

Calorimetric study of selected NZP-type of ceramic materials

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Abstract

Sodium zirconium phosphate, NZP, ideally $\text{NaZr}_2(\text{PO}_4)_3$, is a potential host matrix for nuclear waste. Thermophysical properties of these materials are necessary to assess the thermal stability of these compounds. This paper presents the synthesis and calorimetric measurements of some NZP-type compounds containing alkaline earth elements. It also describes the indigenously developed room temperature drop calorimeter for low temperature calorimetric measurements. Calibration of the instrument is done with standard reference materials. Enthalpy increment of these materials is measured using this setup in the temperature range 373–873 K, and specific heat data are derived. Temperature dependence of enthalpy increment and specific heat of these materials, and the influence of the chemical composition on these properties are discussed.

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1. Introduction

Nuclear fuel cycle wastes can be considered to include any waste material produced in the process of generating electric power using nuclear fuel. The primary objective of the Synroc strategy [1] for HLW management is to provide a waste form which has a much greater resistance to leaching by ground waters than borosilicate glass and which is capable of maintaining its integrity in suitable geological environments for periods exceeding one million years.

The other novel materials for immobilizing HLW are materials based on the crystal structure of NZP [2,3]. Among the various crystalline forms considered, sodium zirconium phosphate, NZP, ideally $\text{NaZr}_2(\text{PO}_4)_3$, was first reported as potential host for nuclear waste by Roy et al. [4]. Its unique crystal structure allows a single phase being maintained with various combinations of elements [5] with the general formula $[\text{M}'_1][\text{M}''_2]\text{A}_2^{\text{VI}}\text{B}_3^{\text{IV}}\text{O}_{12}$. The populated M' site will accept the entire group IA and IIA set of elements and related larger monovalent and divalent elements. The entire rare earth and actinide series is also reported to substitute in this site [6]. The usually unpopulated M'' site only accepts Na and K. Substitution into the

six coordinated zirconium site will in general accept most of the larger trivalent, tetravalent and pentavalent cations, while substitution into the smaller tetrahedrally co-ordinated phosphate site is limited to the smaller trivalent, tetravalent and hexavalent cations.

Though plenty of information on their crystal structure and other properties like ion-exchange capacity are available, thermodynamic information on these materials is not available or is scanty. A few measurements of specific heat obtained by DSC were used in calculating thermal conductivity of these materials by some of the authors [7]. In view of this, the measurement of thermodynamic quantities like $(H_T^0 - H_{298.15}^0)$ was taken up. Specific heat data are needed for these materials if they are to find application as radwaste disposal matrices. The thermal expansion value of several NZP materials has been reported from this laboratory [8]. Higher specific heat coupled with low thermal conductivity is a recommended feature for the waste immobilization matrices. Our apparatus was used to measure low temperature specific heat capacity of uranium–thoria solid solutions and it was reported in an earlier work from this laboratory [9]. This paper describes the method of measuring $(H_T^0 - H_{298.15}^0)$ and deriving specific heat data in the case of NZP materials such as $\text{Ca}_{1/2}\text{Hf}_2(\text{PO}_4)_3$ (CaHfP), $\text{Ca}_{1/2}\text{Zr}_2(\text{PO}_4)_3$ (CaZrP), $\text{Sr}_{1/2}\text{Ti}_2(\text{PO}_4)_3$ (SrTiP), and $\text{Sr}_{1/2}\text{Zr}_2(\text{PO}_4)_3$ (SrZrP) by employing our

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calorimeter. The data are reported as a function of temperature in the range 373–873 K.

