High Microwave Susceptibility of NaH$_2$PO$_4$·2H$_2$O: Rapid Synthesis of Crystalline and Glassy Phosphates with NASICON-Type Chemistry[1]

B. Vaidhyanathan and K. J. Rao[2]

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

High microwave susceptibility of **NaH$_2$PO$_4$·2H$_2$O has been discovered. This hydrated acid phosphate of sodium can be heated upto 1000 K or more when exposed to 2.45 GHz microwaves. Using this, a novel microwave-assisted preparation of a number of important crystalline and glassy materials with NASICON-type chemistry has been accomplished in less than 8 min which is only a fraction of the time required for conventional synthetic procedures. The present single-shot approach to the preparation of phosphates is attractive in terms of its simplicity, rapidity, and general applicability. A "step-ladder" heating mechanism has been proposed to account for the high microwave absorbing ability of NaH$_2$PO$_4$·2H$_2$O.** © 1997 Academic Press

INTRODUCTION

NASICON is the acronym for sodium (Na) super ion conductor, a class of complex crystalline materials based on NaZr$_2$(PO$_4$)$_3$ (NZP), exhibiting high Na$^+$ ion conductivity (1). We use this term to describe a family of phosphates, both in crystalline and glassy states, of the general chemical formula A_xB_y(PO$_4$)$_3$ (A is an alkali ion, B is a tri- tetra- or pentavalent element), the chemistry of which is similar to the original NASICON compound NZP. The covalent network skeleton of NASICONs is remarkably stable toward temperature and chemical substitution (2, 3). It is suggested that they are likely to be very useful for nuclear waste disposal since heavier radioactive elements can be loaded in their structure (4) by substitution. NASICONs are also important for their "net zero thermal expansion" behavior (5). It has been found that some NASICON-type chemical compositions (with the general formula $A_xB_yP_3O_{12}$) can be vitrified, and several studies have reported on the result-

ing glasses (6, 7). However, the procedures presently available for the preparation of both crystalline and glassy NASICON materials are tedious and involved. For example, crystalline NZP itself has been synthesized using a two-step furnace heating for 28 h and with intermediate grinding (8). The time required for the preparation of Na$_3$Fe$_2$(PO$_4$)$_3$ is about 16–20 h (9). Even the NASICON glass preparation necessitates a step-wise heating schedule and requires at least 12 to 15 h (10).

Microwave irradiation has recently been used for the synthesis of inorganic materials. The microwave route to synthesis offers several advantages over conventional methods, the foremost of which are the very short time scales required for the preparation and the selectivity in energy transfer from the microwave field (11). Reaction yields and structural uniformity of products have been reported to be better than in traditional methods (12–18). A critical requirement in using microwaves is the coupling of (at least one of) the reactants to the microwave field in order to initiate and drive the microwave assisted reactions. In this context, a number of oxides (V$_2$O$_5$, CuO, NiO, WO$_3$, MnO$_2$, ZrO$_2$, silica gel, etc.) and a few halides (AgI, CuI) are found to be good microwave susceptors (19, 20). Carbon powder (both amorphous and graphitic forms) absorbs microwaves efficiently and heats up rapidly (21–23). Several mineral compounds (CuFeS$_2$, Fe$_3$O$_4$, PbS, etc.) are also known to be good microwave absorbers (24). However, several hydrated salts which couple to microwaves initially become microwave inert after the dehydration step. To date, no good room-temperature microwave-absorbing phosphate susceptor has been reported. Therefore, preparation of phosphate-based materials which require high temperatures of reaction has not been possible using microwaves. In this paper we report for the first time the unique microwave-absorbing ability of a hydrated phosphate namely NaH$_2$PO$_4$·2H$_2$O (NHP) and describe a simple and fast procedure for the synthesis of some crystalline and glassy phosphates with NASICON chemistry.

