Microwave-Assisted Synthesis of MPS_3 Materials (M = Mn, Cd) Using a Dewar-Ampoule Device

A. Villanueva,[a] M. C. Morales-Varela,[a] and Eduardo Ruiz-Hitzky*[a]

Keywords: Transition metals / Microwave-assisted reactions / Layered compounds / Synthesis design / Solid-phase synthesis

We report on an easy procedure for the synthesis of inorganic solids such as MPS_3 materials (M = Mn, Cd) which uses a simple device consisting of a silica ampoule that is divided into a Dewar zone (*hot* zone) and a nonisolated part (*cold* zone), which is able to operate inside domestic microwave ovens. This is a rapid and advantageous method applied for the first time to the preparation of inorganic solids. It involves a heat concentration within the Dewar zone that allows the required temperature for the reaction between the components to be reached. In this way, a mixture of S, P, and a transition metal such as Mn or Cd, placed in the Dewar zone gives MPS_3 compounds. The temperature gradient assures the vapor phase transport to the *cold* zone. The resulting MPS_3 crystals are deposited within a few minutes in the *cold* area, in contrast to other conventional procedures requiring long periods of treatment or more complicated procedures for the synthesis of similar products.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Microwave-assisted reactions are of increasing interest in different fields of synthetic chemistry to yield both inorganic materials (as in the solid-state synthesis of functional ceramics[1−5]) and organic compounds (as synthesis on supported phases[1,6]). Usually, the reactions developed under microwave (MW) heating show remarkable improvement over those carried out under conventional heating in an extraordinary acceleration of the processes. This is particularly true for solid-state reactions, as for instance, the synthesis of vanadates,[3] chromates,[4] and metal−chalcogenides.[5] In general, the MW treatment of mixtures of pure or combined elements such as metal oxides, nitrates, or carbonates, produces enough heat to induce a rapid transformation of the reagents, to give the corresponding inorganic materials through solid-state reactions, often with excellent yields. A successful control of these reactions depends on the intrinsic properties of the involved solids, mainly related to their conductivity behavior. The energy necessary for the MW-assisted solid-state reactions is given by the absorption of high frequency waves, related to the so-called tangent loss ($\tan \delta$), which is the ratio between the dielectric loss (ε'') and the dielectric constant (ε') of the material.[7] The tangent loss indicates the efficiency of the solid material towards the conversion of MW energy into thermal energy mainly associated with two mechanisms: dipole rotation and electrical conductivity (either ionic or electronic). In solid-state reactions, no relaxation process except for the conduction process of both electrons and ions, takes place because the molecular dipoles are fixed, leading to high loss tangent values.[1] This has been observed particularly for reactions involving semiconductors or ion-conducting solids, in which the increased temperature produces an increase of the electrical conductivity and therefore gives exponential MW energy absorption and rapid heating, that is, the so-called *thermal runaway*.[2]

Transition-metal phosphorus trisulfides (MPS_3; M = Mn, Cd) are the compounds selected in this paper to show the advantages of using the Dewar ampoule device. This is a family of layered compounds[8] with interesting properties as host lattices for intercalation of organic compounds,[9] and lithium insertion,[10] and is indeed useful as electrodes for lithium-batteries and in nonlinear optical devices. The structure of MPS_3 compounds derives from that of $CdCl_2$, and is closely related to the structure of transition-metal dichalcogenides.[11] Conventional synthesis of MPS_3 materials by ceramic methods needs a heating treatment program at temperatures in the 550−800 °C range, from one to several weeks[12] making the process too long for practical purposes. It is assumed that in these conditions a vapor phase transport mechanism occurs,[13] but the nature of the transported species is so far unknown. MPS_3 compounds can be alternatively prepared by coordination of $[P_2S_6]^{4-}$ anions to M^{2+} cations in aqueous solutions, as in the reaction at room temperature between $MnCl_2$ and sodium hexathiohypophosphate[14] [Equation (1)].

$$2\,MnCl_2 + Na_4P_2S_6 \rightleftarrows 2\,MnPS_3 + 4\,NaCl \qquad (1)$$

---

[a] Instituto de Ciencia de Materiales de Madrid, CSIC,
Cantoblanco, 28049 Madrid, Spain
E-mail: eduardo@icmm.csic.es

DOI: 10.1002/ejic.200300654 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

This procedure is also long and tedious, because the sodium hexathiohypophosphate is a noncommercial product that needs to be prepared in the laboratory by reaction of sodium sulfide and phosphorus trichloride.[15] In addition, the reaction yield is lower than that of the ceramic method (about 67 %, from our experiments).