2. Experiment

Preparation of these compounds is described in detail in the previous work [7]. These compounds were synthesized by solid-state reactions starting from the following materials. ZrO_2 (Nuclear Fuel Complex (NFC), India), HfO_2 (NFC, India), TiO_2 (Alpha, USA), $CaCO_3$ (Sarabhai, India), $SrCO_3$ (Sarabhai, India) and $NH_4H_2PO_4$ (CDH, India). Stoichiometric amounts of the reactants were ground together using an agate mortar and pestle and heated in air at 623 K for about 8 h. The amorphous mass so obtained was ground well and calcined in air at 873 K for about 7 h, and subsequently at 1200 K for about 15 h. The powder mixture was ground again and heated in air at 1473 K for 5 h. The powders were then compacted into small discs of 12.5 mm diameter and 2–3 mm of thickness under a load of 4 tons. Then the pellets were sintered in air

at 1473 K for 24 h. The products were characterized by X-ray powder diffraction. After characterization these pellets were again reground and made into smaller pellets of 6 mm diameter and 2–4 mm thick for calorimetric measurements.

In order to measure the enthalpies/heat capacities of a variety of materials over a range of temperatures, a drop calorimeter has been setup and details of the same are reported elsewhere [10]. The calorimeter setup in the present study is of normal drop isoperibol type, where the sample is heated and dropped into a calorimetric vessel maintained at a fixed temperature (300 K). The calorimeter consists of three parts and they are calorimetric vessel, thermopile and the furnace.

A brass cup has been chosen as calorimetric vessel, as it is readily available, and it is amenable to machining and soldering. The brass cup with diameter of 7.5 cm and has depth of 4 cm. The thermopile is made of thirty-five pairs of chromel–alumel thermocouples, connected in series, and one set of junctions is maintained at a fixed temperature, and the other junctions in contact with the calorimetric vessel. Normally an insulator is used between the calorimetric vessel and the thermocouple junction. If the insulator is not used, the junctions will be electrically shorting the signal and the resulting signal is equivalent to that of a single thermocouple. Chromel–alumel thermocouple wire has been selected for making the thermopile. A schematic diagram of the indigenously developed calorimetric set-up is shown in Fig. 1. Each pair of thermocouple wires of 10 cm length is spot welded and the spot welded junctions are in turn soldered to the brass vessel. Twenty-five pairs of thermocouple were soldered on the walls and 10 pairs of the thermocouples at the bottom of the vessel and one of the alumel leads is grounded through a resistor. The other lead wire (chromel) is connected to the inverting input of the operational amplifier, through a resistor. The output signal obtained is that of the added signal due to each thermocouple pair as in the conventional thermopile. The advantages of this design over the normal thermopile are: (i) the response is fast because the junctions are spot welded to the cup. In normal thermopile there will be an insulator between the junction and the cup. (ii) In normal thermopile if one of the thermocouples gives away, it has to be replaced. In the present design, thermopile works even if one or two thermocouples give away. Only the output is reduced correspondingly.

The receiving vessel is enclosed in a stainless steel double-walled vessel, for water circulation and it is always maintained at 298 ± 2 K (over 2 h duration).

The resistive heating furnace made of nichrome wire was used for heating the specimen to the desired temperature. The furnace temperature is controlled using a PID temperature controller with an accuracy of ± 1 K. The sample temperature is monitored separately with another type–K thermocouple. The sample holder is made of