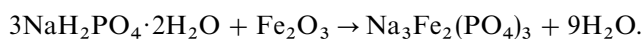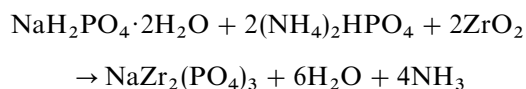[2] To whom correspondence should be addressed. E-mail: kjrao@sscu.iisc.ernet.in.

EXPERIMENTAL

A number of phosphates, some of them containing water of hydration, have been tested for their microwave-absorbing abilities. In a typical experiment, 5–10 g of the salt powders taken in a silica crucible is exposed to microwaves (for about 5–10 min) inside a domestic microwave oven (Batliboy, Eddy operating at 2.45 GHz and with several power level settings up to a maximum of 980 W). Table 1 lists some of the phosphates subjected to microwave irradiation and the observations made. The temperature of the material under microwave irradiation is measured intermittently using a Pt/Rh thermocouple as described earlier (19, 22). The weight-loss measurements have been carried out using a Sartorius balance (accuracy $= 10^{-4}$ g). To get more insight into the microwave coupling characteristics of $NaH_2PO_4 \cdot 2H_2O$, the decomposition of $NaH_2PO_4 \cdot 2H_2O$ was examined using thermogravimetry (TGA: Heating rate; 10 K/min, in air ambient) and differential thermal analysis (DTA: CAHN Instruments, CA).

Formation of crystalline NASICON compounds $NaZr_2(PO_4)_3$ and $Na_3Fe_2(PO_4)_3$ can be represented by

$$NaH_2PO_4 \cdot 2H_2O + 2(NH_4)_2HPO_4 + 2ZrO_2$$

$$\rightarrow NaZr_2(PO_4)_3 + 6H_2O + 4NH_3$$

$$3NaH_2PO_4 \cdot 2H_2O + Fe_2O_3 \rightarrow Na_3Fe_2(PO_4)_3 + 9H_2O.$$

Appropriate amounts of starting materials were therefore thoroughly mixed (batch weight = 7–10 g) and exposed to microwave radiation. The mixture melts partially during microwave irradiation and copious bubbling of the material is seen. The effervescence is observed in two regimes (first after 30 s; second after 80 s) following which the sample becomes red hot (within 3 min). After 7 min, the irradiation was terminated and the samples were allowed to cool inside the oven. The products were characterized using a Philips X-ray diffractometer (Model PW 1050/70).

Several NASICON-type glassy materials of the general formula $Na_xB_yP_3O_{12}$ (where B = Ga, V, Nb) have also been prepared using the same microwave heating technique. Starting materials included Na_2CO_3, Ga_2O_3, V_2O_5, and Nb_2O_5 in addition to $NaH_2PO_4 \cdot 2H_2O$. Batch weight of 5–10 g of appropriate amounts of starting materials were thoroughly mixed and irradiated with microwaves in clean silica crucibles. The duration of exposure was just about 5–7 min. Good melts were found to form within 5 min and were stirred once or twice in between to ensure homogenization. Melts were quenched between polished stainless steel plates. Disks of quenched samples so obtained were confirmed to be amorphous by X-ray diffraction (XRD) and glassy by differential scanning calorimetry (DSC). The preparation conditions and the observed glass transition temperatures (T_g) are given in Table 2. However, it may be noted that among the initial glass forming mixtures, V_2O_5 was also found to be a good microwave susceptor in addition to $NaH_2PO_4 \cdot 2H_2O$.

RESULTS AND DISCUSSION

Table 1 lists some of the alkali phosphates and their behavior under microwave irradiation. It is evident that though most of the hydrates absorb microwaves to begin

TABLE 1
Microwave Susceptibility of Different Compounds Examined[a]

