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### ► To cite this version:

Hieu Pham Sy, Doan Pham Minh, Abdoul Razac Sane, Hoan Nguyen Xuan, Nawal Semlal, et al.. Binary and ternary alkali polyphosphates (MPO<sub>3</sub>, M = Li, Na, K) for thermal energy storage. Journal of Thermal Analysis and Calorimetry, 2021, 146, pp.2027-2033. 10.1007/s10973-020-10346-1 . hal-03012742

**HAL Id: hal-03012742**


**<https://imt-mines-albi.hal.science/hal-03012742v1>**

Submitted on 20 Nov 2020

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# Binary and ternary alkali polyphosphates ( $MPO_3$ , $M = Li, Na, K$ ) for thermal energy storage

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## Abstract

Up-to-date, solar salt (a mixture of 60 mass%  $NaNO_3$  and 40 mass%  $KNO_3$ ) is practically the only media for thermal energy storage (TES) in concentrated solar power (CSP). This commercial product's utilization is limited below 550 °C to avoid an irreversible thermal decomposition. The development of new performing TES materials is decisive for the deployment of CSP technology. Our recent work reported promising results obtained with mono-alkali polyphosphate ( $M-PO_3$ ) as TES materials. These materials can work up to around 900 °C, but their melting point is still high, which is at least 628 °C. In order to lower their melting point, binary and ternary mixtures of alkali polyphosphates are investigated in this work. Different mixtures made of two or three alkali polyphosphates were prepared and studied using thermal analysis methods. The most promising mixture found in this work was the ternary  $Li-Na-K-PO_3$ , which contained 33.3% (mol%) of each alkali metal. This mixture can be used as a liquid TES material in the temperature range of 398 to 900 °C. The results open new prospects for the development of the thermal energy storage field.

**Keywords** Alkali polyphosphate · Thermal energy storage · Ternary ·  $Na-K-Li-PO_3$

## Introduction

Solar energy is the most abundant energy source and can be accessed from different countries. Solar energy includes all technology allowing the transformation of sunlight to usable energies. This includes photovoltaic (PV), solar thermal electricity, and solar heating and cooling as the leading

existing technologies [1]. However, the main drawbacks of solar energy remain in its daily intermittence as well as its seasonal character. Thus, thermal energy storage (TES) is indispensable to compensate for these drawbacks and the dephasing between energy production and consumption.

At a large industrial scale, thermal energy storage is mostly applied in concentrated solar powers (CSP). Sunlight focused from a large area into a small beam by using lenses or mirrors, and sun-tracking systems can be used or stored for further utilization [2]. In a given CSP system, solar salt—a mixture of 60 mass%  $NaNO_3$  and 40 mass%  $KNO_3$ —is the most common commercial liquid material [2, 3]. It is currently used in different CSP plants such as ANDASOL [4–7], GEMASOLAR [8], or recently NOOR I [9]. However, solar salt and other formulations of alkali nitrates and nitrites have different disadvantages and drawbacks. Their utilization is limited at 500 °C to avoid the complete chemical decomposition. Solar salt is used as the main component of fertilizer, and its massive utilization in CSP plants can affect agricultural activities. To limit the corrosion of storage tanks, salts of high purity are required, which incurs a high cost to the CSP plant fact; molten salts can account for up to 49% of CSP plant's cost [10].

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These last decades are remarked by numerous studies on the development of new materials for TES purpose [11–15]. Studies about materials for sensible heat storage, wherein the charge/discharge phases take place by increasing/decreasing the temperature without phase change, respectively, it is obvious that both liquid and solid materials are developed. Solid materials are mostly related to concretes, natural rocks, and refractory ceramics [16–20]. Concerning liquid materials, work has been devoted to nitrate-, carbonate-, chloride-, fluoride-based salts, as well as pure metals (Sn, Pb, and Zn) and alkali hydroxide [21]. However, they have either a high melting point or high risk of corrosion and flammability.