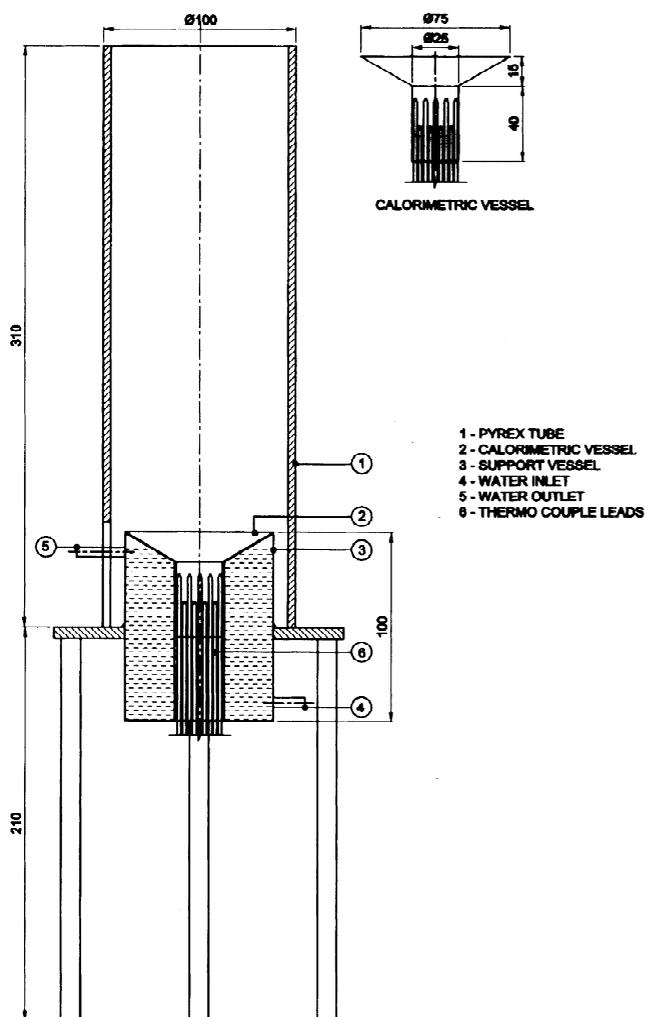


Fig. 1. Schematic diagram of drop calorimeter.

pyrophyllite material, which is pre-heated to 1573 K for removing moisture and to improve its hardness. The sample holder is cut across the diameter and fixed to two stainless steel pieces. A mechanism is provided to move the pyrophyllite pieces apart whenever required. The sample holder along with the mechanical arrangement is fixed on a laboratory stand.

The sample was loaded in the pyrophyllite sample holder assembly and was placed in the uniform temperature zone of the furnace. The sample is heated to a desired temperature in air using a temperature controller. When the specimen is thermally equilibrated with the desired temperature, the sample is dropped into the calorimetric vessel by moving apart the split sample holder system. The distance between the furnace and the calorimetric vessel is around 310 mm. Once the sample is dropped from the furnace into the calorimetric vessel, the heat released by the sample is sensed by the thermopile. The thermopile output is recorded using the operation amplifier and its output is fed into a Keithley high-impedance multimeter, which is provided with a serial interface. The analog signal from the multimeter is digitally stored in an IBM-compatible personal computer at regular interval of 1 s. The program for data collection from the multimeter is written using Quick Basic software, with a provision for online display of the signal.

3. Validation of the technique

The standard material synthetic sapphire (~0.05–0.1 g, SRM-720, α -Al₂O₃) obtained from NIST, USA is taken as the reference material for verifying the enthalpy increment associated with the unknown sample. In order to check the validity of this technique, the thorium dioxide pellet

Table 1
Enthalpy increment of ThO₂

| Temp. (K) | $(H_T^0 - H_{298}^0)$ J mol ⁻¹ | | |
|-----------|--|----------|-------------|
| | Measured | Expected | % Deviation |
| 673 | 96.19 | 97.71 | 1.55 |
| 673 | 96.38 | 97.71 | 1.36 |
| 673 | 98.88 | 97.71 | -1.20 |
| 673 | 99.07 | 97.71 | -1.39 |
| 773 | 127.01 | 125.67 | -1.06 |
| 773 | 123.81 | 125.67 | 1.48 |
| 773 | 128.64 | 125.67 | -2.37 |
| 773 | 125.41 | 125.67 | 0.21 |
| 873 | 154.99 | 154.15 | -0.54 |
| 873 | 153.84 | 154.15 | 0.20 |
| 873 | 154.67 | 154.15 | -0.34 |
| 873 | 153.52 | 154.15 | 0.41 |
| 973 | 180.22 | 183.10 | 1.57 |
| 973 | 184.22 | 183.10 | -0.61 |
| 973 | 182.12 | 183.10 | 0.54 |
| 973 | 186.16 | 183.10 | -1.67 |