Compound	Microwave exposure time	Observations and inference	Temperature reached in 5 min
$NaH_2PO_4 \cdot 2H_2O$	7 min	The two coordinated water molecules get completely removed after 50 s. The third water fully leaves after 125 s and the material is melted within 150 s. The weight loss observed corresponds to $3H_2O$ molecules.	951 K
$Na_2HPO_4 \cdot 2H_2O$	9 min	No weight loss, no red hotness and no melting observed, i.e., not a good microwave susceptor.	328 K
$Na_3PO_4 \cdot 12H_2O$	7 min	Weight loss observed. Found dehydrated. But no further microwave absorption noticed after 2 min. No melting or red hotness seen.	365 K
KH_2PO_4	9 min	No microwave absorption. No weight loss and no melting.	316 K
$(NH_4)_2HPO_4$	8 min	No weight loss and no melting. Not a good microwave susceptor.	323 K
$Na_2B_4O_7 \cdot 10H_2O$	7 min	Weight loss observed. Found dehydrated. A porous product obtained. But no melting or red hotness observed even after 6 min.	395 K
$NaBO_2 \cdot 4H_2O$	7 min	Found dehydrated. Weight loss observed. A rubbery product seen. But no further absorption or melting of the material seen.	385 K

[a] $ZnSO_4 \cdot 7H_2O$, $NiC_2O_4 \cdot 2H_2O$, and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ have also been subjected to microwave irradiation. They only get dehydrated and no further microwave absorption or melting is noticed.

TABLE 2
List of NASICON-Type Glasses and Crystalline Materials
Prepared by Microwave-Assisted Method

Material	Preparation time	T_g (K)[a]
Glasses		
Na$_3$Ga$_2$P$_3$O$_{12}$ (NGP)	6 min	680 (688)
Na$_4$VP$_3$O$_{12}$ (NVP)	6 min	578 (580)
Na$_4$NbP$_3$O$_{12}$ (NNP)	7 min	701 (710)
Crystalline		Lattice parameters (Å)
NaZr$_2$(PO$_4$)$_3$ (NZP)	7 min	$a = 8.801$ (8.804)
		$c = 22.747$ (22.757)
Na$_3$Fe$_2$(PO$_4$)$_3$ (NFP)	7 min	$a = 15.122$ (15.127)
		$b = 8.722$ (8.722)
		$c = 8.790$ (8.793)
		$\beta = 125°\ 02'$ (125° 12')

[a] T_g denotes glass transition temperature and the literature values are given in parentheses.

FIG. 1. (a) The temperature profile of NaH$_2$PO$_4$·2H$_2$O as a function of microwave exposure time and (b) the weight loss observed as a function of exposure time. Lines are drawn as a guide to the eye.

with, the microwave absorption ceases after the stage of dehydration and no further heating of the sample was noticed. Only in the case of NaH$_2$PO$_4$·2H$_2$O does microwave absorption continue to occur even after dehydration and anhydrous NaH$_2$PO$_4$ heats to high temperatures. The material melts and turns red hot. The melt could be quenched and transparent NaPO$_3$ glass ($T_g = 550$ K) was obtained. The time–temperature profile of NaH$_2$PO$_4$·2H$_2$O during microwave heating is given in Fig. 1a. It clearly indicates a rapid initial increase of temperature followed by a level-off region. Weight-loss measurements were also carried out as a function of microwave exposure time and the results are shown in Fig. 1b. Dehydration appears to take place in two steps; The first step which apparently starts within 30 s of exposure (appearance of bubbles) is completed within 50–60 s (when the effervescence stops temporarily). This may correspond to the removal of 2 H$_2$O molecules in the formula (see below). The second stage begins around 80 s and lasts up to 120–130 s. This stage corresponds to the removal of one more H$_2$O molecule from the structure resulting from a condensation reaction. The time and temperatures corresponding to the removal of these water molecules are marked (points 1 and 2) in Fig. 1a. The microwave exposure time required for the melting—as observed visually—of the dehydrated sample (point 3) is also indicated by an arrow in Fig. 1a.