Our research team is the first to work on liquid polyphosphate materials for thermal energy storage [22]. Alkali polyphosphates have the common chemical formula of  $(MPO_3)_n$ , with  $M = \text{Na, K, or Li}$ , and  $n$  can reach up to a dozen units [23]. Our previous work shows that the mono-alkali polyphosphates have melting points of 628, 657, and 812 °C for Na, Li, and K salts, respectively [22]. These melting points are still high for sensible heat storage. Thus, the present research aims to lower the melting point of alkali polyphosphate salts by studying different binary and ternary systems. The final objective is to design a liquid TES material with a low melting point and a large working temperature, making it possible for further industrial utilization.

## Materials and methods

Sodium dihydrogen phosphate hydrate ( $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , Fisher Scientific, > 98%), potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ , Fisher Scientific, > 98%), lithium dihydrogen phosphate ( $\text{LiH}_2\text{PO}_4$ , Aldrich, > 98%) under fine powder form were used as received without further modification.

The study of the binary system ( $\text{Li-Na-PO}_3$ ,  $\text{Na-K-PO}_3$ ,  $\text{K-Li-PO}_3$ ) was carried out according to the standard synthesis method used for  $\text{NaPO}_3$  [24–26] following these steps: a mixture containing two phosphate salts with specified respected molar ratio was well crushed mechanically to obtain the fine mixture powders. The molar ratio of a given mixture of the binary systems was calculated according to Eq. (1). Then, the mixture was placed in a nonporous and inert ceramic crucible. This mixture was then heated under the air atmosphere up to 700 °C with a heating rate of 5 °C  $\text{min}^{-1}$  using a muffle furnace (Nabertherm P320). The temperature was kept at 700 °C for 60 min then the solid product was freely cooled down to room temperature. The obtained solid product was then characterized by different techniques such as TG–DTA, DSC, FTIR, and thermal conductivity.

$$\text{Molar \% of } M_i = \frac{\text{Number of moles of } M_i}{\sum \text{Number of moles of } M_i} \times 100 \quad (1)$$

with  $M_i$  is K, Na, or Li.

Using the same synthesis method, 26 mixtures of the ternary  $\text{Na-K-Li-PO}_3$  system were prepared and characterized. The mol% of each alkali metal varied from 10 to 80 mol%. Figure 1 represents the initial composition of the binary and ternary systems.

TG–DTA analysis was performed with a TA Instruments SDTQ600 analyzer with a heating rate of 5 or 10 °C  $\text{min}^{-1}$  under air flux (100 mL  $\text{min}^{-1}$ ). The specific heat capacity of the synthesized materials was measured by differential scanning calorimetry in a DSC 404 F1 Pegasus® with an initial mass of approximately 30 mg. The measurement was carried out in a dynamic argon atmospheric (gas flow rate of 50 mL  $\text{min}^{-1}$ ). Graphite crucibles with pierced lids were employed for the measurement. The sample was heated between room temperature and 800 °C at a heating rate of 20 °C  $\text{min}^{-1}$ . FTIR spectrum was recorded with a Shimadzu FTIR 8400S spectrometer.

The thermal conductivity of the ternary  $\text{Na-K-Li-PO}_3$  containing 33.33 mol% Na, 33.33 mol% K and 33.33 mol% Li was investigated. Two sets of measurements have been done. The first one was carried out by NETZSCH using their model LFA 467 HyperFlash® at different temperatures of 25, 50, 100, 150, and 200 °C. This set of measurements was limited at 200 °C because of the technical requirement of the equipment. The second one was carried out by Linseis using their model LFA-1000/1250 for three temperatures of 29, 200, and 700 °C. For each measurement, the salt powder was pressed to a pellet ( $\phi$  12.6 mm; thickness ~2.5 mm). The measurement was repeated five times at each temperature, and the average value is considered. Prior to the measurement, the front and the back of the sample were coated with graphite to enhance the emission and absorption properties.

