

AN IMPROVED PROCEDURE FOR THE CRYSTAL GROWTH
OF β -LiIO₃

Oswaldo Luiz Alves* and Josué Mendes Filho[§]

* Instituto de Química, UNICAMP, CP 6154,
13100 Campinas, São Paulo, Brasil.

[§] Departamento de Física, UFC, CP 3010, 60000
Fortaleza, Ceará, Brasil.

Abstract. Single crystals of β -LiIO₃ phase have been grown from aqueous solution by isothermal evaporation. High quality crystals of, typically, 4 mm x 4 mm x 3 mm in size are obtained without the use of seeds.

Several authors have studied the growth of single crystals of LiIO₃ from aqueous solution by isothermal evaporation¹⁻⁵. These crystals exhibit a rich polymorphism characterized by the presence of several phases. The hexagonal α -LiIO₃ (P6₃) phase, stable at room temperature, has interesting non-linear optical and piezoelectric properties⁶⁻¹⁰. The temperature dependence of Raman spectrum of α -LiIO₃ was studied by Cerdeira et al.¹¹ and the results are in complete agreement with X-ray diffraction and DTA data¹.

The others two phases, know as β and γ , are obtained by heating the α phase to 285°C and 245°C respectively. The tetragonal β -LiIO₃ (P4₂/n) phase is also stable at room temperature. All attempts to grow good crystals of β -LiIO₃ by the methods described in the literature have failed to give crystals of good size and quality. The present work reports an improved procedure to grow larger and more perfect single crystals of β -LiIO₃ for studies of dependence of the polarized Raman spectra on the pressure and temperature.

The LiIO₃ powder was prepared by reaction, in aqueous solution, of recrystallized HIO₃ (C. Erba, RP) with Li₂CO₃ (Mallinckrodt, AR) in a 2:1 molar ratio. The product was recrystallized twice from deionized water, giving well-formed crystals. About 10 g of ground LiIO₃ were sealed in a silica tube and kept at 290.0 ± 5.0°C for four hours. The furnace was then cooled slowly to the room temperature (this takes over two hours) and the product was transferred to a 50 ml round-bottom flask. The small quantities of iodine formed during the heating were removed by a vacuum aspirator at 100°C, until the solid became nearly white (1-2 hours). It was then dissolved in deionized water at room temperature (84 g/100 ml), filtered to obtain a clear solution (pH ~7) and kept at 80 ± 2°C in a cylindrical glass vessel (8 cm long and 3 cm in diameter) without the use of seeds for three days. Most of the crystals grown by this procedure had a size of about 4 mm x 4 mm x 3 mm.

The monocrystalline nature of these crystals was checked by Laue back-reflection and powder diffraction patterns. With the first technique, half of the crystals obtained showed a sharp and well defined spot indicating no evidence of large scale faults or defects. The X-ray powder pattern are shown in the Table I.

Recent studies of polarized Raman spectra of β -LiIO₃ prepared by this procedure have indicated a new reversible phase transition when the crystals are compressed hydrostatically at 50 kbar, at room temperature¹². Our high pressure X-ray measurements confirm this transition; the space group of high pressure form is P2/n, which is a sub-group of tetragonal symmetry¹³.

Table I. X-Ray Powder Pattern of β -LiIO₃.

$d(\text{\AA})$ calculated ^a	$d(\text{\AA})$ observed ^b	(hkl)
6.87	6.94 (6.91)	110
6.15		001
5.19	5.03 (5.19)	101
4.86		200
4.58		111
4.34		210
3.81	3.83 (3.811)	201
	3.63	
3.55	(3.438)	211
3.43	3.44 (3.432)	220
3.24		300
3.07	(3.074)	002
3.07		310
3.00		221
2.93	2.94 (2.928)	102
2.87	2.87 (2.862)	301
2.81		112
2.75	2.75 (2.745)	311
2.60		202
	2.43	
2.29	2.29	

^a Calculated using the parameters from ref. 13.

^b This work; the values in brackets are from ref. 1.

In conclusion, using this procedure one can obtain single crystals of β -LiIO₃ of good quality which can be used successfully in polarized spectroscopic studies.

Acknowledgement. The authors to thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico of Brazil (CNPq) and Financiadora de Estudos e Projetos (FINEP) for financial assistance to O.L.A.

References

1. S. Matsumura, *Mat. Res. Bull.*, **6**, 469 (1971).
2. J.M. Desvignes and M. Remoissenet, *Mat. Res. Bull.*, **6**, 705 (1971).
3. Yu. G. Abgbolyan, L.S. Tatevosyan and R.O. Sharkhatunyan, *Sov. Phys. Crystallogr.*, **20**, 549 (1976).
4. R.O. Sharkhatunyan, A.G. Nalbondian, A. Kh. Eritsyanyan and K.P. Bobadzhanyan, *Sov. Phys. Crystallogr.*, **20**, 668 (1976).
5. B.I. Kidyavov and P.L. Mitnitskii, *Sov. Phys. Crystallogr.*, **22**, 634 (1977).
6. G. Nath and S. Haussühl, *Appl. Phys. Letters*, **14**, 154 (1969).
7. F.R. Nash, J.G. Bergman, G.D. Bayde and E.H. Tunner, *J. Appl. Phys.*, **40**, 5201 (1969).
8. A.J. Campillo and C.L. Tong, *Appl. Phys. Letters*, **16**, 242 (1970).
9. J. Jerphagnon, *Appl. Phys. Letters*, **16**, 298 (1970).
10. G. Nath, H. Mehmanesch and M. Gsanger, *Appl. Phys. Letters*, **17**, 286 (1970).
11. F.E.A. Melo, F. Cerdeira and V. Lemos, *Solid State Commun.*, **41**, 281 (1982).
12. V. Lemos, J. Mendes Filho, F.C.A. Melo, R.S. Katiyar and F. Cerdeira, *Phys. Rev. B*, **28**, 2985 (1983).
13. J. Mendes Filho, V. Lemos, F. Cerdeira, R.M. Hazen and L.W. Finger, *Phys. Rev. B*, **30**, 7212 (1984); J. Mendes Filho, V. Lemos, F. Cerdeira, R.M. Hazen, L.W. Finger and O.L. Alves, *Anais do XVI Cong. Lat.-Amer. de Quím.*, p. 340, Rio de Janeiro (1984).