JOURNAL OF MATERIALS SCIENCE **40** (2005) 6565–6569

# A microwave-assisted route for the solid-state synthesis of lead pyrophosphate, $Pb_2P_2O_7$

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In this study, we have developed a new method based on microwave heating for the preparation of lead pyrophosphate compound, $Pb_2P_2O_7$. The favoring of microwave heating as synthesis technique is based on the fact being much faster, cleaner and economical than conventional techniques. By following this new route, the lead pyrophosphate, $Pb_2P_2O_7$, was obtained as a pure phase. The products were characterized by X-ray powder diffraction (XRD) and Fourier Transform IR (FTIR) spectroscopic techniques. Comparing the experimental XRD and FTIR data of the synthesized products with the reported literature data has revealed that there was mutually an excellent agreement. © *2005 Springer Science + Business Media, Inc.*

## 1. Introduction

In recent years, the phosphatic metal compounds, e.g., orthophosphates, pyrophosphates and triphosphates have attracted very much attention due to theirs applications as catalysts, molecular sieves and ion exchangers for various organic and inorganic processes [1, 2]. The cited features of these materials have also of biological importance [3]. Because of theirs magnetic and florescence properties, they are technologically important materials, as well [4]. Additionally, the phosphatic compounds are used as raw materials or additives in the industrial production of metal surface treating materials, detergents and pigments [5].

In conventional methods, preparation of metal phosphate compounds and phosphatic materials generally involves long reaction times and high temperatures. Up to date, a large number of metal phosphates were prepared by a solid-state reaction or hydrothermal process with long period [6]. Since the reactions are completed in short time periods (usually between 10–30 min) by applying microwave irradiation, microwave-assisted synthesis reactions have also been used for phosphatic materials as well as many inorganic materials in recent years [7].

Microwaves belong to the portion of the electromagnetic spectrum with wavelenghts ranged from 1 mm to 1 m. This range corresponds to frequencies between 300 MHz and 300 GHz. For microwave heating processes, two frequencies most commonly used are 0.915 and 2.45 GHz. But the most of chemical syntheses were commonly performed with the frequencies of 2.45 GHz. The microwave method offers several advantages over conventional methods. Among these, the most outstanding one is that being very short of time scale required for the preparation of materials [8]. Microwave synthesis also gives rise to high reaction yields and the products having uniform structure. Therefore, this method is preferred to the traditional methods, recently [7].

Most of phosphate compounds are not susceptible to microwaves and therefore it is difficult to use microwaves for the preparation of phosphates except when one of other reactants is a microwave susceptor. But recently, it has been found that crystalline $NaH_2PO_4{\cdot}2H_2O$ is a good microwave susceptor [7]. When the $NaH_2PO_4{\cdot}2H_2O$ is exposed to microwave radiation, a heating process occurs due to the presence of water molecule in the crystalline structure. This type of microwave susceptibility was also reported for the some other crystalline hydrates [9].

### 1.1. Preparation of the lead pyrophosphate, $Pb_2P_2O_7$

In context of conventional techniques, several synthesis methods were developed for the lead pyrophosphate, $Pb_2P_2O_7$. For example, Brixner *et al.* [10] synthesized the cited compound by solid-state reaction method. In this method, a reaction was carried out with the lead carbonate, $PbCO_3$, and the ammonium dihydrogen phosphate, $NH_4H_2PO_4$, according to following equation:

$$\begin{aligned}2PbCO_3(s) + 2(NH_4)H_2PO_4(s) &\rightarrow Pb_2P_2O_7(s)\\ &+2NH_3(g)\uparrow + 3H_2O(g)\uparrow + 2CO_2(g)\uparrow \qquad (1)\end{aligned}$$

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DOI: 10.1007/s10853-005-1809-y

Firstly, the initial mixture of raw materials was heated at 300°C for a period of 10–14 h. After the homogenization of the product, a second heating step was applied at 700°C for extra 3 h.

Again in scope of conventional techniques, Eysel *et al.* [11] discovered a second synthesis route. They obtained the $Pb_2P_2O_7$ as a result of direct solid-state reaction, where an appropriate stoichiometric mixture of the reactants PbO and $NH_4H_2PO_4$ was initially heated in a Pt-crucible at 600°C for 3 days and then the obtained product was sintered at 700°C for 4 days.

If we compare two routes mentioned above, in both case, the reaction time is too long for the synthesis of $Pb_2P_2O_7$. But in our work, we developed a new method with short time scale for the synthesis of the lead pyrophosphate. In this new method, the reaction was completed within 10 min and it is based on microwave-assisted solid-state reaction.