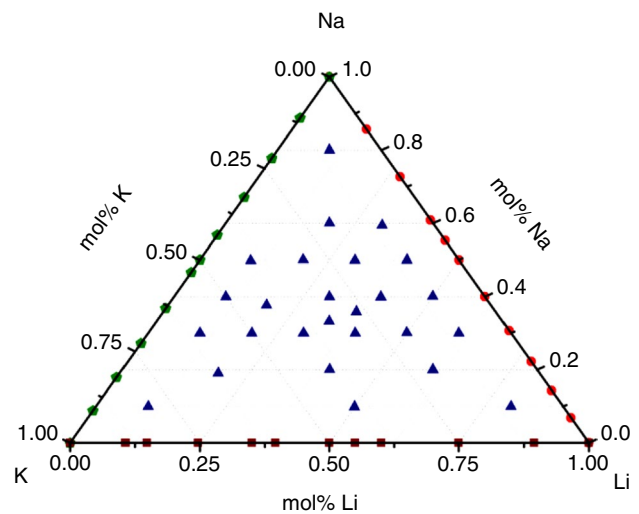


Fig. 1 The initial composition for the prepared samples in the binary and ternary  $\text{Na-K-Li-PO}_3$  system

## Results

### Characterization of the binary Na-K-PO<sub>3</sub>

As previously specified, the melting point of a given mono-alkali polyphosphate or a mixture of alkali polyphosphates (binary or ternary systems) was determined by TG–DTA analysis. As example, Fig. 2 shows the TG–DTA analysis of the binary mixture Na-K-PO<sub>3</sub> prepared from 50 mol% NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O and 50 mol% KH<sub>2</sub>PO<sub>4</sub> after sustained treatment at 700 °C for 60 min under air atmosphere. The melting point of this mixture was observed at 540 °C. This analysis was consecutively repeated 4 times (with the same sample) between 30 and 700 °C, and a very good repeatability was obtained. This also shows the thermal stability of this mixture during heating/cooling cycles.

The evolution of the melting point of the binary Na-K-PO<sub>3</sub> system is presented in Fig. 3. The mono-alkali polyphosphate salts of this binary system, (NaPO<sub>3</sub>)<sub>n</sub> and (KPO<sub>3</sub>)<sub>n</sub>, had a melting point at 628 and 812 °C, respectively [22, 27]. As expected for a binary system, the melting point of a given mixture prepared from these two components was lower than those of the single salts. Among different compositions investigated in this work, the lowest melting point of this binary system was found at 540 °C for the equimolar mixture (50 mol% of each single salt). The shape of the obtained Na-K-PO<sub>3</sub> diagram shows quite similarly to George works [27]. Using NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O and KH<sub>2</sub>PO<sub>4</sub> as precursors, the formation of 3NaPO<sub>3</sub>·KPO<sub>3</sub> was observed, which melts incongruently at 552 °C to form crystalline NaPO<sub>3</sub> and a liquid containing 0.31 mass% KPO<sub>3</sub>. Then, the eutectic formation took place at 547 °C according to the following reaction [27]:

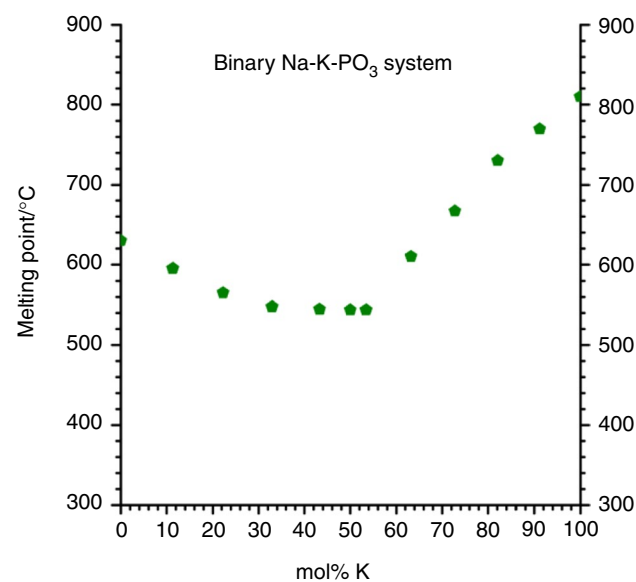
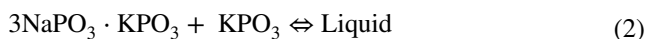


Fig. 3 Melting point of the binary Na-K-PO<sub>3</sub> determined by TG–DTA



FTIR analysis was carried out with the equimolar mixture of the binary Na-K-PO<sub>3</sub>, which had the lowest melting point for this binary system (Fig. 4). All the spectra have similar vibration peaks of P–O bonds in the wavelength range of 1400–600 cm<sup>-1</sup> [28, 29], except for the relative intensity of the FTIR signal. FTIR and TG–DTA analyses allow predicting that the resulting binary Na-K-PO<sub>3</sub> was stable during different thermal treatments.