The two stages of weight loss can be correlated to the respective temperatures of decomposition since the time axis is common to both Figs. 1a and 1b. Thus, loss of two water molecules of hydration can be interpreted to occur around 410 K and the loss of the additional water molecule from condensation (acid phosphate → metaphosphate) around 560 K in microwave experiments. This is corrobor-

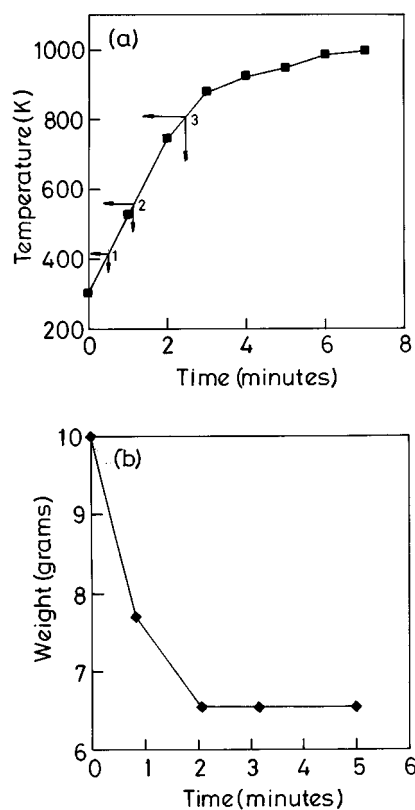ated by TGA/DTA measurements shown in Fig. 2. The TGA results confirm the two-step dehydration procedure at temperatures 382 and 471 K (points 1 and 2 in TGA curve), respectively. Incidence of these transitions are confirmed by DTA also (points b and c, respectively). The first endothermic peak in DTA (point a) is due to melting of NaH$_2$PO$_4$·2H$_2$O which occurs at ≈333 K without any loss of water. The melting point of the dehydrated product is found to be 612 K (point d in the DTA thermogram). We consider the temperatures obtained from microwave heating experiments as erroneous because of our inability to monitor the temperatures or any other suitable property continuously during irradiation. It is partly a manifestation of the very rapid heating process also.

A discussion of the origin of this unique microwave behavior of NaH$_2$PO$_4$·2H$_2$O is in order. Microwave irradiation can be expected to activate the rotational degrees of freedom in the water molecules (of hydration) present in the sample NaH$_2$PO$_4$·2H$_2$O. The sample first melts as a consequence forming a highly concentrated solution of NaH$_2$PO$_4$ in water. In the second stage the H$_2$O molecules escape from the solution leaving behind "hot" NaH$_2$PO$_4$ which we suspect is itself sufficiently microwave absorbing
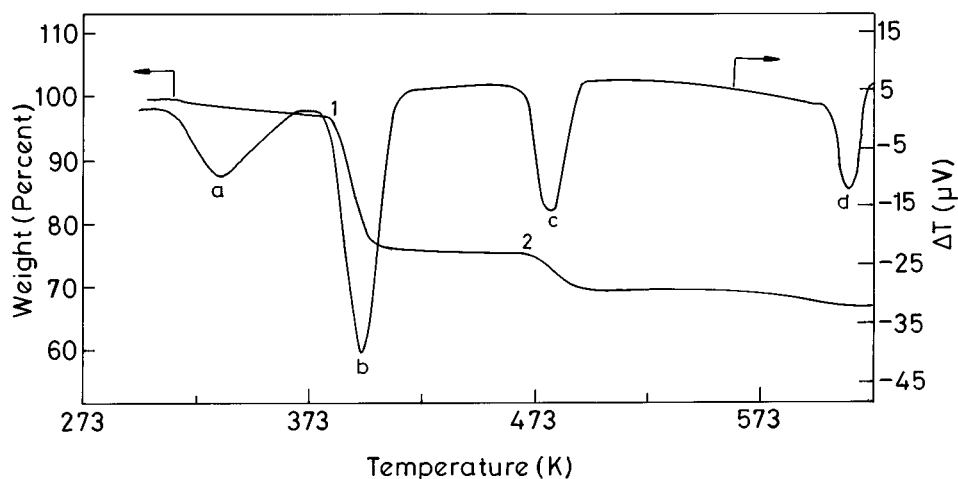
FIG. 2. TGA and DTA thermograms of $NaH_2PO_4 \cdot 2H_2O$. Points 1 and 2 in the TGA curve represent the first and second stages of dehydration. The incidence of these transitions are denoted as b and c in the DTA curve.