## 2. Experimental procedure

### 2.1. Reagents and equipments

The reagents, $PbO_2$, $(NH_4)_2HPO_4$ and $NaH_2PO_4 \cdot 2H_2O$, were used as the starting materials. All commercial reagents were analytical grade and supplied from the Riedel Company.

Microwave reactions were carried out in the open air by a domestic type of microwave oven, Arçelik MD-560 (2.45 GHz, 750 W), which was made in Turkey.

The XRD data were collected using a Rikagu X-ray diffractometer (Model, Dmax 2200) with a Cu $K_\alpha$ radiation (40 kV, 20 mA, $\lambda = 1.54056$ Å). Infrared spectrum was obtained using Perkin Elmer, BX-2 FTIR spectrophotometer in the 4000–400 $cm^{-1}$ regions with KBr disc samples. Average particle size of the sample was measured by Mastersizer 2000-5.1 instrument, which was made by Malvern Instruments Ltd. The measurement was based on laser light technology.

### 2.2. Synthesis procedure

Appropriate amounts of the $PbO_2$, $(NH_4)_2HPO_4$ and $NaH_2PO_4 \cdot 2H_2O$ were weight according to molar ratio of 2:2:1. The initial reagents were well mixed and grounded homogeneously in an agate mortar. Then, the mixture was transferred into an alumina ceramic crucible and exposed to microwave radiation in the microwave oven for a period of 10 min. The sample was allowed to cool inside the oven. While the initial color of the mixture material was black, the final product was entirely white. Experiments were repeated several times for reproducibility test. The product was mainly characterized by XRD and FTIR techniques. Finally, average particle size of the sample was also determined.

## 3. Results and discussion

### 3.1. Evaluation of the X-ray diffraction data

The XRD data of the products are given in Fig. 1. As shown, these data belong to the $Pb_2P_2O_7$ compound and exhibit excellent agreement with the data of JCPDS card no: 43-469 (Fig. 1 and Table I). The crystal structure of $Pb_2P_2O_7$ was known as triclinic and the unit cell parameters are $a = 6.9766$, $b = 12{,}7660$, $c = 6{,}9624\ 0$ Å, $\alpha = 91.14°$, $\beta = 90.31°$, $\gamma = 83.23°$, $Z = 4$ and the space group is $P\bar{1}$.

Basic chemical reaction for the microwave-assisted synthesis of $Pb_2P_2O_7$ can be represented by the chemical equation below, taking into account XRD, IR and stoichiometric data:

$$\begin{aligned} &2PbO_2(s) + 2(NH_4)_2HPO_4(s) + NaH_2PO_4 \cdot 2H_2O(s) \\ &\quad \rightarrow Pb_2P_2O_7(s) + NaPO_3(g)\uparrow \\ &\quad +4NH_3(g)\uparrow + 6H_2O(g)\uparrow + O_2(g)\uparrow \end{aligned} \tag{2}$$

When the reactants were exposed to microwave radiation, a fast heating process was observed. The initial material mixture melted and turned to white-hot in a short time. During the process, sodium metaphosphate, $NaPO_3$, was obtained as a side product with respect to chemical equation given above. The $NaPO_3$ melts at 625°C and molten state of it is a fair microwave absorber at this temperature [12]. Along with formation of this new absorber $NaPO_3$, the microwave absorbers in the reaction medium become coupled to each others and lead to reach the temperature to a higher value than of 625°C [7].

Although the formation of $NaPO_3$ product is necessary according to chemical reaction stoichiometry (Equation 2), the $NaPO_3$ peaks given in literature (JCPDS card numbers: 2-776, 2-826, 3-394, 3-688, 11-648, 11-383, 11-650 and 36-243) could not be observed

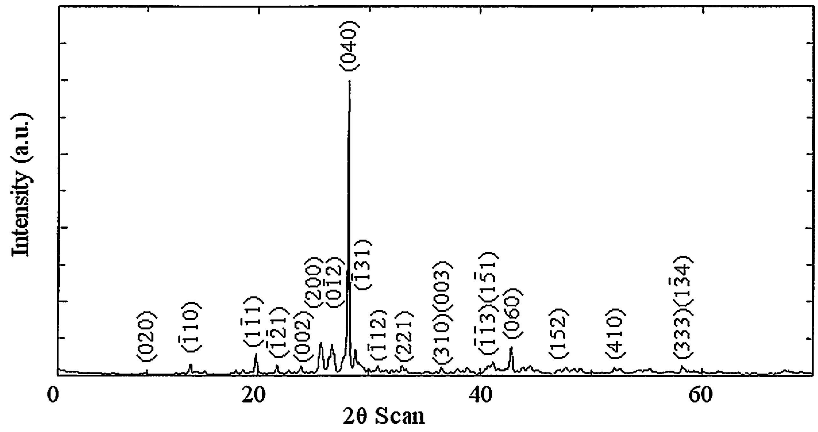

*Figure 1* X-ray powder diffraction pattern of $Pb_2P_2O_7$ (High intensity of the Miller indices were pointed out in the figure).

