaque to transparency together with the Al-content. The compositions of two single-crystal specimens,  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  (opaque) and  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$  (transparency), synthesized at 1173 and 1373 K, respectively, were determined to be  $\text{Li}:\text{Al}:\text{Co}:\text{O} = 1.0:0.3:0.7:2$ , and  $\text{Li}:\text{Al}:\text{Co}:\text{O} = 1.0:0.7:$

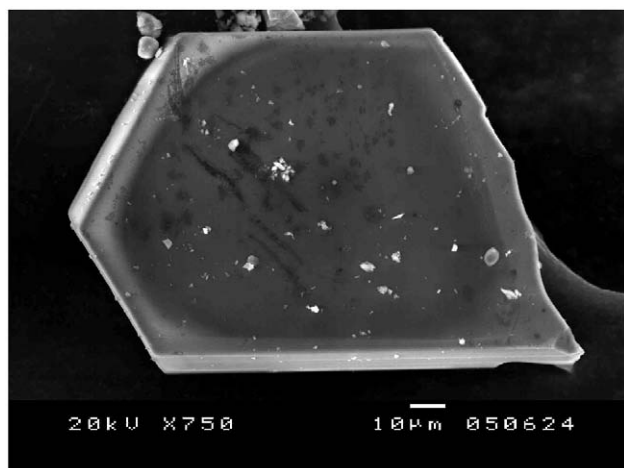


Fig. 1. SEM photograph of  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$  single crystal.

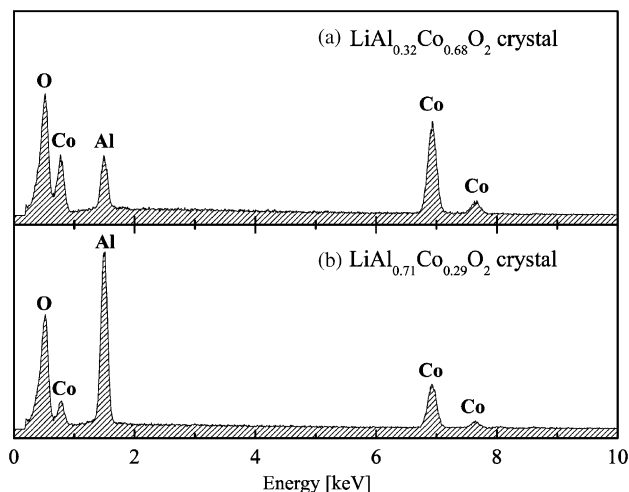


Fig. 2. Typical EDX spectra of (a)  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and (b)  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$  single crystals.

$0.3:2$ , respectively, which agree well with the structural formulae. Fig. 2 shows the EDX spectra of these single-crystal specimens. The maximum Al-content in the  $\text{LiAl}_y\text{Co}_{1-y}\text{O}_2$  crystals in the present experiment was  $y = 0.75$  from the results of EDX analysis.

X-ray precession photographs of these single crystals showed the trigonal symmetry and space group of  $R\bar{3}m$ , which is isostructural with  $\text{LiCoO}_2$  and  $\alpha\text{-LiAlO}_2$ . We could not find any superstructures in this study. The lattice parameters, which were determined by least-squares refinement using  $2\theta$  values of 25 strong reflections in the range  $26\text{--}36^\circ$  and  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) on an automated Rigaku AFC-7S four-circle diffractometer, were  $a = 2.8056(11) \text{ \AA}$ ,  $c = 14.1079(15) \text{ \AA}$ , and  $c/a = 5.028$  for  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$ , and  $a = 2.8023(7) \text{ \AA}$ ,  $c = 14.184(4) \text{ \AA}$ , and  $c/a = 5.061$  for  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$ , respectively. These values agree quite well with the reported powder data [3–5] for  $\text{LiAl}_y\text{Co}_{1-y}\text{O}_2$ ; e.g.  $a = 2.8108(3) \text{ \AA}$ ,  $c = 14.137(1) \text{ \AA}$ ,  $c/a = 5.030$  for  $y = 0.30$  and  $a = 2.8008(2) \text{ \AA}$ ,  $c = 14.1960(7) \text{ \AA}$ ,  $c/a = 5.069$  for  $y = 0.70$ , respectively [3].