Results and Discussion

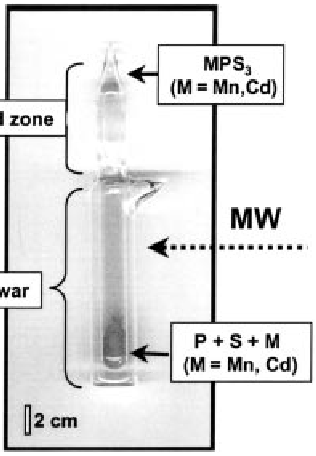

Figure 1. A picture of the Dewar ampoule highlighting its different parts and the process of MPS$_3$ crystallization

Figure 1. shows the apparatus developed for the MPS$_3$ synthesis, which essentially consists of a silica (quartz) ampoule with two different zones. One of the zones is furnished with a vacuum thermal barrier [i.e., it is a Dewar container (*hot* zone)], while the other zone is thermally deshielded (*cold* zone). Such a device was inspired by the typical two-zone furnace used to grow single crystals. The novelty of this design is that it operates inside a domestic MW oven, and this configuration allows the temperature to be reached so as to activate certain solid-state reactions. A sufficiently high temperature cannot be obtained in conventional reactors (e.g. standard sealed silica ampoules). For the first time, we have successfully applied this methodology to the preparation of well-crystallized MPS$_3$ layered solids, selected as an example in view of its difficult synthesis by the classical ceramic process. The attempts to produce these solid-state reactions using small amounts of metals inside conventional silica ampoules (i.e., classical quartz reactors) with MW irradiation always failed. Apparently, in an unshielded ampoule fast heat dissipation precludes the system from reaching a temperature high enough to afford the solid-state reaction. By contrast, the reaction is completed after a few minutes with MW irradiation when the Dewar ampoule apparatus is used, giving almost quantitative amounts of the corresponding metal phosphorus trisulfides. The driving idea to design such a device was to avoid the heat dissipation in the region of the reactor where the components are placed, thus assuring the increase of temperature required to produce the reaction. In our example, the MPS$_3$ compounds are deposited in the *cold* zone as relatively large crystals due to the temperature gradient that promotes the vapor-phase transport of the synthesized materials.

The nonmetallic elements, sulfur and phosphorus are insulators and practically transparent to MW, although theoretically they could be activated in the presence of a metal incorporated in the form of a fine powder. Under these conditions, the metal simultaneously acts as a reagent and as a MW absorber, because it couples very effectively with microwave radiation. This is the case for the reactions between sulfur and transition metals such as Ta, Cr, Fe, and Mn, which produces the corresponding sulfides.[16] In a similar way, we have tried to prepare MPS$_3$ compounds (M = Mn and Cd) by MW irradiation of a mixture of their three integrating elements using a conventional reactor (sealed, evacuated, single-quartz ampoule), using the same domestic MW oven. As indicated above, the reactions were always unsuccessful, even after a long time of treatment. It could be maintained that under these conditions, the temperature reached is always lower than that required for the activation of the solid-state reaction. We have also unsuccessfully tried to carry out the MnPS$_3$ synthesis using mixtures of manganese metal and P$_2$S$_5$, or working under different conditions in a set of experiments involving conventional ampoules. In contrast, the Dewar ampoule offers a way to produce the phosphorus trichalcogenides quickly with excellent yields.

The details for the use of the Dewar ampoule with starting reagent mixtures of sulfur, phosphorus, and the selected transition metal (Mn or Cd), or alternatively mixtures of manganese, sulfur, and P$_2$S$_5$ (with stoichiometric MPS$_3$ ratios) are described in the Exp. Sect. Emission of very intense light of different colors is produced during the reactions, which are completed after 25−40 minutes of MW irradiation.