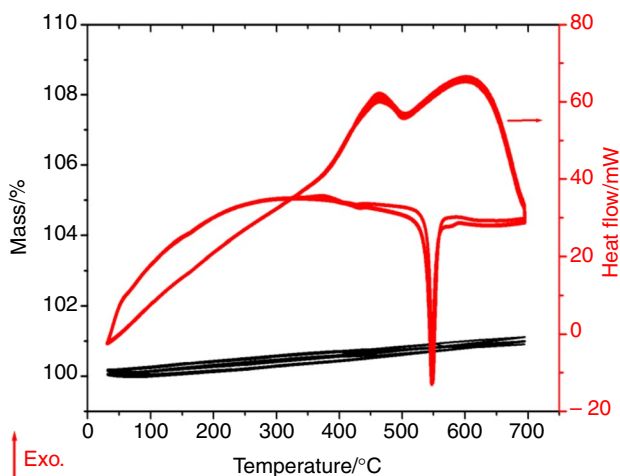


Fig. 2 TG–DTA analysis (4 cycles) of the mixture Na-K-PO<sub>3</sub> (50 mol% NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O and 50 mol% KH<sub>2</sub>PO<sub>4</sub>)

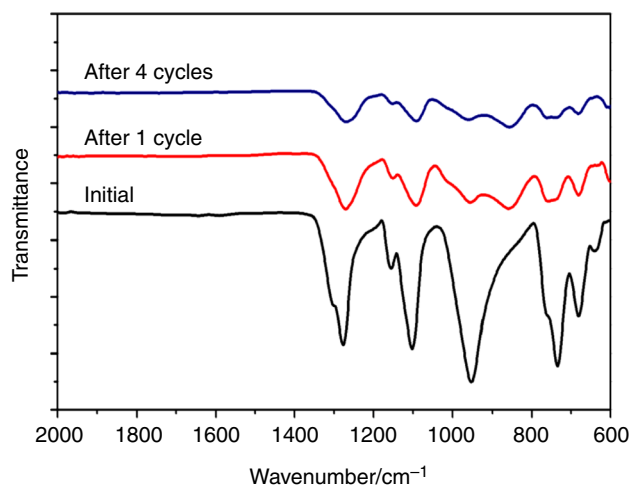


Fig. 4 FTIR of the binary Na-K-PO<sub>3</sub> (50 mol% NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O – 50 mol% KH<sub>2</sub>PO<sub>4</sub>) before and after TG–DTA analysis

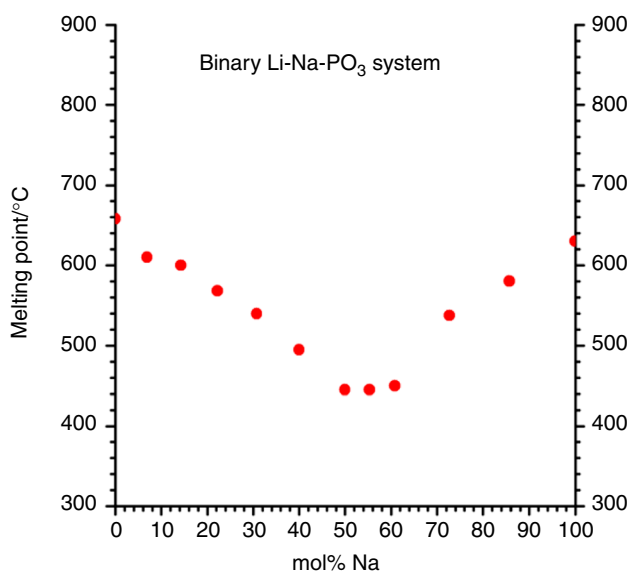


Fig. 5 Melting point of the binary Li-Na-PO<sub>3</sub> determined by TG-DTA

### Characterization of the binary Li-Na-PO<sub>3</sub>

The mono-alkali polyphosphate salts of this system are NaPO<sub>3</sub> and LiPO<sub>3</sub>, which have the melting point at 628 and 657 °C, respectively [22, 30, 31]. As expected, mixing these single salts allowed decreasing the melting point (Fig. 5). Among the different compositions of this binary system investigated in this work, the lowest melting point was obtained at 445 °C for the equimolar mixture (50 mol% of each single alkali polyphosphate). This melting point was much lower than that obtained with the binary Na-K-PO<sub>3</sub> above. TG-DTA and FTIR analyses were also performed