either due to increased dielectric loss or due to the nearness of a dielectric anomaly. This material then continues to be heated even further where upon in the third stage the chemically bound water (-H and -OH groups) in the structure of NaH_2PO_4 is eliminated by condensation. Anhydrous $NaPO_3$ melt is formed as a result. Molten $NaPO_3$ is itself a fair microwave absorber at this temperature (≈ 820 K). However, like other molten salt systems (19) $NaPO_3$ melt also reaches a temperature at which the microwave coupling is just sufficient to maintain a constant temperature. No significant escalation of temperature is observed above this point. It would be worth mentioning here that powders of neither pure $NaPO_3$ crystals nor $NaPO_3$ glass is found to be a microwave absorber at laboratory temperature. However, a hot $NaPO_3$ melt (melted using an electric furnace) was found to absorb microwaves when exposed and to reach the same flat temperature regime in the microwave oven. Thus, there are four essential stages in the microwave heating; (i) $NaH_2PO_4 \cdot 2H_2O$ crystals → hydrate melt, (ii) hydrate melt → anhydrous NaH_2PO_4, (iii) anhydrous NaH_2PO_4 → molten $NaPO_3$, (iv) molten $NaPO_3$ → stable high temperature melt of $NaPO_3$. These stages and their order are so critical for the microwave heating of $NaH_2PO_4 \cdot 2H_2O$ that they suggest a "step-ladder" heating mechanism.

The same step-ladder mechanism does not seem to operate in other hydrated salts ($Na_3PO_4 \cdot 12H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $NaBO_2 \cdot 4H_2O$, $ZnSO_4 \cdot 7H_2O$, $NiC_2O_4 \cdot 2H_2O$, and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) which we investigated for comparison and included in Table 1. The microwave absorbtion ceases after the stage of dehydration in these hydrates. Even among phosphates the differences in the microwave response is noteworthy. When there is no water of crystallization present (e.g., KH_2PO_4 and $(NH_4)_2HPO_4$), the material

is not heated to high enough temperature by microwaves and condensation–dehydration does not occur. In the case of $Na_2HPO_4 \cdot 2H_2O$ which has similar water molecules of crystallization as $NaH_2PO_4 \cdot 2H_2O$, microwave irradiation (even 10 min exposure) does not raise the temperature of the sample and no dehydration occurs. This profound difference in the behavior of the two hydrated sodium acid phosphates is noteworthy. We suggest that it is due to an enhanced barrier to rotation of H_2O molecules in disodium salt compared to dihydrogen salt. Such barrier-increasing effects are known in solution chemistry where effect of ionic substitutions on rotational barriers have been studied (25). The increase in barrier height can be visualized to be caused by the substitution of the H^+ ion in H-bonded structure by a Na^+ ion which leads to a geometrically tight-packed structure. This results in increased energy of excitation of the rotational degree of freedom and makes it unfavorable for transfer of energy from microwave field (energy mismatch). Such an argument implies that the energy transfer from microwave field to the rotational modes in these hydrates occurs through a resonance phenomenon. Absence of microwave absorption in other phosphates not having water of crystallization in the structure can also be due to the absence of a rotational mode of matching energy.