TABLE I The literature and observed XRD data of $Pb_2P_2O_7$ (JCPDS card no: 43-469)

| $2\theta$ | $I$ | $d$ | $d_{obs.}$ | $h$ | $k$ | $l$ | $2\theta$ | $I$ | $d$ | $d_{obs.}$ | $h$ | $k$ | $l$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 13.979 | 4 | 6.3300 | 6.3210 | 0 | 2 | 0 | 40.760 | 9 | 2.2119 | 2.2110 | −2 | 4 | 0 |
| 14.386 | 4 | 6.1520 | 6.1500 | 0 | −1 | 1 | 41.174 | 14 | 2.1906 | 2.1890 | −1 | −1 | 3(1 −5 1) |
| 15.282 | 5 | 5.7930 | 5.7900 | −1 | 1 | 0 | 41.557 | 5 | 2.1713 | 2.1690 | 2 | 5 | 0 |
| 18.048 | 4 | 4.9110 | 4.9020 | −1 | 0 | 1 | 41.673 | 5 | 2.1655 | 2.1640 | 0 | 2 | 3 |
| 18.705 | 6 | 4.7400 | 4.7360 | −1 | −1 | 1 | 42.049 | 5 | 2.1470 | 2.1520 | −1 | 4 | 2 |
| 19.099 | 3 | 4.6430 | 4.6920 | 0 | 2 | 1 | 42.295 | 5 | 2.1351 | 2.1350 | 3 | 3 | 0 |
| 19.846 | 14 | 4.4700 | 4.4710 | 1 | −1 | 1 | 42.621 | 12 | 2.1195 | 2.1190 | −3 | 1 | 1 |
| 19.981 | 7 | 4.4400 | 4.4360 | −1 | 1 | 1 | 42.776 | 14 | 2.1122 | 2.1120 | 0 | 6 | 0 |
| 21.749 | 9 | 4.0830 | 4.0810 | −1 | −2 | 1 | 43.220 | 5 | 2.0915 | 2.0900 | −3 | 2 | 0 |
| 23.334 | 5 | 3.8090 | 3.8640 | 1 | 3 | 0 | 43.406 | 4 | 2.0830 | 2.0800 | −2 | −5 | 1 |
| 23.694 | 5 | 3.7520 | 3.8670 | 1 | −2 | 1 | 43.741 | 7 | 2.0678 | 2.0650 | 0 | −5 | 2 |
| 23.940 | 10 | 3.7140 | 3.7120 | −1 | 2 | 1 | 43.915 | 6 | 2.0600 | 2.0600 | 2 | −3 | 2 |
| 24.843 | 8 | 3.5810 | 3.5730 | 0 | 3 | 1 | 44.987 | 5 | 2.0134 | 2.0170 | −1 | −6 | 1 |
| 25.569 | 12 | 3.4810 | 3.4900 | 0 | 0 | 2 | 45.353 | 10 | 1.9980 | 1.9900 | 1 | 5 | 2 |
| 25.696 | 20 | 3.4640 | 3.4660 | 2 | 0 | 0 | 46.978 | 5 | 1.9326 | 1.9320 | −3 | 3 | 0 |
| 25.825 | 12 | 3.4470 | 3.4500 | 2 | 1 | 0 | 46.978 | 5 | 1.9326 | 1.9320 | −2 | −1 | 3 |
| 26.418 | 18 | 3.3710 | 3.3730 | 0 | −1 | 2(−1 −3 1) | 47.671 | 8 | 1.9061 | 1.9060 | 2 | 6 | 0 |
| 26.659 | 16 | 3.3410 | 3.3430 | 0 | 1 | 2 | 48.463 | 8 | 1.8768 | 1.8760 | 2 | −4 | 2 |
| 26.848 | 16 | 3.3180 | 3.3180 | 1 | 3 | 1 | 49.002 | 6 | 1.8574 | 1.8550 | −2 | −5 | 2 |
| 27.472 | 5 | 3.2440 | 3.2530 | −2 | 1 | 0 | 49.002 | 6 | 1.8574 | 1.8550 | −2 | 4 | 2 |
| 27.831 | 12 | 3.2030 | 3.2070 | 2 | 2 | 0 | 50.967 | 4 | 1.7930 | 1.7890 | 1 | −4 | 3 |
| 28.144 | 100 | 3.1680 | 3.1660 | 0 | 4 | 0 | 50.967 | 4 | 1.7930 | 1.7890 | −3 | 2 | 2 |
| 28.803 | 20 | 3.0970 | 3.0970 | −2 | −1 | 1(2 0 1) | | | | | | | |
| 29.014 | 8 | 3.0750 | 3.0670 | 0 | −2 | 2(−1 −1 2) | | | | | | | |
| 29.150 | 25 | 3.0610 | 3.0610 | −1 | 3 | 1 | | | | | | | |
| 29.346 | 8 | 3.0410 | 3.0410 | 1 | 1 | 2 | | | | | | | |
| 29.554 | 5 | 3.0200 | 3.0260 | 1 | 4 | 0 | | | | | | | |
| 30.001 | 14 | 2.9760 | 2.9770 | −1 | 1 | 2 | | | | | | | |
| 30.367 | 5 | 2.9410 | 2.9290 | −2 | 1 | 1 | | | | | | | |
| 30.850 | 9 | 2.8960 | 2.8930 | 2 | 2 | 1 | | | | | | | |
| 31.204 | 5 | 2.8640 | 2.8650 | 0 | 4 | 1 | | | | | | | |
| 31.589 | 5 | 2.8300 | 2.8290 | 1 | 2 | 2 | | | | | | | |
| 32.054 | 7 | 2.7900 | 2.7950 | −1 | −4 | 1 | | | | | | | |
| 32.520 | 4 | 2.7510 | 2.7530 | 1 | −2 | 2(1 4 1) | | | | | | | |
| 32.976 | 9 | 2.7140 | 2.7140 | 0 | −3 | 2 | | | | | | | |
| 33.368 | 5 | 2.6830 | 2.6810 | 2 | −2 | 1 | | | | | | | |
| 35.121 | 5 | 2.5530 | 2.5530 | −1 | 4 | 1 | | | | | | | |
| 35.350 | 4 | 2.5370 | 2.5340 | −2 | 3 | 0 | | | | | | | |
| 36.055 | 4 | 2.4890 | 2.4900 | 2 | 4 | 0 | | | | | | | |
| 36.513 | 6 | 2.4588 | 2.4600 | −2 | −1 | 2 | | | | | | | |
| 36.513 | 6 | 2.4588 | 2.4600 | −2 | 0 | 2 | | | | | | | |
| 36.637 | 4 | 2.4508 | 2.4510 | 2 | 0 | 2 | | | | | | | |
| 38.777 | 7 | 2.3203 | 2.3310 | 3 | 1 | 0(0 0 3) | | | | | | | |
| 38.961 | 5 | 2.3098 | 2.3100 | 3 | 0 | 0 | | | | | | | |
| 39.226 | 3 | 2.2948 | 2.2950 | −1 | 5 | 0 | | | | | | | |
| 39.853 | 4 | 2.2601 | 2.2660 | 1 | 4 | 2 | | | | | | | |
| 40.490 | 5 | 2.2260 | 2.2260 | −3 | 1 | 0 | | | | | | | |
| 40.593 | 6 | 2.2206 | 2.2210 | −2 | −3 | 2(−2 2 2) | | | | | | | |