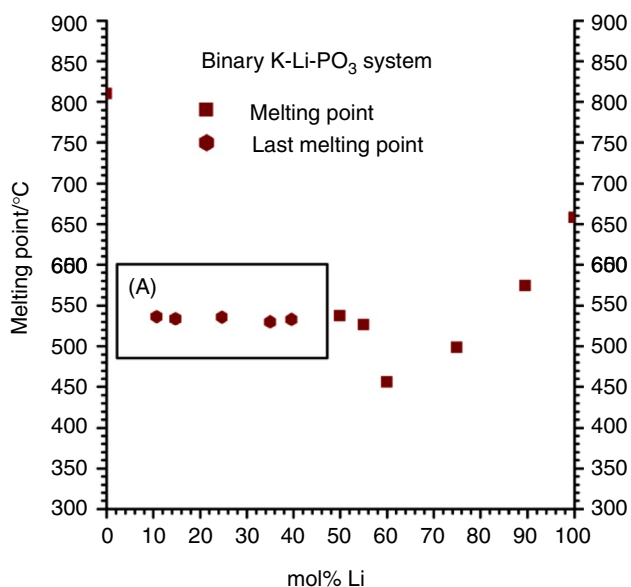


Fig. 6 Melting point of the binary K-Li-PO<sub>3</sub> determined by TG-DTA

with the eutectic mixture of the binary Li-Na-PO<sub>3</sub>. The results obtained (*not shown here*) also confirm the good thermal stability of this eutectic during different heating/cooling cycles under the air atmosphere.

### Characterization of the binary K-Li-PO<sub>3</sub>

Figure 6 shows the evolution of the melting point of the binary K-Li-PO<sub>3</sub> system. Lithium polyphosphate and potassium polyphosphate have the melting point at 657 and 812 °C, respectively [22, 31]. For mixtures containing more than 50 mol% of lithium polyphosphate, the melting point's determination was easy, with usually a net peak of melting (heating step) or crystallization (cooling step), as illustrated in Fig. 7a. On the other hand, for the mixtures having less than 50 mol% of lithium polyphosphate, the melting determination becomes more complicated because at least two major peaks appeared for heating step, as illustrated in Fig. 7b. This must be due to the presence of the

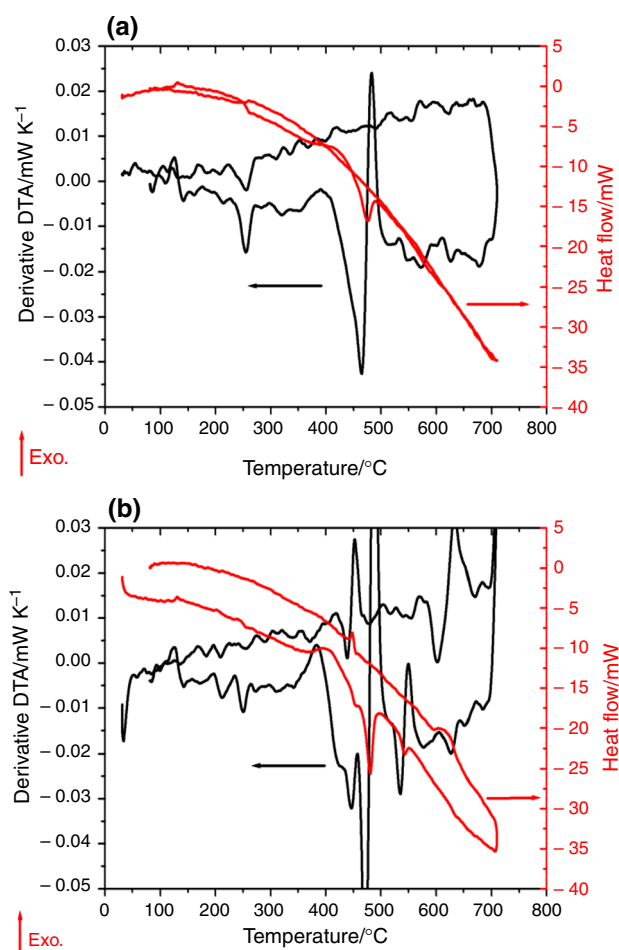


Fig. 7 Illustration of the binary K-Li-PO<sub>3</sub> with: **a** one melting peak (40 mol% KPO<sub>3</sub> and 60 mol% LiPO<sub>3</sub>); and **b** two melting peaks (75 mol% KPO<sub>3</sub> and 25 mol% LiPO<sub>3</sub>)

