

## *Section 2: Phosphor Preparation*

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## Section 2

### PHOSPHOR PREPARATION\*

The following methods are essentially the preparation procedures used by the writer (W. Lehmann) to make the phosphors described in this report. Many points probably are trivial to the professional phosphor chemist but they are certainly not so to the novice or to anyone preparing phosphors only once in a while.

Almost all good inorganic phosphors consist of a crystalline “host material” in which small amounts of certain impurities, the “activators” are dissolved. The activators are primarily responsible for the luminescence. Other impurities, the “co-activators,” are necessary in some (not in all) cases to dissolve the activator impurities into the host crystal. Co-activators do not, or only to a very minor degree, participate in the luminescence process. Both activators and (if necessary) co-activators are diffused into the host crystal at elevated temperatures, the “firing.” Even the final host material frequently is formed only during the firing by solid-state reactions between several starting materials. The firing temperature often is little below the melting temperature of the host material. If that is impractical because of excessively high-melting temperatures of the host material, the crystallization is facilitated at lower temperatures by addition of a “flux” (frequently a halide) to the raw mix before firing.

#### 2.1 Starting Materials

Commercially available high-purity grade chemicals (e.g., analytical reagent grade, luminescent grade) are adequate to prepare most of the phosphors. Only sulfide-type phosphors are exceptions because they are sensitive to undesired impurities, sometimes down to the parts per million range. Sufficiently pure ZnS and CdS are available not to require additional purification for the preparation of ZnS-type phosphors. However, the chemicals needed to prepare CaS-type phosphors are not normally available in the required purity. Section 3 of this report describes some techniques that can be used to purify commercial compounds to prepare CaS-type phosphors.

The chemicals mentioned in the individual recipes are those that usually are the most readily available. They can frequently be exchanged with others. For instance,  $\text{CaCO}_3$  can frequently be replaced by  $\text{CaO}$ ,  $\text{CaO}_2$ ,  $\text{Ca}(\text{NO}_3)_2$ , or  $\text{Ca}(\text{OH})_2$ . Similarly,  $\text{MnCO}_3$  can be replaced by  $\text{MnO}_2$ ,  $\text{MnO}$ ,  $\text{MnS}$ ,  $\text{MnSO}_4$ ,  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and so on. What counts are only the necessary amounts of the particular chemical elements measured in moles, and that the used compounds decompose readily during the firing of the phosphor to provide the necessary building blocks to the final material.

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

## 2.2 Amounts

The recipes in this report are given in whole molar units to make them as clear as possible. Whenever such large amounts of phosphors are not needed or wanted, all amounts can be reduced by constant factors as long as the molar ratios between the individual components in the recipe are maintained. However, it is impractical to reduce the amounts to less than about 1 or 2 g of the final phosphor. The materials become poorly reproducible with such very small amounts.

The weightings of the starting materials are not very critical. Phosphor properties vary relatively little only with a variation of the starting material ratios. Roughly, the amounts of the chemicals involved in the formation of the host materials need to be weighed only within  $\pm 1\%$  of the mentioned proportions, sometimes even within still wider tolerances. The smaller amounts of the activating chemicals involved are even less critical. Variations of  $\pm 10\%$  of the mentioned activator concentrations normally have little effect on the performance of the final phosphor.

## 2.3 Mixing

Very thorough mixing of the starting materials before firing is extremely important for the successful preparation of a good phosphor. Some of the best methods are:

**Slurrying** The finely powdered starting materials are mixed into water, alcohol, or any other inert and volatile liquid to a uniform slurry. Water-soluble activator chemicals, etc. can be added dissolved in water. The slurry is dried and the dried material, which sometimes is a more or less hard crust, is powderized in a mortar as well as possible. This method has been used for most of the recipes of this report.

**Wet Ball-Milling** The slurry prepared above is ball-milled with porcelain pebbles for a time (about 1–2 hours) to ensure a moist thorough mix and, in particular, a breakup of all possible lumps in the slurry. The slurry is then dried in air and the dry material is mechanically powderized. This method is a bit cumbersome and it is impractical for small samples (a few grams); otherwise it is the most ideal.