Table 2
Enthalpy increment of Ca_{1/2}Hf₂(PO₄)₃ and Ca_{1/2}Zr₂(PO₄)₃

| Temp. (K) | $(H_T^0 - H_{298}^0)$ J mol ⁻¹ | |
|-----------|---|---|
| | Ca _{1/2} Hf ₂ (PO ₄) ₃ | Ca _{1/2} Zr ₂ (PO ₄) ₃ |
| 373 | 14 480 | 22 000 |
| 423 | 21 480 | 48 050 |
| 448 | – | 47 080 |
| 473 | 70 480 | 45 430 |
| 523 | 58 010 | – |
| 548 | 74 930 | 82 750 |
| 598 | 119 220 | 104 260 |
| 623 | 114 990 | 111 860 |
| 673 | 170 300 | 112 450 |
| 698 | 158 890 | – |
| 723 | – | 147 980 |
| 773 | – | 163 690 |
| 823 | – | 192 590 |
| 848 | – | 207 690 |

supplied by Nuclear Fuel Complex (Hyderabad, India) has been chosen as the unknown material. During a drop experiment, one sample and two standards were thermally equilibrated at the experimental temperature and dropped into the calorimetric vessel maintained at 298 ± 2 K. The experiments at each temperature were done in an air atmosphere involving the sequential dropping of Al₂O₃, ThO₂ and Al₂O₃ covering the temperature range 673–973 K. The output of the calorimetric vessel was amplified and stored in the computer continuously. The output from the computer gives the trace of the temperature change of the sample as a function of time. The data are plotted as function of time and peaks will be obtained corresponding to the heat output from the sample and the standard. The area under the curves was calculated using standard software. Using the relationship between the known enthalpy increment and area under the signal of standard, the enthalpy increment for unknown sample is obtained.

Table 3
Enthalpy increment of Sr_{1/2}Ti₂(PO₄)₃ and Sr_{1/2}Zr₂(PO₄)₃

| Temp. (K) | $(H_T^0 - H_{298}^0)$ J mol ⁻¹ | |
|-----------|---|---|
| | Sr _{1/2} Ti ₂ (PO ₄) ₃ | Sr _{1/2} Zr ₂ (PO ₄) ₃ |
| 373 | 26 030 | 17 250 |
| 423 | 36 220 | 32 610 |
| 448 | 36 660 | 41 780 |
| 473 | 49 730 | 49 520 |
| 523 | 53 190 | 65 800 |
| 598 | 85 150 | – |
| 623 | 110 730 | 91 820 |
| 673 | 139 320 | 107 680 |
| 698 | 125 360 | 126 960 |
| 723 | 155 350 | 141 720 |
| 773 | 153 930 | 164 940 |
| 798 | 179 510 | 168 630 |
| 823 | 178 460 | 184 360 |
| 848 | 221 600 | 193 460 |
| 873 | – | 198 780 |

Table 4

Calculated heat capacity values of $\text{Ca}_{1/2}\text{Hf}_2(\text{PO}_4)_3$, $\text{Ca}_{1/2}\text{Zr}_2(\text{PO}_4)_3$, $\text{Sr}_{1/2}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Sr}_{1/2}\text{Zr}_2(\text{PO}_4)_3$ ^a