in the XRD pattern. Moreover, we could not find any fundamental vibration bands belong to $NaPO_3$ in the IR spectrum of product (Fig. 2) by comparing to literature spectra [13]. In this context, it was concluded that sodium metaphosphate must be sublimated when the temperature was reached to higher values than 625°C.

## 3.2. Evaluation of the FTIR data

In order to confirm the functional groups of the lead pyrophosphate, $Pb_2P_2O_7$, we had taken the FTIR spectra of the synthesized product (Fig. 2). The main band assignments for the fundamental modes of $P_2O_7^{4-}$ anions were presented in Table II. The frequencies of the $P_2O_7^{4-}$ group were assigned on the basis of the characteristic vibrations of the P–O–P bridge and $PO_3$ groups. As the P–O bond in the $PO_3$ group is stronger than that in the P–O–P bridge, the vibrational frequencies of $PO_3$ are expected to the higher frequencies. The symmetric and antisymmetric stretching frequencies of $PO_3$ in $P_2O_7^{4-}$ are observed in the regions 1117 to 998 $cm^{-1}$. Antisymmetric and symmetric POP stretching modes were observed in the region of 900–714 $cm^{-1}$. The bands due to $\delta$(OPO), $\delta$($PO_3$) and $\delta$(POP) deformations are also quite consistent with the frequencies region of 595–464 $cm^{-1}$. We had seen that experimental IR bands could be attributed to the literature assignments of diphosphate functional groups [14, 15].

