

# Flux growth and crystal structure determination of trilithium niobate

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## Abstract

Single crystals of trilithium niobate,  $\text{Li}_3\text{NbO}_4$ , have been grown for the first time by a slow-cooling flux method using  $\text{LiCl}$  as a flux. Single crystals are transparent colourless cubes with 100–600  $\mu\text{m}$  edges. The crystal structure of  $\text{Li}_3\text{NbO}_4$  has been determined from single crystal X-ray data. This compound belongs to a cubic system, space group  $\bar{1}43m$ , the unit cell dimensions are  $a = 8.412(2)$  Å,  $V = 595.2(4)$  Å<sup>3</sup> and  $Z = 8$ . The structure comprises characteristic  $\text{Nb}_4\text{O}_{16}$  clusters which form a body-centred cubic lattice with Li ions located among the  $\text{Nb}_4\text{O}_{16}$  clusters. The  $R$  factor ( $wR$ ) is 0.045. Well-developed facets of the crystals are  $\{100\}$ . The X-ray and pycnometric densities are in good agreement:  $D_x = 3.967$  mg m<sup>-3</sup> and  $D_m = 3.95$  mg m<sup>-3</sup> respectively. The space group presented here contradicts that reported by previous researchers.

**Keywords:**  $\text{Li}_3\text{NbO}_4$ ; trilithium niobate; Single crystal; Flux growth; Crystal structure determination

## 1. Introduction

In the phase diagram of the system  $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$ , four different compounds are present:  $3\text{Li}_2\text{O} \cdot \text{Nb}_2\text{O}_5$ ,  $\text{Li}_2\text{O} \cdot \text{Nb}_2\text{O}_5$  (LN),  $\text{Li}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5$  and  $\text{Li}_2\text{O} \cdot 14\text{Nb}_2\text{O}_5$  [1]. In particular,  $\text{LiNbO}_3$  (LN) has wide device potential: acousto-optic, nonlinear-optic, electro-optic, piezoelectric and pyroelectric. So, synthesis of the single crystalline LN has been investigated extensively by many researchers for a long time [2–4]. As little attention has been given to the other three compounds, little is known about them. In this paper, we focus our interest on the title compound of trilithium niobate,  $\text{Li}_3\text{NbO}_4$ . Blasse [5] previously reported crystallographic data by the XRD method for the polycrystalline compound. Grenier and Bassi [6] reported crystallographic data by the neutron diffraction method, although the synthetic method of the specimen was not given.

$\text{Li}_3\text{NbO}_4$  is the Li-richest compound among the four compounds mentioned above [1]. The Li element that constitutes the compound tends to remove at high temperature, therefore this compound seems not to be

so stable at high temperature. The cationic ratio of Li:Nb may deviate from 3:1, stoichiometric composition, to an Li-poor site with increasing heating temperature. The present authors have studied the crystal growth of the multi-component oxides, unstable at high temperature, by the flux method using alkaline halides as solvents (fluxes) [7–9]. Here, we will report the crystal growth of the  $\text{Li}_3\text{NbO}_4$  using  $\text{LiCl}$ , one of the alkaline halides, as a flux.  $\text{LiCl}$  solvent has  $\text{Li}^+$  ion commonly with solute of  $\text{Li}_3\text{NbO}_4$ . The melting point of  $\text{LiCl}$  is 606 °C, its boiling point is 1382 °C and its density at 0 °C is 2.07 mg m<sup>-3</sup>. Results of structure determination using single crystals are also described.

## 2. Experimental details

### 2.1. Sample preparations

The solute was prepared from  $\text{Li}_2\text{CO}_3$  and  $\text{Nb}_2\text{O}_5$  with a purity better than 99.9%. These reagents were weighed in molar ratio 3:1, 1:1 and 1:3, and were mixed thoroughly in a plastic pot on a roller mixer for 6 h. This mixture was directly used as a solute (nutrient) for the flux growth experiment.  $\text{LiCl}$  (m.p. 606 °C, b.p. 1382 °C,  $d_0 = 2.07$  mg m<sup>-3</sup>) was used as a flux (solvent). A 20 wt.% mixture of the solute together with  $\text{LiCl}$  solvent, a total charge of 60 g, was

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Table 1

Growth procedure of the  $\text{Li}_3\text{NbO}_4$  single crystals by the flux method using LiCl as a flux