**Dry Ball-Milling** The dry powder mix is ball-milled with porcelain pebbles for 1–2 hours. This method avoids the time-consuming drying of the slurry but it works only for powders, which stay free flowing all the time. Some materials (e.g., ZnO) are not free flowing and cannot be mixed this way.

**Mortaring** The dry powders are simply mixed by mortaring together to make the mix as uniform as possible. This method is least time-consuming and most practical for small samples but the mixes are less uniform down to the microscopic scale than any one prepared by the other methods. Corresponding non-uniformities of the final phosphor may be the result. Whenever such non-uniformities occur, firing not only once but also several times and mortaring every time in between can usually eliminate them. Several firing steps are appropriate in many cases for other chemical reasons.

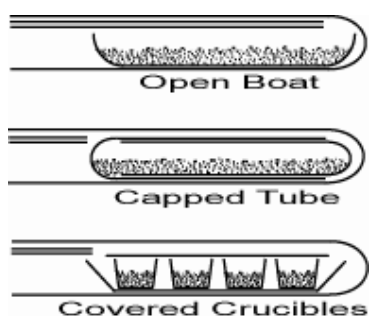
## 2.4 Containers

The best container material for the preparation of most phosphors is clear quartz glass (silica). Only some materials (the alkali elements, in particular) react too badly with quartz

glass at firing temperatures and are better fired in other container materials. Pure alumina serves fairly well in these cases.

Phosphor raw mixes not containing volatile (at firing conditions) constituents are best fired in open boats so that the charge is fully exposed to the desired atmosphere surrounding the material. Raw mixes which do contain volatile constituents (e.g., halides) are better fired in loosely covered containers permitting some contact with the surrounding atmosphere but still keeping at least some of the volatile part in the container. Capped silica tubes are widely used in our laboratory; they consist of two tubes each closed at one end and both loosely fitting into each other. Loosely covered crucibles are appropriate wherever alumina is the container material.

All these containers are placed near the closed ends of bigger firing tubes made of silica. Some typical arrangements are shown in Figure 1. Only these ends of the firing tubes are in the furnaces during firing.



**Figure 1** Schemata of different containers during phosphor firing.

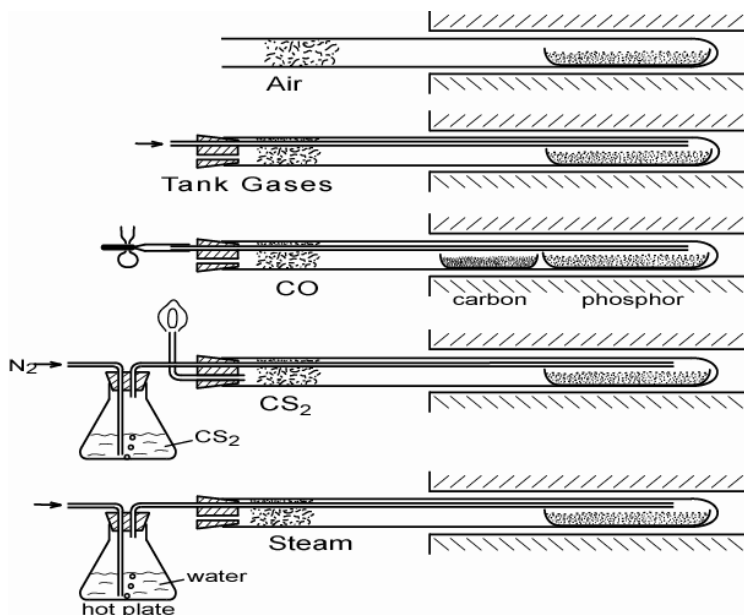
## 2.5 Furnace

Phosphor firing requires an electric furnace permitting temperatures between about 500°C and at least 1200°C, better up to about 1400°C. Any desired temperature should be maintained during firing by means of an automatic temperature controller to within  $\pm 20^\circ\text{C}$  or better. A simple on-off control is acceptable.

A reliable temperature control clearly is one of the weak points of phosphor preparation. The writer has yet to see a furnace whose temperature does not occasionally deviate from that indicated by the controller. The only way to eliminate this problem is frequent re-calibration of furnace and controller by means of a good thermocouple and a millivolt comparator.

