Journal of Thermal Analysis and Calorimetry, Vol. 78 (2004) 707–713

MICROWAVE ASSISTED LOW TEMPERATURE SYNTHESIS OF SODIUM ZIRCONIUM PHOSPHATE ($NaZr_2P_3O_{12}$)

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Abstract

Sodium zirconium phosphate [$NaZr_2P_3O_{12}$], a potential ceramic matrix for fixation of high level nuclear waste, was synthesized by heating the mixture of sodium carbonate [Na_2CO_3], zirconyl nitrate hydrate [$ZrO(NO_3)_2\cdot 5H_2O$] and ammonium dihydrogen phosphate [$NH_4H_2PO_4$] in air, in a resistance heated furnace and a microwave heating system respectively in the temperature range 450 to 650°C. The mixture heated for 1 h in a resistance furnace at 450°C yielded a poorly crystalline $NaZr_2P_3O_{12}$ [NZP]. Increasing the temperature to 650°C produced a highly crystalline product. The same mixture heated in a microwave oven at 450°C for 1 h however, yielded the most crystalline NZP.

In an alternate method, the mixture of sodium dihydrogen phosphate (NaH_2PO_4), Zirconium dioxide (ZrO_2) and diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] heated in resistance furnace at 650°C for the same period did not react in air. It also did not yield the pure product at 450°C when heated in microwave assembly for 1 h.

Keywords: ceramic matrix, microwave processing, nuclear waste, sodium zirconium phosphate (NZP), XRD

Introduction

Sodium zirconium phosphate ($NaZr_2P_3O_{12}$) (NZP) was reported to be the potential material for replacement of glass which is used to date for fixation of high level nuclear waste [1]. The thermodynamic stability of NZP and its unique property of accommodating 40 to 45 elements in the periodic table in its lattice without altering the basic structure, makes its choice natural as replacement for glass. In addition to metastability of glass, the processes involved in the incorporation of the fission products in the glass matrix require high temperatures at which the volatility of the fission products present in the form of oxides is significant. Any new material developed for substitution of glass should therefore be synthesized at low temperatures at which the vapor pressure of the oxides of the fission products is negligibly small. In the method reported by

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1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

NIST laboratory for synthesis of NZP, the mixture of sodium dihydrogen phosphate (NaH_2PO_4), zirconium dioxide (ZrO_2) and diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] was heated to 1200°C in air for nearly 24 h in the conventional resistance heated furnace to get pure product. In the present work we report the process by which NZP can be prepared in highly crystalline form at temperature as low as 450°C.

Experimental

Sodium carbonate [Na_2CO_3], ammonium dihydrogen phosphate [$NH_4H_2PO_4$] and zirconyl nitrate hydrate [$ZrO(NO_3)_2 \cdot 5H_2O$] used in the synthesis of NZP were better than 99% purity and were procured from M/S Merck, Central Drug House and Thomas Baker companies, respectively. The mixture of these components in appropriate proportion was heated in air in the range 450 to 650°C in the silicon carbide furnace (henceforth referred as resistance furnace) and specially fabricated microwave system for the same time interval of 1 h. The thermogravimetry (TG) and differential thermal analysis (DTA) curves were recorded for the mixture using simultaneous recording TG/DTA unit (Setaram, Model 92-16.18) and the home built DTA apparatus. The details of experimental conditions employed are marked in figure. Identification of the reaction products obtained at different temperatures was done employing X-ray diffractometer (Model:PW-1710). The diffraction patterns were recorded with CuK_α radiation at the scanning rate of $0.5° \ 2\theta \ min^{-1}$.

Result and discussion

The TG curve recorded in argon for the mixture of Na_2CO_3, $ZrO(NO_3)_2 \cdot 5H_2O$ and $NH_4H_2PO_4$ is shown in Fig. 1a. The corresponding DTA plot recorded simultaneously is presented in Fig. 1b. The first step in TG corresponds to dehydration followed by the second nearly overlapping step, which could involve the mass loss due to denitration and elimination of CO_2 from the mixture. Among the prominent DTA peaks recorded in a simultaneous TG/DTA system, the first is endothermic and corresponds to the elimination of water from the mixture. This is followed by two prominent exothermic peaks (a sharp peak followed by a broad one) which could be attributed to the oxidation of evolved ammonia by zirconyl nitrate followed by a solid-state reaction between the components to yield $NaZr_2P_3O_{12}$.