The MPS$_3$ resulting materials were characterized by XRD, FTIR spectroscopy and SEM-EDX analyses. Figure 2 shows the XRD patterns of MnPS$_3$ prepared by conventional procedures, that is, either from the ceramic method using a standard furnace (10 days, 700 °C, see A in Figure 2), or from soft conditions through a reaction involving various steps [Equation (1), see B in Figure 2], or by the MW-assisted synthesis using the Dewar ampoule (Figure 2, C and D). The XRD diagram of the reaction product obtained from the aqueous solution method [Equation (1)] corresponds to an ill-crystallized solid in view of the broad and low intensity *hkl* reflections attributed to MnPS$_3$ materials. All the diffraction peaks of the compound prepared by the ceramic method (Figure 2 A) fit very well with the corresponding ASTM file (No. 33−903), the diffractogram being very similar to the sample resulting from 25 minutes of MW irradiation of stoichiometric mixtures of Mn, P, and S (see D in Figure 2). Small differences in the relative intensities of the reflections of the two materials are attributed to preferred orientation effects: the [00 l] reflections of MnPS$_3$ (in particular for $l = 2$) are increased with respect to other reflections in the sample prepared by conventional techniques, while in the material prepared by the method reported here other reflections are relatively enhanced (like the [$\bar{1}$30] and [200] reflections, see Figure 2). The sample prepared from 30 minutes MW irradiation of Mn, P_2S_5, and S stoichiometric mixtures shows additional low intensity peaks identified as P_2S_5, MnP_4, and other byproducts of variable P, S, and Mn composition.

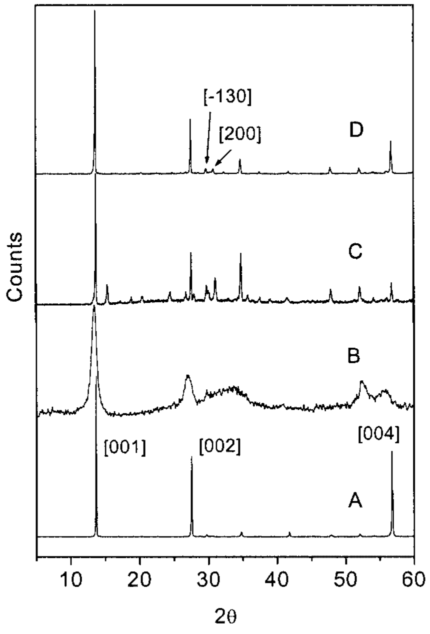

Figure 2. XRD diffraction patterns of $MnPS_3$ synthesized by: A) conventional heating of Mn + P + 3S (700 °C, 10 days); B) reaction of $Na_4P_2S_6$ with $MnCl_2$ in aqueous solution; C) MW-assisted reaction of 2Mn + P_2S_5 + S (30 min); D) MW-assisted reaction of Mn + P + 3S (25 min); traces A and D correspond to pure and highly crystalline $MnPS_3$, the differences between them being related to preferred orientations

Figure 3 shows the IR spectra (800−400 cm^{-1} region) of the reaction products obtained by the two methods that give the best results, that is, conventional heating and MW-assisted reactions involving the Mn + P + 3S mixture. The similarity between the compounds prepared by the two procedures is again evidenced by their coincidence in frequency and intensity of the IR absorption bands, the most characteristic of them appearing in the 700−400 cm^{-1} spectral region. According to Mathey and co-workers,[17] and Joy and Vasudevan,[18] the strong intensity band that appears at 573 cm^{-1} is attributed to P−S stretching vibrations $\nu_{P-S}(PS_3)$, whereas the ν_{P-P} vibration band appears at 440 cm^{-1}.

SEM images of the $MnPS_3$ products obtained by both procedures, the conventional ceramic method, and MW-assisted reactions show crystals of lamellar shape and average particle sizes of about 100 and 20 µm, respectively (Figure 4). The differences in the crystal size can be attributed to the different nucleation and crystal growth rates achieved by MW or conventional heating.

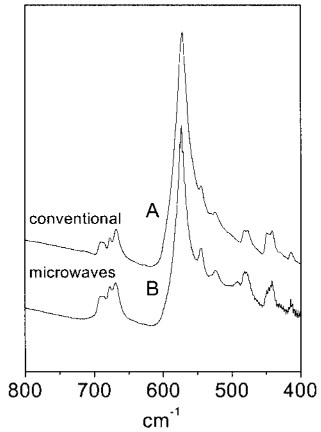

Figure 3. IR spectra (800−400 cm^{-1} region) of $MnPS_3$ obtained by: A) conventional heating of Mn + P + 3S (700 °C, 10 days); B) MW-assisted reaction of Mn + P + 3S (25 min)