We have thus identified the uniquely effective microwave coupling and the step-ladder heating mechanism in $NaH_2PO_4 \cdot 2H_2O$ and we now discuss the preparation of several NASICON materials. First, two important crystalline compounds of the NASICON family have been synthesized. Figure 3 gives the X-ray diffractograms of the microwave-prepared crystalline NASICONs ($NaZr_2(PO_4)_3$ and $Na_3Fe_2(PO_4)_3$). The good crystallinity and the phase purity are evident. The calculated lattice parameters of the product NASICONs match well with the literature data (see
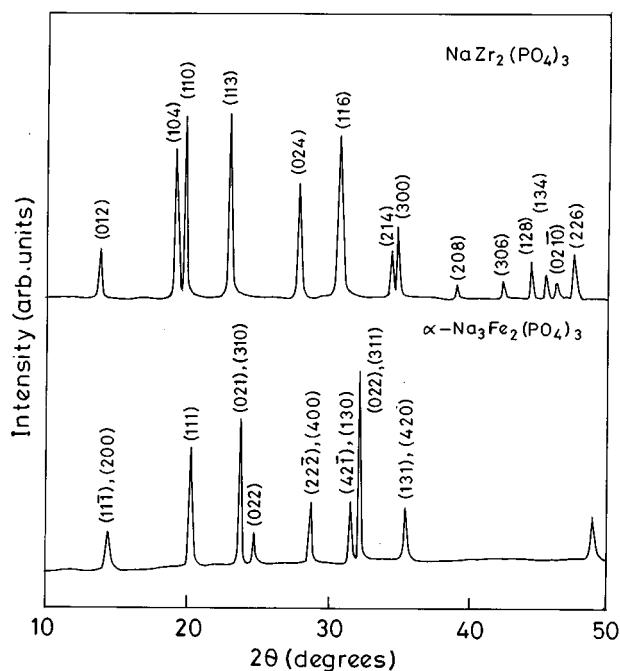
FIG. 3. X-ray diffractograms of the microwave-prepared crystalline NASICONs (wavelength of X-rays used CuKα = 1.5418 Å).

FIG. 4. Time–temperature profile of the NGP glass composition under microwave irradiation.

Table 2). Also, the full width at half maximum (FWHM) of the initial X-ray peaks have been measured as 0.20° in the case of (022) reflection of microwave prepared NFP which is the highest intensity peak. Other peaks had similar FWHM values. This result agrees well with the same data of the conventionally prepared (using ceramic method) Na₃Fe₂(PO₄)₃ compound (9). The microwave-assisted preparation of the above crystalline phosphates required less than 8 min which is only a fraction of the time required in conventional methods. Also, the present method does not necessitate intermediate grinding and hence is a single-shot process. In a microwave-assisted reaction, since the crucible is not heated directly and only the reactants (at least one of them) couple to microwaves, contamination by the crucible material is virtually completely eliminated (19, 26, 27). The rapidity of the microwave heating method also minimizes the loss of components from the reaction mixture (which normally occurs during prolonged heating of the material).

Various NASICON-type glasses were also prepared using NaH₂PO₄·2H₂O as a component of the batch mixtures. They are listed in Table 2 along with the measured glass transition temperature (T_g). The T_g values agree well with the reported data (given in parentheses) (9). The infrared spectroscopic investigations on a gallium-containing glass (NGP) (measurements were conducted on a pellet made by using KBr and the sample powders and vibrational bands were observed at 1170, 1060, 980, 665, 550, 480, and 340 cm⁻¹) confirmed the high quality of the resulting glass
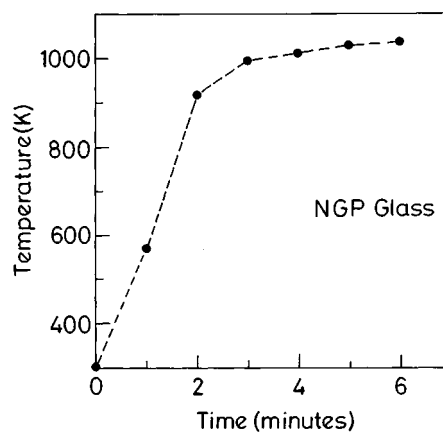
(9). The time–temperature profile during the microwave preparation of the NGP glass composition is shown in Fig. 4. This shows a sharp initial rise of temperature and then a levelling-off region, indicating features of auto-temperature-control, which we discussed in an earlier publication (19).

CONCLUSIONS

Thus, a microwave method of preparing crystalline and glassy NASICONs has been found to be possible by the discovery of the unique microwave coupling behavior of NaH₂PO₄·2H₂O. The method is found to be simple, fast, and quite general.

ACKNOWLEDGMENT

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