## 2.6 Firing Atmospheres

The various phosphors are fired in different atmospheres depending on the materials and the desired reactions. Oxygen-dominated phosphors (oxides, silicates, phosphates, etc.) may be fired in oxidizing (air,  $\text{O}_2$ ), inert ( $\text{N}_2$ , Ar), or reducing atmospheres ( $\text{CO}$ , forming gas,  $\text{H}_2$ ,  $\text{NH}_3$ ). Sulfurization of sulfide phosphors may be achieved by firing either in  $\text{H}_2\text{S}$  or in an inert gas loaded with  $\text{CS}_2$ . Many of these gases are interchangeable. It makes no difference, for instance, whether a phosphor is fired in  $\text{N}_2$  or in Ar. Some arrangements used to handle the various gases in the firing tubes are shown in [Figure 2](#) assuming the phosphor containers are both open boats.



**Figure 2** Schemata of different containers during phosphor firing.

**Air** Firing a phosphor in air requires nothing but the container in the firing tube whose open end is left open or, at most, closed by a bit of loose glass wool to prevent dust particles from drifting in during firing.

**Gases from tanks** (or other supplies) These can be piped into the firing tubes via long and thin gas inlet tubes (silica) reaching as far into the firing tubes as possible. The open ends of the latter are closed by ordinary rubber stoppers with two holes for gas inlet and outlet. The stopper is protected against radiant heat by a bit of loose glass wool in front of it. If the phosphor is fired in  $H_2$  or in  $H_2S$ , it is extremely important first to flush all air out the firing tube with an inert gas (e.g.,  $N_2$ ) before admitting the final gas; otherwise the effect (explosion) will be spectacular when the firing tube enters the furnace. **Be extremely cautious!**

**CO** This gas is about the most convenient for firing an oxygen-dominated phosphor in a reducing atmosphere. Some carbon black is placed in a separate open container next to the phosphor container in the firing tube. The air is flushed out by plain  $O_2$  and the gas inlet tube is then closed (*but leave the inlet open*). When the charge enters the furnace, some of the carbon black burns to CO in situ.

**$CS_2$**  An inert carrier gas (e.g.,  $N_2$ ) bubbles through a flask containing some liquid  $CS_2$  in front of the firing tube. Do not heat the flask; the vapor pressure of the  $CS_2$  is high enough at room temperature. Escaping unused  $CS_2$  gas can be burned at the end of an outlet tube. As in cases of  $H_2$  and  $H_2S$ , be very careful to flush all the air out the firing tube before admitting the  $CS_2$ -loaded gas.

**Steam** This arrangement resembles that used for  $CS_2$ . A carrier gas (air,  $N_2$ , etc.) bubbles through a flask containing some water in front of the firing tube. The vapor pressure of the water is too low at room temperature to have much effect, so it is necessary to heat the flask to gentle boiling. The tube connection between flask and firing tube should be as short and straight as possible; otherwise condensing liquid water might block the gas flow.

## 2.7 Treatments after Firing

Fired phosphors often (not always) are slightly sintered cakes that have to be powderized to obtain the desired fine powder. This powderizing usually is possible by gentle grinding or milling. Avoid all hard milling because it is likely to damage the phosphor. Phosphors coming out the furnace as badly sintered lumps indicate that something is wrong; most likely the firing temperature was too high.

Some phosphors require special washings after firing, usually to remove one or the other undesired residues (e.g., halides). Such cases are noted in the recipes of this report. Phosphors of recipes that do not mention a washing do not need it.

All phosphors should finally be screened to remove undesired big particles. A 200-mesh stainless steel sieve is adequate for most general purposes but some special applications may require finer screens. Some phosphors are free flowing and easily screened. Others tend to lump and are not screenable with any reasonable effort. Such materials can easily be made free flowing by addition of small amounts (roughly 1/10% by weight) of some additives like very fine  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ , etc. Unfortunately there is no general rule to pick the best additive; to find one remains up to the ingenuity of the experimenter. Phosphors that stubbornly refuse to become free flowing with any additive can still be wet screened in a suspension in water, methanol, etc. However, this still requires subsequent drying, of course.

All phosphors that are not immediately used up for some application should be stored in **closed and labeled** containers. Closed containers obviously are necessary for any phosphor that is not completely stable in room air (e.g.,  $\text{CaO}$ ) but they are a good practice also for all others. Remember that good phosphors are precious materials.