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solute: $\text{Li}_2\text{CO}_3, \text{Nb}_2\text{O}_5$
flux: LiCl
↓
melt in Pt crucible
↓
keep at 800 °C for 10 h
↓
cool down to 620 °C at a rate of 10 °C h <sup>-1</sup>
↓
furnace cool
↓
solidified mass ( $\text{Li}_3\text{NbO}_4$ single crystals + LiCl)
↓
dissolve LiCl in water
↓
single crystals of $\text{Li}_3\text{NbO}_4$

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put into a platinum crucible of 70 mm diameter and 70 mm depth. The crucible, without lid, was then placed in a vertical tubular electric furnace with SiC heater and was heated up to 800 °C. The mixture was kept at that temperature for 10 h to soak, slowly cooled at 10 °C h<sup>-1</sup> to 620 °C, and rapidly cooled down to room temperature. Crystal growth has been carried out in air. Single crystals were separated from the solidified mass by dissolving LiCl in water. Table 1 represents the schematic flow of the growth procedure.

## 2.2. Characterizations

The morphological properties and the impurity of the crystals were investigated by optical microscopy, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The density of the crystals was measured by means of a pycnometer using H<sub>2</sub>O at 20 °C. The contents of Li and Nb were analysed by inductive coupled plasma atomic emission spectrometry (ICP-AES) after fusion of the sample with  $\text{NH}_4\text{HSO}_4$  [10], and oxygen was determined by a helium carrier fusion thermal conductivity method using both a nickel capsule and tin as a melting flux in a graphite crucible [11]. A crystal structure analysis was carried out using an X-ray powder diffractometer and a four-circle X-ray diffractometer with graphite monochromatized Mo K $\alpha$  radiation.

## 3. Results and discussion

It is known that LiCl evaporates itself and/or in the form of dimer at high temperature. Not only by the effect of slow-cooling, but also by the effect of evaporation of solvent, saturation of the solution was achieved. As a result, single crystals of transparent colourless cubes with 100–600  $\mu\text{m}$  edges were success-

fully extracted from all of three different starting compositions. Chemical analysis for these cubic crystals showed that the chemical composition of the compound corresponded almost to Li:Nb:O = 3:1:4 in an atomic ratio. Crystals grew mainly at the bottom of the crucible, because the density of the objective compound is about two times higher than that of the flux material. LiCl acted as a good intermediate for crystal growth of the double oxide  $\text{Li}_3\text{NbO}_4$ . No significant levels of Cl or Pt from the flux or the crucible were detected in the crystals by EDX analysis. The sizes of single crystals obtained were relatively large when the solute was settled as  $\text{Li}_2\text{CO}_3$ : $\text{Nb}_2\text{O}_5$  = 1:1 in molar ratio. Fig. 1 shows a SEM photograph of the single crystals of  $\text{Li}_3\text{NbO}_4$  obtained from this solute. Good crystallinity is essentially confirmed by the observation using optical microscopy and SEM, both for the external surfaces and for the fluted surfaces of the single crystals.

After Blasse [5],  $\text{Li}_3\text{NbO}_4$  was first prepared by heating of  $\text{Li}_2\text{CO}_3$  and  $\text{Nb}_2\text{O}_5$  in the molar ratio 3:1 at 950 °C for 24 h in air. Results of the XRD method of  $\text{Li}_3\text{NbO}_4$  were reported: cubic system,  $a$  = 8.433 Å. The crystal structure determination was, however, made with the polycrystalline sample and the  $R$  factor was fairly large at 0.23. The space group was not given. Grenier and Bassi [6] also reported the crystal structure of this compound by the neutron diffraction method: cubic system, space group  $I23$ ,  $a$  = 8.429(2) Å.  $R$  factor ( $wR$ ) 0.06. The synthetic method of the specimen was not mentioned.

Structure determination using a single crystal was performed [12]. It belongs to a cubic system. Well-developed facets of the crystals are {100}. Space group  $I\bar{4}3m$ ; lattice parameters  $a$  = 8.412(2) Å,  $V$  = 595.2(4) Å<sup>3</sup> and  $Z$  = 8.  $R$  factor ( $wR$ ) 0.045. This value is