The use of TG and DTA in the present study facilitated anchoring of temperature for the synthesis of NZP. Similar approach was adopted by Ferragina *et al.* [2] to follow the formation of zirconium phosphate from the thermal decomposition patterns of dried gel containing surfactant moiety.

The DTA curves (Fig. 2) recorded separately for $ZrO(NO_3)_2 \cdot 5H_2O$, $(NH_4)H_2PO_4$ and the mixture lends support to the above conclusion. It is interesting to note that the temperature of denitration (Fig. 2b) nearly coincides with that for deammoniation (Fig. 2c) thereby increasing the probability of the nitrate ammonia reaction in presence of solid nascent reactant substrates (ZrO_2, P_2O_5, etc.) formed during the thermal

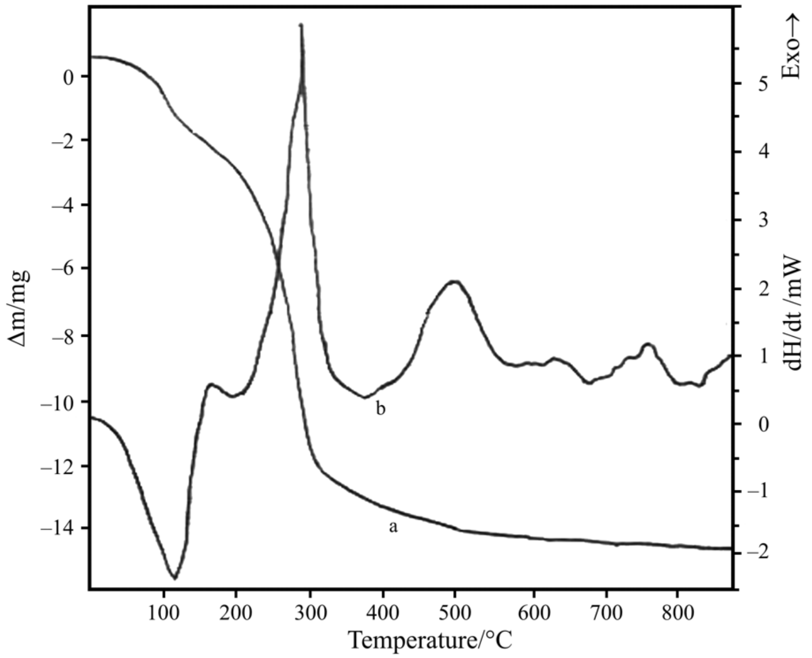

Fig. 1 a – TG and b – DTA of mixture of Na_2CO_3, $ZrO(NO_3)_2{\cdot}5H_2O$ and $(NH_4)H_2PO_4$

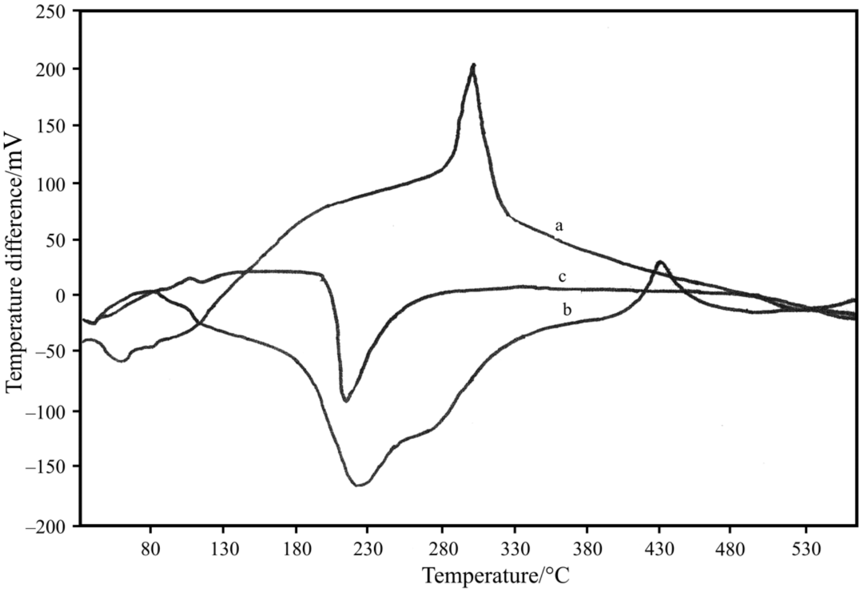

Fig. 2 DTA of mixture of a – Na_2CO_3, $ZrO(NO_3)_2{\cdot}5H_2O$, $(NH_4)H_2PO_4$, b – $ZrO(NO_3)_2$ and c – $(NH_4)H_2PO_4$