#### 3.2. Structure refinement

The intensity data were collected by the  $2\theta\text{--}\omega$  scan mode with a scan rate of  $2^\circ/\text{min}$  at 298 K on the four-circle diffractometer (operating conditions: 50 kV, 40 mA). The fluctuation of the intensities, monitored by examining a set of three standard reflections ((110), (009), (104)) taken after every 150 reflections, was within 1.21% for  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and 1.04% for  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$ . A summary of the crystallographic and experimental data is given in Table 1.

Structure refinements were carried out using the Xtal 3.4 program [9]. Structure factors were obtained after averaging the equivalent Bragg intensities, which were corrected for Lorentz and polarization factors, scale factors,

Table 1  
Crystallographic and experimental data for  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$

	$\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$	$\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$
Structural formula	$\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$	$\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$
Crystal system	Trigonal	Trigonal
Space group	$R\bar{3}m$	$R\bar{3}m$
$a$ (Å)	2.8056(11)	2.8023(7)
$c$ (Å)	14.1079(15)	14.184(4)
$V$ (Å <sup>3</sup> )	96.17(8)	96.46(5)
$Z$	3	3
Crystal size (μm)	150 × 150 × 150	300 × 100 × 10
Temperature (K)	298	298
Maximum $2\theta$ (°)	135	135
Absorption correction method	Gaussian integration	
Transmission factors		
Min.	0.298	0.587
Max.	0.408	0.948
Measured reflections	668	2308
$R_{\text{int}}$	0.022	0.053
Independent reflections	264	262
Observed reflections ( $>3\sigma$ )	264	260
Number of variables	10	10
$R$	0.032	0.036
$wR$ [ $w = 1/\sigma^2 F$ ]	0.024	0.035
Extinction parameter $g$	228(10)	56(21)

and absorption and extinction effects. Neutral atomic scattering factors for all atoms were applied in the refinement.

The crystal structures of  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$  were first refined using the atomic coordinates of  $\text{LiCoO}_2$  ( $R\bar{3}m$  space group; Li at the  $3a$  site, Al and Co at the  $3b$  site and O at the  $6c$  site). In the present refinements, the Co and Al atoms were statistically distributed only in the  $3b$  site. The refined occupancy parameters of Co/Al were in good agreement with the results of chemical analysis. The evidence of the location of the Al atoms in the pseudotetragonal coordination ( $6c$  site), reported in  $\text{LiAl}_{0.2}\text{Co}_{0.8}\text{O}_2$  [3], could not be observed in the present electron density distribution maps using the computer program PRIMA [10], as shown in Fig. 3. Furthermore, in the final stage of the refinements, an additional Li occupation model at the  $3b$  site was introduced, such as in the “lithium overstoichiometric”  $\text{Li}_{1.1}\text{CoO}_2$  [11,12]. However, such a substitution model did not improve both the  $R$  values and the structural parameters for these compounds. Finally, the structures were refined to  $R = 3.2\%$  and  $wR = 2.4\%$  for  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$ , and  $R = 3.6\%$  and  $wR = 3.5\%$  for  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$ , respectively. The final atomic coordinates and displacement parameters are given in Tables 2 and 3.

### 3.3. Structural discussions

The structure refinement revealed that the chemical compositions of the present single-crystal samples were  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$ , respectively (Table 1), which were well consistent with the chemical analysis results. In comparison with the structural data of  $\text{LiCoO}_2$