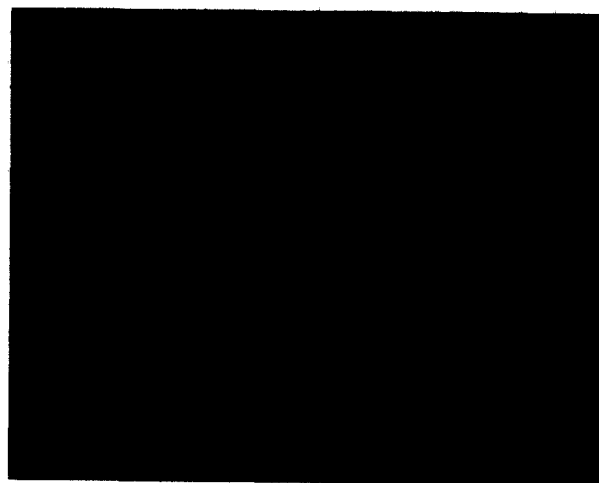


Fig. 1. External morphology of the  $\text{Li}_3\text{NbO}_4$  crystals extracted from a solution using LiCl as a flux.

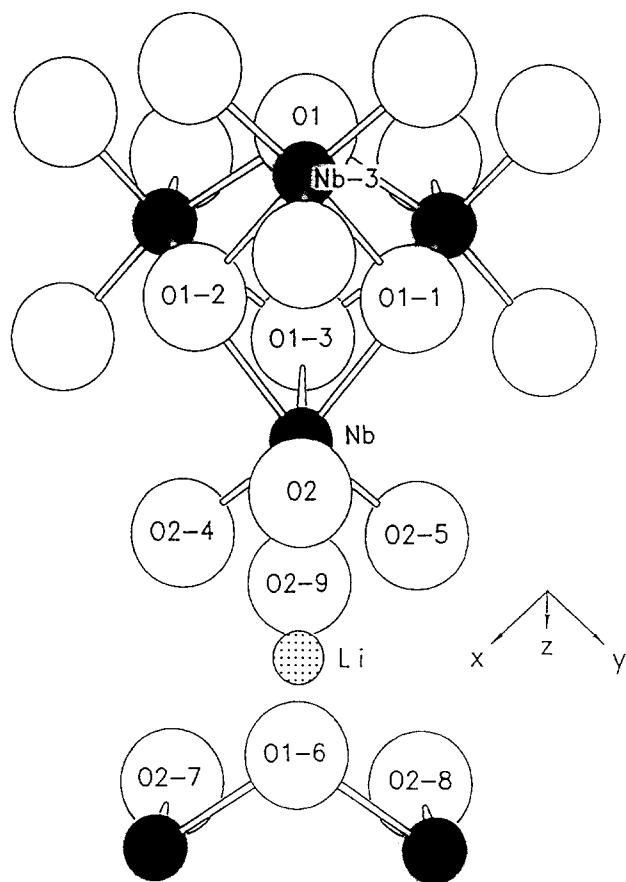


Fig. 2. A view of the  $\text{Nb}_4\text{O}_{16}$  cluster and an Li ion with coordinating  $\text{O}^{2-}$  ions. Filled, dotted and open circles represent  $\text{Nb}^{5+}$ ,  $\text{Li}^+$  and  $\text{O}^{2-}$  ions respectively. Atomic nomenclature is abbreviated: for example, O 1-2 represents  $\text{O}(1^{\text{ii}})$ .

smaller than those found by previous researchers [5,6]. The measured pycnometric density is in good agreement with the X-ray density:  $D_m = 3.95 \text{ mg m}^{-3}$  and  $D_x = 3.967 \text{ mg m}^{-3}$  respectively. The structure comprises characteristic  $\text{Nb}_4\text{O}_{16}$  clusters, which form a body-centred cubic (b.c.c.) lattice with Li ions located among the  $\text{Nb}_4\text{O}_{16}$  clusters. O ions coordinate to Nb and Li in an octahedral manner. Fig. 2 shows a view of the  $\text{Nb}_4\text{O}_{16}$  cluster and an Li ion with coordinating  $\text{O}^{2-}$  ions. Filled, dotted and open circles represent  $\text{Nb}^{5+}$ ,  $\text{Li}^+$  and  $\text{O}^{2-}$  ions respectively. Atomic nomenclature is abbreviated: for example, O 1-2 represents  $\text{O}(1^{\text{ii}})$ . Selected geometric parameters, interatomic distances and angles, are listed in Table 2. The single crystal X-ray data on  $\text{Li}_3\text{NbO}_4$  are summarised in Table 3; previously reported results of the structure analysis by both X-ray [5] and neutron [6] methods are co-listed in the table. The atomic positional parameters reported by Grenier and Bassi [6] are similar to those reported here, but the space group determined by them ( $I23$ ) is incorrect. As a result, the space group  $I43m$  is newly proposed here.