decomposition of reactants. The width of the second broad exothermic peak in Fig. 1b is typical of solid- solid reaction and would therefore correspond to the formation of $NaZr_2P_3O_{12}$ (NZP) from ZrO_2, P_2O_5 and Na_2CO_3. From the stoichiometry of the reaction the contribution of the evolved CO_2 to the enthalpy is expected to be relatively small compared to the strong exothermic effects involved in the oxidation of ammonia and formation of NZP from the solid components in the mixture.

The results of TG and DTA suggest that the formation of NZP from the reaction components is complete by 650°C. The X-ray diffraction pattern of the product obtained by heating the reaction mixture in conventional furnace at 650°C confirmed the results of thermal analysis. The X-ray diffraction pattern recorded for the product could be identified with that of pure $NaZr_2P_3O_{12}$ (Fig. 3a). The same mixture heated at 450°C for 1h in the same furnace however produced poorly crystalline NZP (Fig. 3b). The mixture on heating in microwave system at 450°C however, transformed completely into highly crystalline NZP (Fig. 4a).

The standard NZP sample for which X-ray pattern was reported by NIST [3] was prepared by heating the mixture of NaH_2PO_4, ZrO_2 and $(NH_4)_2HPO_4$ in the conventional resistance furnace at 1200°C overnight by repeated grinding. The mixture

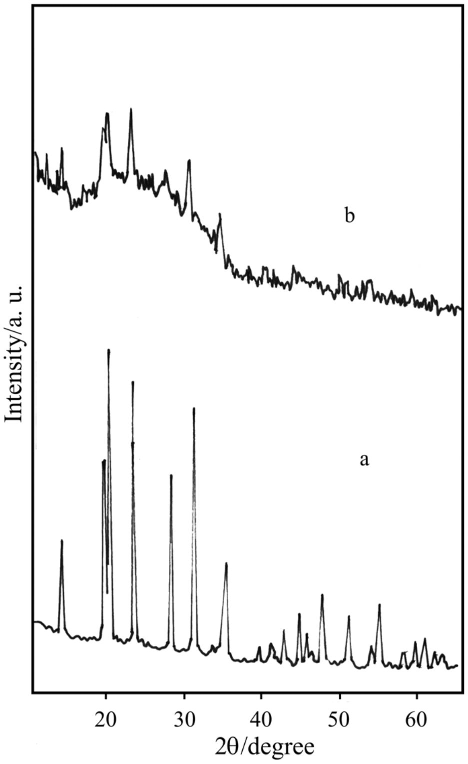

Fig. 3 XRD of product formed by heating mixture of Na_2CO_3, $ZrO(NO_3)_2{\cdot}5H_2O$ and $(NH_4)H_2PO_4$ in resistance heated furnace at a – 650°C and b – 450°C

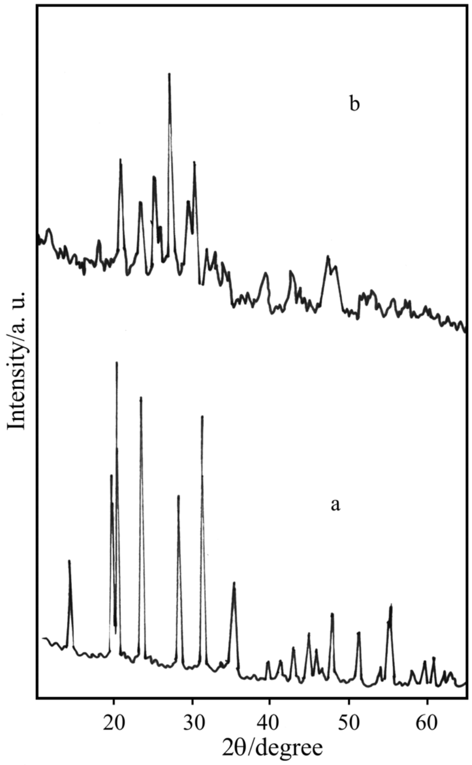

Fig. 4 XRD of product formed by heating mixture of a – Na_2CO_3, $ZrO(NO_3)_2\cdot 5H_2O$ and $(NH_4)H_2PO_4$ in microwave system at 450°C and b – NaH_2PO_4, ZrO_2 and $(NH_4)_2HPO_4$ in microwave system at 650°C

of same components of appropriate stoichiometry heated at 650°C for 1 h in the present experiments in the resistance furnace did not indicate the formation of NZP (Fig. 4b). Heating this mixture in microwave system for 1 h at 450°C yielded the X-ray pattern with sharp peaks, but with no evidence for the formation of NZP.

