

Section 3:
Purification of Some Starting
Materials

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Section 3

PURIFICATION OF SOME STARTING MATERIALS*

The normal purities (analytical reagent grade, luminescent grade, etc.) of commercially available starting materials are good enough to prepare almost every phosphor mentioned in this cookbook. Only some CaS-type phosphors are exceptions. Some impurities (e.g., Mn) show up in the CaS-type phosphors in concentrations as low as 1 ppm. Consequently, harmful impurities (mainly metals like Mn, Fe, etc.) in the starting materials are better kept below this level.

3.1 Carbonates (described using the example of CaCO_3)

Prepare two separate solutions.

Solution A: Dissolve 1 g-mole of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (= 236 g) in about 1 liter water at room temperature. Add a few cubic centimeters of freshly prepared NH_4 -sulfide solution; stir. Let stand overnight. Then filter through a milli-pore filter (0.45 μm pore size).

Solution B: Dissolve about 1.1 g-mole of the $(\text{NH}_4)_2\text{CO}_3$ (= 105 g) in 1 liter water at room temperature. The carbonate usually comes in big chunks which take considerable time to dissolve. It helps to crush the chunks but do not try to speed up the dissolution by heating. Do not filter this solution.

Slowly add solution A to B (or vice versa) while stirring. White CaCO_3 precipitates and some CO_2 develops.

Let settle.

Decant the excess liquid.

Wash the carbonate in de-ionized water several times (stir, let settle, decant).

Dry with methanol in filter funnel and then completely in open air.

Properties

Mg carbonate prepared in this way is of somewhat uncertain composition. It is best converted to MgO by heating in an open boat, air ~ 500 – 1000°C , for $\sim \frac{1}{2}$ hour.

CaCO_3 precipitates and settles readily. It can be converted to CaO by firing in an open quartz boat, air, ~ 1000 – 1200°C , for $\sim \frac{1}{2}$ hour.

SrCO_3 and BaCO_3 both precipitate in too fine particles which almost behave like a gel in the water and do not readily settle. Both are better prepared via the oxalates.

* This section is from W. Lehmann's *Phosphor Cookbook*.

3.2 Sulfates (described using the example of SrSO_4)

Prepare two separate solutions.

Solution A: Dissolve 1 g-mole (= 212 g) of $\text{Sr}(\text{NO}_3)_2$ in about 1 liter water. Add a few cubic centimeters of freshly prepared NH_4 sulfide solution; stir. Let stand overnight. Then filter through a milli-pore filter (0.45 μm pore size).

Solution B: Dissolve about 1.1 g-mole of the $(\text{NH}_4)_2\text{SO}_4$ in 1 liter water. Add a few cubic centimeters of NH_4OH ; stir. Filter through a milli-pore filter (0.45 μm pore size).

Slowly pour solution A into B (or vice versa) while stirring. White sulfate will precipitate.

Let settle.

Decant the excess liquid.

Wash in de-ionized water several times (stir, let settle, decant).

Dry with methanol in filter funnel over filter paper and then completely in open air.

Properties

Mg sulfate cannot be prepared in this way (MgSO_4 = epsom salt).

CaSO_4 precipitates as gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. It can be converted to the more stable anhydrite by heating in open boats, air ~ 500 – 1000°C , for about $\frac{1}{2}$ hour.

Sr and Ba sulfates precipitate immediately as anhydrous sulfates. SrSO_4 is still manageable but BaSO_4 tends to be of too fine particles which behave almost like a gel in the water and do not readily settle.

3.3 Oxalates (described using the example of BaC_2O_4)

Prepare two separate solutions.

Solution A: Dissolve 1 g-mole (= 273 g) of Ba-acetate, $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2) \cdot \text{H}_2\text{O}$ in about 1 liter water at room temperature. Add a few cubic centimeters of freshly prepared NH_4 sulfide solution, stir. Let stand overnight. Then filter through a milli-pore filter (0.45 μm pore size).

Solution B: Dissolve about 1.1 g-mole (= 138 g) of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, in 1 liter water at room temperature. Add NH_4OH to make the solution slightly alkaline. Then filter through a milli-pore filter (0.45 μm pore size).

Slowly pour solution A into B (or vice versa) while stirring. White BaC_2O_4 will precipitate out and readily settles down.

Let settle.

Decant the excess liquid.

Wash in de-ionized water several times (stir, let settle, decant).

Dry with methanol in a filter funnel over filter paper and then completely in open air.

Properties

Mg oxalate precipitates as $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. It converts completely to MgO by heating in an open boat, air, $\sim 500^\circ\text{C}$, $\sim \frac{1}{2}$ hour.

Ca oxalate precipitates as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. It converts to CaCO_3 by heating in an open boat, air, $\sim 500\text{--}1000^\circ\text{C}$, $\sim \frac{1}{2}$ hour. Further conversion to SrO is not practically possible by firing in an open boat, H_2 , $\sim 1100^\circ\text{C}$, ~ 1 hour.

Sr oxalate precipitates as $\text{SrC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. It converts to SrCO_3 by firing in an open boat, H_2 , $\sim 1100^\circ\text{C}$, ~ 1 hour.

Ba-oxalate precipitates as BaC_2O_4 which can be converted to BaCO_3 by firing in an open boat, air, $\sim 500\text{--}1000^\circ\text{C}$, $\sim \frac{1}{2}$ hour. In contrast to SrCO_3 , BaCO_3 is not as easily converted into the oxide by firing in H_2 .

3.4 Sulfur

Dissolve ordinary precipitated (not sublimed) sulfur in as little CS_2 as possible.

Filter the solution through a dense paper filter. Black impurities (metal sulfides, etc.) will remain on the paper.

Pour the filtered solution into a clean flask; add the same amount (by volume) of pure acetone; stir or shake vigorously. Yellow sulfur will precipitate.

Wash the sulfur several times in acetone (stir, let settle, decant).

Dry in filter funnel over filter paper and then completely in open air.

Properties

This is a coarse yellow powder, sufficiently pure for all preparation work of sulfide-type phosphors.