In conclusion, single crystals of  $\text{Li}_3\text{NbO}_4$  were successfully obtained for the first time by LiCl flux. Single crystals are transparent colourless cubes with 100–600  $\mu\text{m}$  edges. The crystal belongs to a cubic system, the space group is  $I43m$  and the lattice parameters are  $a = 8.412(2) \text{ \AA}$ ,  $V = 595.2(4) \text{ \AA}^3$  and  $Z = 8$ . Characteristic  $\text{Nb}_4\text{O}_{16}$  clusters form a b.c.c. lattice with Li ions situated among the  $\text{Nb}_4\text{O}_{16}$  clusters. The  $R$  factor ( $wR$ ) is 0.045. The X-ray and pycnometric densities are in good agreement:  $D_x = 3.967 \text{ mg m}^{-3}$

Table 2  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Nb–Nb <sup>iii</sup>	3.3381(7)	Nb–Li	2.846(4)
Nb–O(1i)	2.130(4)	Nb–O(1ii)	2.130(4)
Nb–O(1iii)	2.130(4)	Nb–O(2)	1.858(3)
Nb–O(2iv)	1.858(3)	Nb–O(2v)	1.858(3)
Li–O(2iv)	2.145(5)	Li–O(2v)	2.145(5)
Li–O(2ix)	2.057(6)	Li–O(1vi)	2.414(7)
Li–O(2vii)	2.095(5)	Li–O(2viii)	2.095(5)
O(1)–O(1iii)	2.593(5)		
O(1i)–Nb–O(1ii)	75.0(1)	O(1i)–Nb–O(2)	92.6(1)
O(1i)–Nb–O(2iv)	164.2(1)	O(1i)–Nb–O(2v)	92.6(1)
O(2)–Nb–O(2iv)	97.8(1)	O(2iv)–Li–O(2v)	81.5(2)
O(2iv)–Li–O(2ix)	93.8(2)	O(2iv)–Li–O(1vi)	88.2(2)
O(2iv)–Li–O(2vii)	92.7(2)	O(2iv)–Li–O(2viii)	166.5(3)
O(2ix)–Li–O(1vi)	177.3(2)	O(2ix)–Li–O(2vii)	98.8(2)
O(2vii)–Li–O(1vi)	79.3(2)	O(2vii)–Li–O(2viii)	90.2(2)
Nb–O(1i)–Nbiii	103.2(2)		

Symmetry codes: (i)  $x, -x, -x$ ; (ii)  $-x, x, -x$ ; (iii)  $-x, -x, x$ ; (iv)  $z, x, x$ ; (v)  $x, z, x$ ; (vi)  $1/2 + x, 1/2 + x, 1/2 + x$ ; (vii)  $1/2 + x, 1/2 - x, 1/2 - z$ ; (viii)  $1/2 - x, 1/2 + x, 1/2 - z$ ; (ix)  $1/2 - x, 1/2 - x, z - 1/2$ .

Table 3  
Crystallographic data on  $\text{Li}_3\text{NbO}_4$

	This study	After Blasse [5] <sup>a</sup>	After Grenier and Bassi [6]
Chemical formula	$\text{Li}_3\text{NbO}_4$	$\text{Li}_3\text{NbO}_4$	$\text{Li}_3\text{NbO}_4$
Synthetic method	Flux growth	Sintering	
Specimen	Single crystal	Polycrystalline	
Shape	Cube		
Crystal colour	Colourless		
Size in edge ( $\mu\text{m}$ )	100–600		
Structure analysis method	X-ray diffraction	X-ray diffraction	Neutron diffraction
Crystal system	Cubic	Cubic	Cubic
Space group	$I\bar{4}3m$		$I\bar{2}3$
Lattice parameter $a$ ( $\text{\AA}$ )	8.412(2)	8.433	8.429(2)
Unit cell volume $V$ ( $\text{\AA}^3$ )	595.2(4)		
Molecules per unit cell $Z$	8		
$R$ factor	0.045	0.23	0.06
X-ray density $D_x$ ( $\text{mg m}^{-3}$ )	3.967		
Observed density $D_m$ ( $\text{mg m}^{-3}$ ) <sup>b</sup>	3.95		

<sup>a</sup> See powder diffraction file, JCPDS card No. 16-459.

<sup>b</sup>  $D_m$  was determined by a pycnometric method using  $\text{H}_2\text{O}$  at 20 °C.

and  $D_m = 3.95 \text{ mg m}^{-3}$  respectively. The space group reported previously is incorrect.

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