

## CLO

## Cloverite (GaPO<sub>4</sub>)

## P(50), Ga(50)

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**Type Materials** 8{[Ga<sub>96</sub>P<sub>96</sub>O<sub>372</sub>(OH)<sub>24</sub>(QF)<sub>24</sub>(H<sub>2</sub>O)<sub>n</sub>] (Q = quinuclidine [1])

**Method** A. Merrouche, J. Patarin, H. Kessler, M. Soulard, L Delmotte, J.-L Guth, J. F. Joly [2]

**Batch Composition** Ga<sub>2</sub>O<sub>3</sub> : P<sub>2</sub>O<sub>5</sub> : HF : 80 H<sub>2</sub>O : 6 Q<sup>a</sup>

### Source Materials

phosphoric acid (Fluka, 85% H<sub>3</sub>PO<sub>4</sub>)

distilled water

gallium sulfate [Ga<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O] (Strem Chemicals, wt.% Ga ~18)<sup>b</sup>

hydrofluoric acid (Fluka, 40% HF)

quinuclidine (Fluka, 97% C<sub>7</sub>H<sub>13</sub>N)

### Batch Preparation (for 1 g product)

- (1) 10.95 g phosphoric acid + 2.2 g H<sub>2</sub>O + 3.14 g gallium sulfate hydrate + 2.2 g H<sub>2</sub>O  
stir until dissolved
- (2) [(1) + 0.2 g HF + 2.7 g quinuclidine], mix until uniform. Initial pH = 4 to 4.5

### Crystallization

Vessel: PTFE-lined autoclave

Temperature: 150°C

Time: 24 hours

Agitation: none

### Product Recovery

- (1) Filter, wash with distilled water, dry at 60°C
- (2) Yield: approximately 60% on Ga<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>

### Product Characterization

XRD: Characteristic strong reflections at d 25.4, 9.1 and 8.5 Å; competing phases are GaPO<sub>4</sub>-a and GaPO<sub>4</sub>-b [2] when the starting molar ratio F/Ga<sub>2</sub>O<sub>3</sub> <0.5 [3]  
Elemental Analysis (anhydrous form): Q<sub>0.14</sub>Ga<sub>0.48</sub>P<sub>0.52</sub>O<sub>2</sub>F<sub>0.13</sub>. Crystal Size and Habit: small cubes, less than 1 μm<sup>c</sup>

### References

- [1] M. Estermann, L B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, Nature 352 (1991) 320
- [2] A. Merrouche, J. Patarin, H. Kessler, M. Soulard, L Delmotte, J.-L Guth, J. F. Joly, Zeolites 12 (1992) 226

- [3] J. Patarin, C. Schott-Darie, A. Merrouche, H. Kessler, M. Soulard, L. Delmotte, J.-L. Guth and J. F. Joly in Proceedings from the 9th International Zeolite Conference, R. von Ballmoos, J. B. Higgins and M. J. Treacy (eds), Butterworth-Heinemann, Stoneham, 1992, p. 263

**Notes**

- a. The acceptable range for HF/Ga<sub>2</sub>O<sub>3</sub> is 0.75 to 2.
- b. Aldrich Ga<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> acceptable substitute.
- c. Crystals are typically cubes with apparent truncatures when large (20 μm or more). Increase in crystal size has been achieved by decreasing the amount of fluoride in the starting mixture to F/Ga<sub>2</sub>O<sub>3</sub> <0.5 [3].