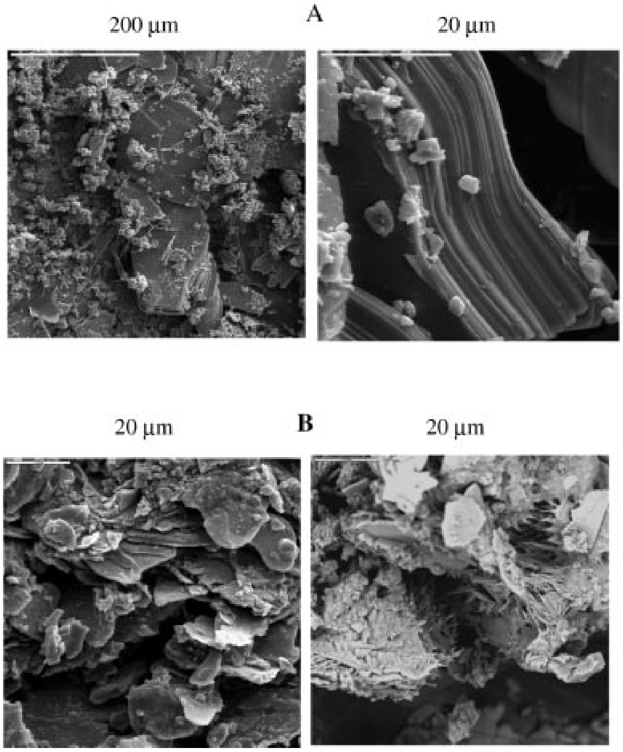

Figure 4. SEM images of $MnPS_3$ obtained by: A) conventional heating of Mn + P + 3S (700 °C, 10 days); B) MW-assisted reaction of Mn + P + 3S (25 min)

The method of preparation of $MnPS_3$ compounds, with MW's and the Dewar ampoule reported above has also been successfully applied to the synthesis of $CdPS_3$ materials. This result indicates the ability to extend the procedure to other members of the MPS_3 family.

Conclusions

We have shown that a simple device such as the Dewar ampoule reported here, when used with an unmodified MW domestic oven, offers a new procedure to reach suitable temperatures(at least when small amounts of powdered metals are used) to allow the efficient and rapid synthesis of solids that are difficult to prepare by other routes, as it is the case of the MPS_3 compounds.

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. MW synthesis of MPS_3 compounds (M = Mn, Cd) under different experimental conditions

Reactor	Starting reagents	Resulting products	Irradiation time	Emitted light
Conventional ampoule	Mn + P + 3 S	no reaction	1−60 min	no emission
Conventional ampoule	Cd + P + 3 S	no reaction	1−60 min	no emission
Conventional ampoule	2 Mn + P_2S_5 + S	no reaction	1−60 min	no emission
Dewar ampoule	Mn + P + 3 S	$MnPS_3$	25 min	purple-blue
Dewar ampoule	2 Mn + P_2S_5 + S	$MnPS_3$	30 min	pink-orange
Dewar ampoule	Cd + P + 3 S	$CdPS_3$	40 min	white-yellow

In addition, the method developed here could be extended to the preparation of other materials with similar synthetic problems, that is, in the cases where the dielectric component prevails over the metallic or semiconducting elements involved in the starting mixture lowering the efficiency of microwave-assisted procedures. This could be the case of different metal oxides, nitrides, carbides, etc.

Experimental Section

General: Conventional ceramic syntheses of MPS_3 materials were carried out as follows: a mixture of S, P and the transition-metal elements was ground in an glove box (Ar) and sealed in a classical quartz ampoule under a vacuum of 10^{-2} Torr. The ampoule was heated to 700 °C at 1 °C/min and maintained at this temperature for 10 days.[12]

Synthesis of MPS_3 Compounds: MPS_3 (M = Mn, Cd) crystals were also prepared by the Dewar ampoule method as follows: 0.3 g of the starting reagents, either as Mn (Aldrich, 99.9 %) or Cd (Aldrich, 99.5 %), P (Aldrich, 99.99 %) and S [(Aldrich) sublimed, 100 mesh, mixture, or as Mn, P_2S_5 (Aldrich, 99 %)] and S were thoroughly mixed in 1:1:3 or 2:1:1 molar ratios, respectively. The mixture was then transferred to the Dewar zone inside a glove box (Ar atmosphere). After vacuum degassing and hermetic flame sealing, the reactor was surrounded by quartz wool to provide insulation for high temperatures and protection against possible explosions (CAUTION!). In this manner, the mixture was MW-treated in a Moulinex Optiquick model (900 W, 2.45 GHz) during various periods of time (from 5 to 40 minutes) by steps of 1−2 minutes to avoid overheating effects that could produce damage. During the reaction, flashes of very intense visible light are produced, their color depending on the nature of the starting reagents (Table 1). The end of the reaction, which occurs after about 25−40 minutes, is clearly indicated by the extinction of the emitted light. At this time, only traces of residual reagents remain coating the bottom of the hot zone of the Dewar ampoule. The resulting MPS_3 compounds were characterized by X-ray diffraction (Siemens D-500 instrument with a Cu anode and Ni filter), IR spectroscopy (Nicolet 20SXC spectrophotometer), and electron microscopy (SEM) (ZEISS DSM-960 microscope working at 20 kV).