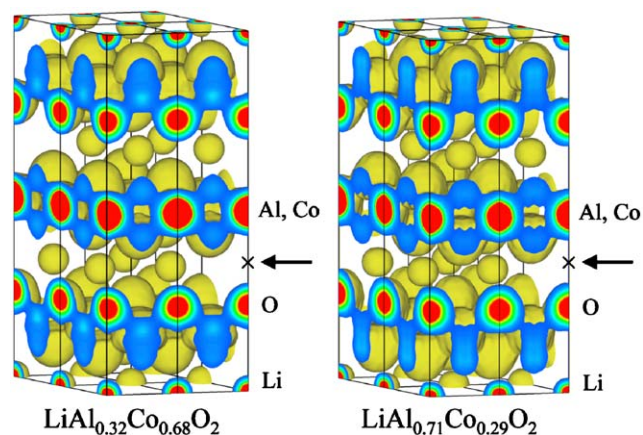


Fig. 3. Three-dimensional electron density distributions of: (a)  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and (b)  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$  obtained by Maximum Entropy Method using the computer program PRIMA [9]. These figures were drawn with VENUS developed by Dilanian and Izumi. Iso-surface density level is equal to  $0.4 \text{ \AA}^{-3}$ . The vacant  $6c$  sites are indicated by arrows in both compounds.

( $z(\text{O}) = 0.23951(15)$ ) [6], the refined oxygen coordination parameter,  $z(\text{O})$ , decreases together with increasing the Al-content (Tables 2 and 3). The precise oxygen positions in this solid-solution compound system were determined for the first time in the present single-crystal study. The negative deviations of the  $z$  parameters from the ideal value of 0.25 compress the (Al, Co) $\text{O}_6$  octahedra and elongate the  $\text{LiO}_6$  octahedra. The selected bond distances and angles are listed in Table 4, together with the data of  $\text{LiCoO}_2$ .

The Li–O distance of  $2.1016(7) \text{ \AA}$  and the O–O' distance ( $3.1327(13) \text{ \AA}$ ) of the  $\text{LiO}_6$  octahedron in  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$  is longer than those in  $\text{LiCoO}_2$  and  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$ . This fact indicates an apparent elongation of the  $\text{LiO}_6$  to the  $c$ -axis direction. This may have a positive effect on Li-ion diffusion, as previously suggested [5]. On the other hand, the (Al, Co)O distances are shortened by the Al-substitution, from  $1.9213(12) \text{ \AA}$  in  $\text{LiCoO}_2$  to  $1.9140(6) \text{ \AA}$  in  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$ . However, the precise changes of the (Al, Co) $\text{O}_6$  octahedral distortion could not be revealed only by the comparison of bond distances and angles, because both the O–O and O–O' distances of the (Al, Co) $\text{O}_6$  octahedra are shortened by the Al-substitution (Table 4).

The structural changes by the Al substitution in the  $\text{LiAl}_y\text{Co}_{1-y}\text{O}_2$  compounds were evaluated using the crystallographic parameters of the  $\text{LiO}_6$  and (Al, Co) $\text{O}_6$  octahedra in the present study. The octahedral volumes and distortion parameters ( $\lambda$  and  $\sigma^2$ ) were calculated with the program VOLCAL [13]. Distortion parameters include the quadratic elongation,  $\lambda$ , which is equal to unity for a regular octahedron and is  $>1$  for a distorted octahedron, and the bond angle variance,  $\sigma^2$ , which is equal to zero for a regular octahedron and is positive for a distorted octahedron, respectively [14].

Fig. 4 shows the relationship between the Al-content and the octahedral volumes. As can be seen from this figure, the

Table 2  
Atomic coordinates, displacement parameters,<sup>a</sup> and site occupancy factors for LiAl<sub>0.32</sub>Co<sub>0.68</sub>O<sub>2</sub>

Atom	Site	x	y	z	U <sub>eq</sub>	U <sub>33</sub>	U <sub>12</sub>	s.o.f.
Li	3a	0	0	0	0.0107(18)	0.0068(18)	0.0063(9)	1
Al	3b	0	0	0.5	0.00278(9)	0.00240(9)	0.00149(4)	0.318(10)
Co	3b	0	0	0.5	0.00278(9)	0.00240(9)	0.00149(4)	0.682(10)
O	6c	0	0	0.23941(8)	0.0050(3)	0.0042(3)	0.00270(13)	1

<sup>a</sup>Displacement parameter conditions are  $U_{11} = U_{22} = 2U_{12}$  and  $U_{13} = U_{23} = 0$ , respectively.