The DTA pattern of the mixture of NaH_2PO_4, ZrO_2 and $(NH_4)_2HPO_4$ recorded in air (Fig. 5) was found to be quite different compared to the DTA curve recorded for the mixture of Na_2CO_3, $ZrO(NO_3)_2\cdot 5H_2O$ and $NH_4H_2PO_4$. The prominent exothermic peak present in the former pattern (Fig. 2a) between 250 to 350°C is virtually absent in Fig. 5. This observation suggests that the prominent exothermic peak in Fig. 2a represents the redox type self-propagating high temperature synthesis (SHS) reaction between the nitrate and ammonium dihydrogen phosphate which facilitates the formation of NZP. The rate of this reaction is further augmented when the mixture is heated in the microwave field. The observed sluggishness of reaction in the case of mixture used in NIST experiment could probably be understood in terms of the absence of such reaction.

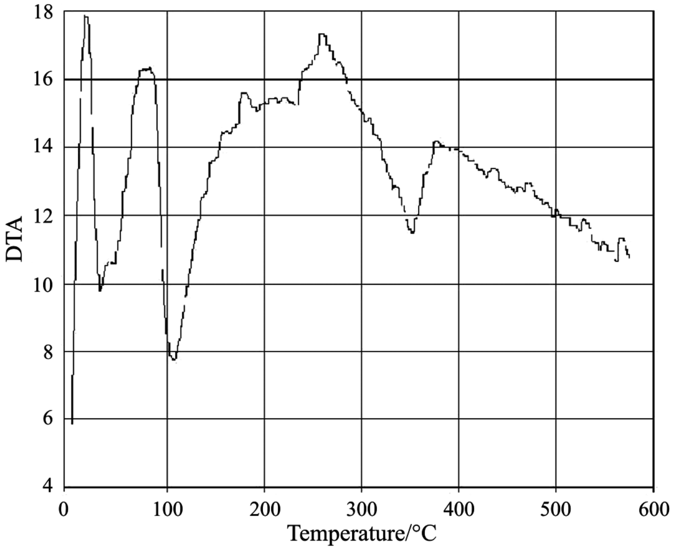

Fig. 5 DTA of mixture of NaH_2PO_4, ZrO_2 and $(NH_4)_2HPO_4$

Conclusions

NZP which could be used as a ceramic matrix for fixation of high level nuclear waste was synthesized by heating the mixture of Na_2CO_3, $ZrO(NO_3)_2·5H_2O$ and $(NH_4)H_2PO_4$ at 450°C in air in microwave oven. The same mixture yielded NZP when heated in air in resistance furnace at 650°C. The mixture of NaH_2PO_4, ZrO_2 and $(NH_4)_2HPO_4$, however, did not produce NZP at 650°C in the resistance furnace and also in microwave system. The possible reason for this difference in the chemical behavior of the two mixtures could be the self-propagating highly exothermic reaction (indicated by DTA) between the nitrate and $(NH_4)H_2PO_4$, accelerating the reaction rate between the reaction components in the mixture consisting of Na_2CO_3, $ZrO(NO_3)_2·5H_2O$ and $(NH_4)H_2PO_4$. Several such reactions involving self-propagating high temperature synthesis (SHS) have been described in [4–7]. The microwave heating apart from lowering of reaction temperature produces materials with remarkably different properties compared to that of the product obtained in normal resistance heating. The reverse temperature gradient prevailing in microwave-heated samples, for instance, has been successfully exploited recently [8] for the production of porous glass composite compacts containing high concentrations of well-defined spherical pores from the gases evolved within the sample during processing.

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The authors thank the Board of Research in Nuclear Sciences (BRNS) of the Department of Atomic Energy (DAE) for the financial support for this work under the project No. 2000/37/19/BRNS/1959 dtd09-02-02.

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