

clave with 200 ml H₂O for 48 h at 300 °C and approximately 90-130 atm. The product was thoroughly washed with deionized water* and dried at 50 °C. Mn₇O₁₃·5H₂O was prepared according to reference (19).

The starting materials are listed in Table 1.

TABLE 1. — Starting compositions for the synthesis of unsubstituted lithiophorite (series 1).

Preparation No.	Molar ratio of cations			Remarks
	Mn	Al	Li	
1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.12, 1.13, 1.14, 1.15, 1.20, 1.21	30	20	10	Stoichiometric ratio
1.8	36	20	10	Mn excess 20 %
1.19	30	26	7	Al excess 30 %, Li deficiency 30 %
1.17	30	24	8	Al excess 20 %, Li deficiency 20 %
1.18	30	22	9	Al excess 10 %, Li deficiency 10 %
1.22	30	18	11	Al deficiency 10 %, Li excess 10 %
1.10, 1.11	27	20	10	Mn deficiency 10 %
1.9, 1.16	24	20	10	Mn deficiency 20 %

In a *second series* of experiments 1 g of a mixture of γ -Al(OH)₃ "Baker's Analyzed" (gibbsite=hydrargillite), Mn₇O₁₃·5H₂O, LiOH·H₂O "Merck", and NaOH p. a. "Merck" was treated in an autoclave in the manner mentioned above for 48 h at 300 °C and 90-130 atm with 200 ml H₂O. In some instances, γ -MnO₂ was used in place of Mn₇O₁₃·5H₂O. γ -MnO₂ was prepared as follows:

450 g (NH₄)₂S₂O₈ p. a. "Merck" were added in small portions to a solution of 200 g MnSO₄·H₂O p. a. "Merck" in 4 L H₂O at 97 °C.

The brownish black precipitate was washed anion-free with deionized water and dried at 60 °C for 190 h.

The starting materials are listed in Table 2.

In a *third series* of experiments 1 g of a mixture of γ -Al(OH)₃ "Baker's Analyzed" (gibbsite=hydrargillite), Mn₇O₁₃·5H₂O (in some instances γ -MnO₂), LiOH·H₂O "Merck", and ϵ -Zn(OH)₂, in varying proportions was treated in an autoclave in the same manner for 48 h at 300 °C with 200 ml H₂O. The ϵ -Zn(OH)₂ was prepared as follows: 2260 ml 0,2 N Zn(NO₃)₂ solution were precipitated in a 3 L beaker with 100,0 ml concentrated NaOH solution (carbonate free) which were added in one go under heavy stirring. The gelatinous precipitation that

* Preparations No. 1.1 to 1.7 proved to have excess Li⁺. The washing process was therefore considerably intensified from No. 1.8 onwards.

TABLE 2. — Starting compositions for Na-substituted lithiophorite (series 2)

Preparation No.	Molar ratio of cations			
	Mn	Al	Li	Na
2.3, 2.19	30	20	8	2
2.20	30	20	7	3
2.4, 2.9	30	20	5	5
2.5, 2.18	30	20	3	7
2.6	30	20	2	8
2.21	30	20	1	9
2.8	30	20	0,4	9,6
2.22	30	20	0	10

forms at first redissolved under stirring. After 4-10 min a well sedimenting precipitate appeared. It was isolated on a glass frit, thoroughly washed with deionized water and dried at room temperature over KOH in a desiccator. It consists of monodisperse, crystalline ϵ -Zn(OH)₂ in the form of distorted bipyramids (20).

The metal ion ratios used for the starting materials are listed in Table 3.

TABLE 3. — Starting compositions for Zn-substituted lithiophorite (series 3)

Preparation No.	Molar ratio of cations			
	Mn	Al	Zn	Li
3.13	30	17	3	10
3.11	30	14	6	10
3.12	30	13	7	10
3.23	30	11	9	10
3.14	30	10	10	10
3.24	30	8	12	10
3.15	30	6	14	10
3.16	30	3	17	10
3.17	30	0	20	10

2. Analytical

Where products were pure with respect to X-ray diffraction, quantitative analyses were done with following procedures: Na and Li were determined by Atomic Absorption Analysis directly in a solution of 600 mg substance