Acknowledgments

The financial support from the CICYT, Spain, (MAT2000−1585-C03−01) is gratefully acknowledged. We would like to express our gratitude to Tomás García-Somolinos for his helpful technical assistance in the Dewar ampoule development. We are indebted to Dr. M. A. Camblor for his helpful discussion and comments incorporated to this article.

---

[1] (Eds.) M. M. Kingston, S. J. Haswell, *Microwave-Enhanced Chemistry*, ACS, Washington, **1997**.

[2] [2a] D. M. P. Mingos, R. Baghurst, *Br. Ceram. Trans. J.* **1992**, *91*, 124. [2b] D. M. P. Mingos, *Adv. Mater.* **1993**, *5*, 857. [2c] D. M. P. Mingos, D. R. Baghurst, *Chem. Soc. Rev.* **1991**, *20*, 1.

[3] B. Vaidhyanathan, K. Balaji, K. J. Rao, *Chem. Mater.* **1998**, *10*, 3401.

[4] M. Iwasaki, H. Takizawa, K. Uheda, T. Endo, M. Shimada, *J. Mater. Chem.* **1998**, *8*, 2765.

[5] [5a] B. Vaidhyanathan, M. Ganguli, K. J. Rao, *Mater. Res. Bull.* **1995**, *30*, 1173. [5b] A. G. Whittaker, M. P. Mingos, *J. Chem. Soc., Dalton Trans.* **1995**, 2073.

[6] [6a] E. Gutiérrez, A. Loupy, G. Bram, E. Ruiz-Hitzky, *Tetrahedron Lett.* **1989**, *30*, 945. [6b] G. Bram, A. Loupy, M. Majdoub, E. Gutiérrez, E. Ruiz-Hitzky, *Tetrahedron* **1990**, *46*, 5167. [6c] R. S. Varma, *Green Chemistry* **1999**, *1*, 43.

[7] (Eds.) W. S. Cheung, F. H. Levien, *Microwaves Made Simple: Principles and Applications*, Artech House, Inc., Norwood, **1985**.

[8] R. Brec, *Solid State Ionics* **1986**, *22*, 3.

[9] [9a] D. O'Hare, *Inorganic Intercalation Compounds* in *Inorganic Materials*, 2nd ed., (Eds: D. W. Bruce and D. O'Hare), John Wiley & Sons, Chichester, **1996**. [9b] R. Clement, *J. Chem. Soc., Chem. Commun.* **1980**, 647. [9c] I. Lagadic, P. G. Lacroix, R. Clement, *Chem. Mater.* **1997**, *9*, 2004. [9d] R. Clement, *J. Am. Chem. Soc.* **1981**, *103*, 6998.

[10] A. H. Thompson, M. S. Whittingham, *Mat. Res. Bull.* **1977**, *12*, 741.

[11] G. Ouvrad, R. Brec, J. Rouxel, *Mat. Res. Bull.* **1985**, *20*, 1181.

[12] [12a] W. Klingen, R. Ott, H. Hahn, *Z. Anorg. Allg. Chem.* **1973**, *396*, 271. [12b] W. Klingen, G. Eulenberger, H. Hahn, *Z. Anorg. Allg. Chem.* **1973**, *401*, 97. [12c] B. E. Taylor, J. Steger, A. Wold, *J. Solid State Chem.* **1973**, *7*, 461.

[13] [13a] A. R. Wildes, M. J. Harris, K. W. Godfrey, *J. Magnet. Magnetic Mater.* **1998**, *177−181*, 143. [13b] A. R. Wildest, S. J. Kennedy, T. J. Hickst, *J. Phys.: Condens. Matter* **1994**, *6*, L335.

[14] R. Clement, P. Garnier, J. Jegoudez, *Inorg. Chem.* **1986**, *25*, 1404.

[15] H. von Falius, *Z. Anorg. Allg. Chem.* **1968**, *356*, 189.

[16] A. G. Whittaker, M. P. Mingos, *J. Chem. Soc., Dalton Trans.* **1995**, 2073.

[17] Y. Mathey, R. Clement, C. Sourisseau, G. Lucazeau, *Inorg. Chem.* **1980**, *19*, 2773.

[18] P. A. Joy, S. Vasudevan, *J. Phys. Chem. Solids* **1993**, *54*, 343.

Received September 17, 2003