## 3.3. Evaluation of the particle size data

Particle size distribution of the sample was determined experimentally. In the curve of volumetric particle size distribution, the maximum is 150 $\mu$m, as shown in

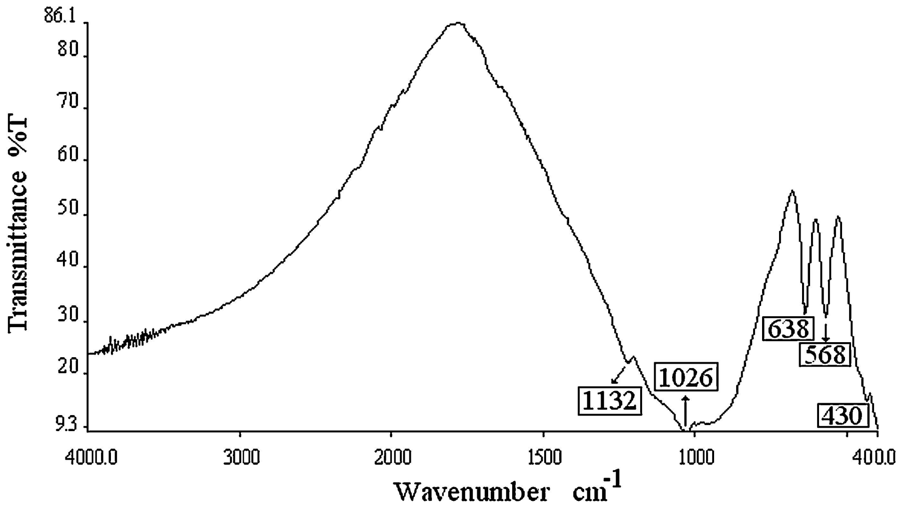

*Figure 2* IR spectrum of $Pb_2P_2O_7$..

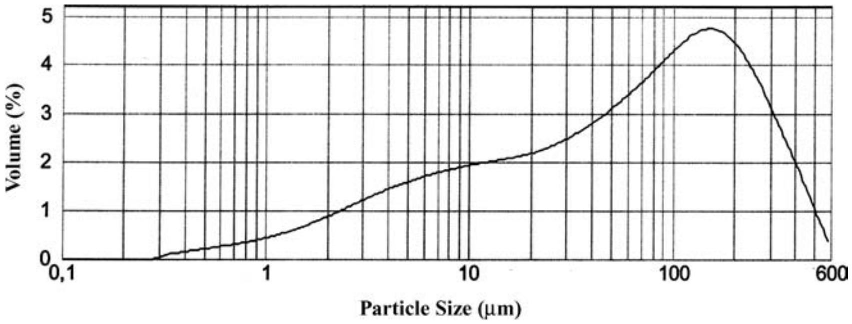

*Figure 3* Particle size distribution of $Pb_2P_2O_7$.

Fig. 3. This result indicates that the crystallinity of sample is quite high. The experimental high intensity cps values (max 2400) in the XRD pattern support also this conclusion.

## 4. Conclusions

The lead pyrophosphate, $Pb_2P_2O_7$, was successfully synthesized by using microwave-assisted solid-state chemical reaction. $Pb_2P_2O_7$ was obtained as a pure phase having a good crystalline form. In the synthesis procedure, the reaction was ended up in 10 min. Comparing to the conventional methods, $Pb_2P_2O_7$ was obtained in a very short time. The energy saving, very high heating rates, considerably reduced processing time and low reaction temperature could be given as advantages for this microwave synthesis route.

TABLE II FTIR spectrum data of $Pb_2P_2O_7$

| Assignments | Frequency ($cm^{-1}$)<br>$Pb_2P_2O_7$ | Literature |
|---|---|---|
| $\nu_{AS}$ ($PO_3$) | 1117—998 | 1108–1005 [14] |
| $\nu_S$ ($PO_3$) | 1065 | 1055 [15] |
| $\nu_{AS}$ (P-O-P) | 900 | 915 [15] |
| $\nu_S$(P-O-P) | 714 | 712 [15] |
| $\delta_{AS}$($PO_3$) | 595–545 | 599–545 [14] |
| $\delta_S$ ($PO_3$) | 497–464 | 485–450 [15] |

## Acknowledgement

Authors would like to thank Turkey Prime Ministry, State Planning Organization for project supporting (DPT-2003-K-120-230) and Balikesir University Research Project Foundation (Fund contract no: 2002-12) for financial support for this scientific study.

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*Received 8 October 2004*
*and accepted 2 May 2005*