Table 3  
Atomic coordinates, displacement parameters,<sup>a</sup> and site occupancy factors for LiAl<sub>0.71</sub>Co<sub>0.29</sub>O<sub>2</sub>

Atom	Site	x	y	z	U <sub>eq</sub>	U <sub>33</sub>	U <sub>12</sub>	s.o.f.
Li	3a	0	0	0	0.0137(15)	0.0121(19)	0.0072(6)	1
Al	3b	0	0	0.5	0.00482(10)	0.00632(13)	0.00203(4)	0.711(6)
Co	3b	0	0	0.5	0.00482(10)	0.00632(13)	0.00203(4)	0.289(6)
O	6c	0	0	0.23877(6)	0.0065(2)	0.0072(3)	0.00305(10)	1

<sup>a</sup>Displacement parameter conditions are  $U_{11} = U_{22} = 2U_{12}$  and  $U_{13} = U_{23} = 0$ , respectively.

Table 4  
Selected bond distances (Å) and angles (deg.) for LiAl<sub>y</sub>Co<sub>1-y</sub>O<sub>2</sub>

	LiCoO <sub>2</sub> <sup>a</sup>	LiAl <sub>0.32</sub> Co <sub>0.68</sub> O <sub>2</sub>	LiAl <sub>0.71</sub> Co <sub>0.29</sub> O <sub>2</sub>
<i>LiO<sub>6</sub> octahedron</i>			
Li–O	2.0934(14)	2.0928(9)	2.1016(7)
O–O	2.8161(5)	2.8056(11)	2.8023(7)
O–O'	3.098(3)	3.1060(14)	3.1327(13)
O–Li–O	84.54(5)	84.18(3)	83.63(3)
O–Li–O'	95.46(5)	95.82(3)	96.37(3)
<i>(Al, Co)O<sub>6</sub> octahedron</i>			
(Al, Co)–O	1.9213(12)	1.9175(8)	1.9140(6)
O–O	2.8161(5)	2.8056(11)	2.8023(7)
O–O'	2.614(2)	2.6146(13)	2.6079(12)
O–(Al, Co)–O	94.25(5)	94.03(3)	94.12(3)
O–(Al, Co)–O'	85.75(5)	85.97(3)	85.88(3)

<sup>a</sup>Data after Akimoto et al. [6].

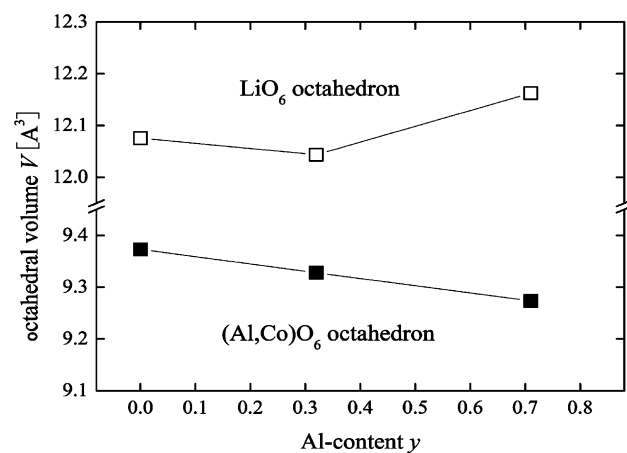


Fig. 4. Relationship between the Al-content  $y$  and the octahedral volumes  $V$  [Å<sup>3</sup>] for LiAl<sub>y</sub>Co<sub>1-y</sub>O<sub>2</sub>.