| Temp. (K) | Heat capacity $\text{J mol}^{-1} \text{K}^{-1}$ | | | |
|--------------|--|---|---|---|
| | $\text{Ca}_{1/2}\text{Hf}_2(\text{PO}_4)_3$ | $\text{Ca}_{1/2}\text{Zr}_2(\text{PO}_4)_3$ | $\text{Sr}_{1/2}\text{Ti}_2(\text{PO}_4)_3$ | $\text{Sr}_{1/2}\text{Zr}_2(\text{PO}_4)_3$ |
| 300 | 222.10 | 227.55 | 268.43 | 225.10 |
| 350 | 276.90 | 251.17 | 286.72 | 247.56 |
| 400 | 331.70 | 274.78 | 305.02 | 270.02 |
| 450 | 386.51 | 298.40 | 323.32 | 292.48 |
| 500 | 441.31 | 322.02 | 341.62 | 314.95 |
| 550 | 496.11 | 345.63 | 359.91 | 337.41 |
| 600 | 550.92 | 369.25 | 378.21 | 359.87 |
| 650 | 605.72 | 392.86 | 396.51 | 382.33 |
| 700 | 660.53 | 416.48 | 414.80 | 404.79 |
| 750 | 715.33 | 440.10 | 433.10 | 427.26 |
| 800 | – | 463.71 | 451.40 | 449.72 |
| 850 | – | 487.33 | 469.69 | 472.18 |

^a Expression used for fitting the enthalpy increment is $A + BT + CT^2$.

Enthalpy increment value of standard alumina (SRM-720) used for calculations is taken from the literature. The results obtained in this measurement for thoria are tabulated in Table 1. The measured data are in good agreement within $\pm 2\%$ error compared to the data reported in the literature [11]. The value obtained using this technique shows that the results are reproducible and accurate, and it serves as a validation of the present apparatus. This has established that the present apparatus can be used to

measure specific heat of ceramic materials from room temperature to high temperatures.

Enthalpy increment of CaHfP, CaZrP, SrTiP and SrZrP was measured in the same manner as described above covering a temperature range 673–973 K. The experiment was repeated to get reproducible values with different masses of sample.

4. Results and discussion

The measured enthalpy increments of NZP materials were fitted to polynomials of temperature of the following form:

$$H_T^0 - H_{298.15}^0 = A + BT + CT^2$$

The constraints attempted were $(H_T^0 - H_{298.15}^0)$ to go through 0 at 298.15 K and the specific heat, that is the derivative of $(H_T^0 - H_{298.15}^0)$, which yields C_p^0 should be the same as the measured value/or the estimated value. Since the experimental value of these materials at room temperature is not reported, Neumann–Kopp's method was followed to estimate the value. After arriving at the C_p^0 value at 298.15 K, we tried to fit the data to the standard equation. It was found that the calculated specific heat values go through 0 at the 298.15 K value; the unexpected peaking or depression in specific heat curve does not reflect the true picture for these compounds. It was concluded that the Neumann–Kopp types of calculation of specific heat for these compounds are not in general valid at 298.15 K. The differentiated form of the enthalpy increment equation is the heat capacity over the given temperature range. The only boundary condition applied for the fitting was:

$$(H_T^0 - H_{298.15}^0) = 0 \text{ at } T = 298.15 \text{ K}$$

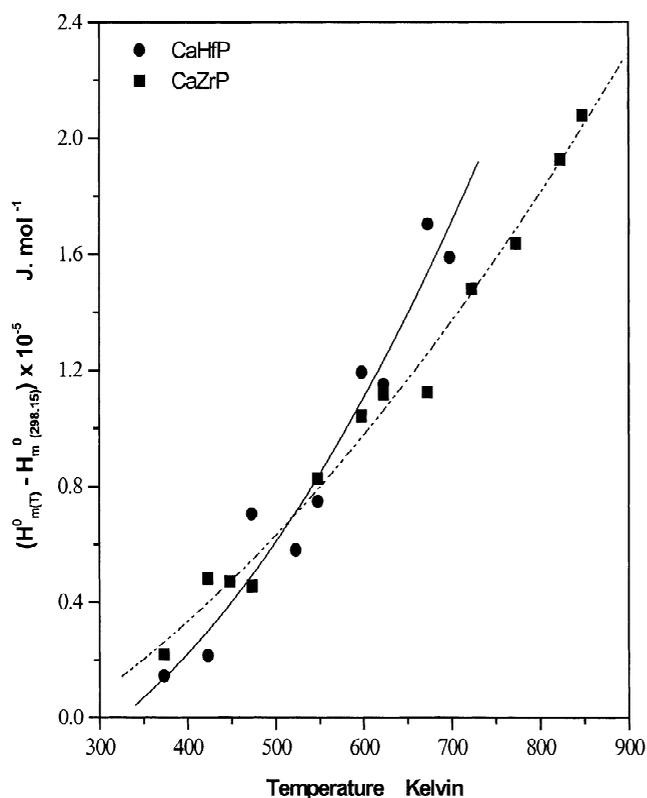


Fig. 2. $(H_T^0 - H_{298.15}^0)$ of $\text{Ca}_{1/2}\text{Hf}_2(\text{PO}_4)_3$ and $\text{Ca}_{1/2}\text{Zr}_2(\text{PO}_4)_3$ compounds.

The measured enthalpy increment values of these materials and the calculated heat capacity values using the measured enthalpy increment at 298.15 K are given in Tables 2–4. The estimated accuracy of the measured data is $\pm 2\%$ in all the temperature ranges.

Enthalpy increment of these compounds is plotted as a function of temperature and shown in Figs. 2 and 3, respectively. The specific heat values indicate that the difference in specific heat of CaHfP and SrTiP materials is much larger than that of CaZrP and SrZrP, respectively. This behavior can be attributed to the probable partial

covalency exhibited by the Hf and Ti elements in the oxide systems. The partial covalency behavior of both Hf and Ti elements in oxide type of compounds is reported by Wang [12]. Powder X-ray diffraction study shows that the cell volume of CaHfP is lower than that of CaZrP indicating partial covalency in the former. It was reported in the earlier work that the thermal expansion of these NZP compounds is very low [7]. The very low thermal expansion value suggests high specific heat for these compounds. The high specific heat is also justified on the high bond strength and stability of these compounds.

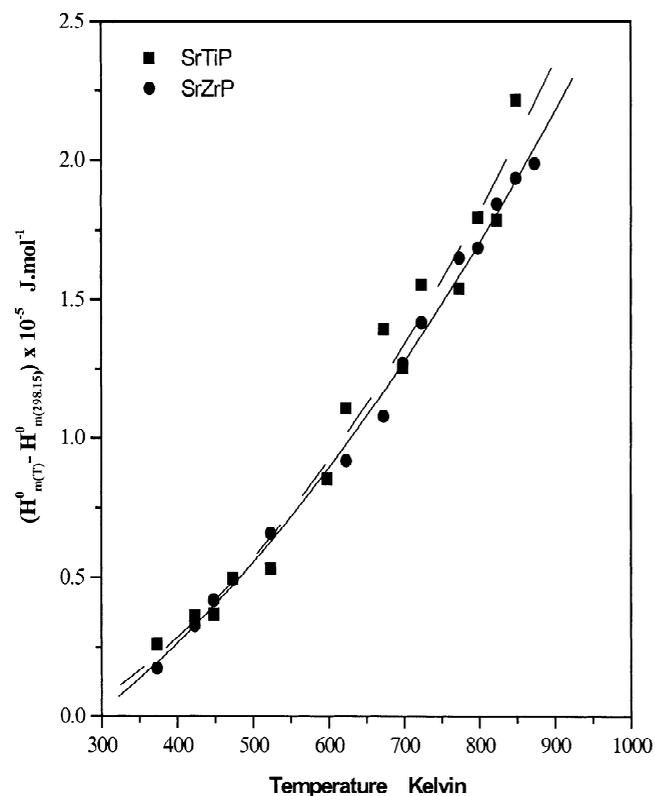


Fig. 3. $(H_T^0 - H_{298.15}^0)$ of $\text{Sr}_{1/2}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Sr}_{1/2}\text{Zr}_2(\text{PO}_4)_3$ compounds.

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