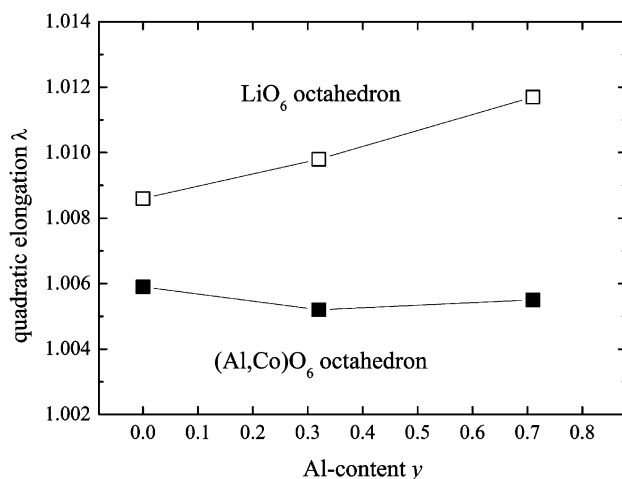


Fig. 5. Relationship between the Al-content  $y$  and the quadratic elongation  $\lambda$  for LiAl<sub>y</sub>Co<sub>1-y</sub>O<sub>2</sub>.

LiO<sub>6</sub> octahedral volume increases together with the Al-content, although the (Al, Co)O<sub>6</sub> octahedral volume decreases linearly. In addition, the distortion parameters,  $\lambda$  (Fig. 5) and  $\sigma^2$  (Fig. 6) of the LiO<sub>6</sub> octahedron indicate that the octahedral distortion increases with the Al-content. In contrast, these parameters of the (Al, Co)O<sub>6</sub> octahedron remain unchanged. From these facts, it is concluded that the Al-substitution strongly affected the distortion of the LiO<sub>6</sub> octahedron in this solid-solution compound system, but hardly affected that of the (Al, Co)O<sub>6</sub> octahedron. The decrease of the (Al, Co)O<sub>6</sub> octahedral volume can be well explained by the difference in size between the Al and Co ions. In fact, the Al–O distance of 1.905 Å in  $\alpha$ -LiAlO<sub>2</sub> [15] is much shorter than the Co–O distance of 1.9213 Å in LiCoO<sub>2</sub> [6].

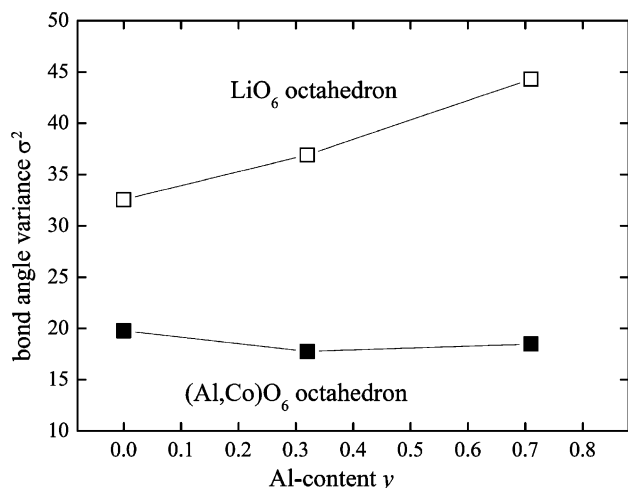


Fig. 6. Relationship between the Al-content  $y$  and the bond angle variance  $\sigma^2$  for  $\text{LiAl}_y\text{Co}_{1-y}\text{O}_2$ .

#### 4. Conclusion

We synthesized single crystals of the  $\text{LiCoO}_2$ – $\text{LiAlO}_2$  solid solution compounds  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$  for the first time. The structure refinement by the single-crystal X-ray diffraction method revealed the precise structural changes by the Al-substitution. The evidence of the location of Al atoms in the pseudotetragonal coordination ( $6c$  site), reported previously in  $\text{LiAl}_{0.2}\text{Co}_{0.8}\text{O}_2$  [3], could not be observed in the present electron density distribution maps in both  $\text{LiAl}_{0.32}\text{Co}_{0.68}\text{O}_2$  and  $\text{LiAl}_{0.71}\text{Co}_{0.29}\text{O}_2$ . The octahedral distortion analysis indicated that the Al-substitution strongly affected the distortion of the  $\text{LiO}_6$  octahedron in this solid-solution compound system,

but hardly affected that of the  $(\text{Al, Co})\text{O}_6$  octahedron. This structural feature by the Al-substitution is thought to be related to the good performance of  $\text{LiAl}_y\text{Co}_{1-y}\text{O}_2$  as a positive electrode material, predicted by the theoretical calculation [1].

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