low-crystallinity/amorphous phase, (Li,K)PO<sub>3</sub> [32] and/or due to the creation of different phases within these mixtures. The zone (A) in Fig. 6 reports the temperature corresponding to the last peak during the heating step. This temperature is practically similar for different mixtures studied, which contained 60 to 89 mol% of potassium polyphosphate. More investigation needs to be performed to understand this thermal behavior for these mixtures. However, it is not the objective of the present study.

### Characterization of synthesized ternary Na-K-Li-PO<sub>3</sub>

The thermal behavior of the ternary mixtures Na-K-Li-PO<sub>3</sub> was much more complicated than that of mono-alkali polyphosphate (M-PO<sub>3</sub>) or binary polyphosphate. In general, several endothermic peaks of low intensity were detected. In some cases, these peaks were not clearly observed by the apparatus available in our laboratory (TA Instruments SDTQ600).

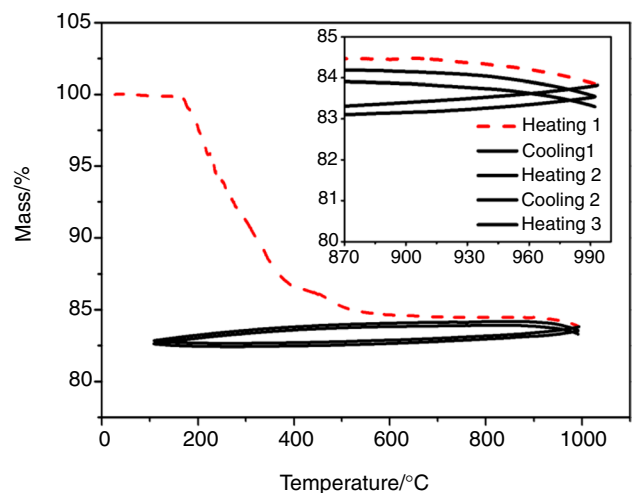
Table 1 shows the results obtained. The melting point of the first 21 mixtures could be determined by TG–DTA analysis. The lowest value was obtained at 398 °C for the mixture containing one-third of each mono-alkali polyphosphate (mixture N°1). Then, the melting point increased progressively up to 556 °C for the mixture N°21. This increase had no evident relationship with the mixture composition. For the mixtures from N°22 to N°26, their melting point could not be detected by TG–DTA analysis. As discussed previously in the binary K-Li-PO<sub>3</sub>, it might be possible that for each composition of these mixtures, low-crystallinity/amorphous phases of (Li,K,Na)PO<sub>3</sub> and/or metaphosphate glass composition [33] were formed. Since the initial mass of each TG–DTA analysis is small (around 20 mg), the DTA signal was not enough to be detected. However, manual verification by heating each mixture in a muffle furnace showed that the mixture composition N°1 had the lowest melting point.

Figure 8 shows the TG curves of the mixture composition N°1 (Table 1), which has a molar composition of 33.3% for each alkali under air atmosphere for three consecutive heating/cooling cycles. Thus, during the first heating, successive mass losses were observed due to the dehydration of alkali orthophosphates to form alkali polyphosphates. The evaporation took place above 900 °C, as highlighted in the insert, leading to a mass loss within the temperature range of 900–1000 °C. During the second and the third heating, no mass loss was observed below 900 °C indicating that the product was thermally stable. On the other hand, the evaporation was observed above 900 °C for each heating. Thus, this mixture can potentially be used as liquid TES material in the temperature range of 398–900 °C. It is worth noting that all alkali polyphosphates mixtures developed in this work have no risk of oxidation under the air atmosphere at high temperature.

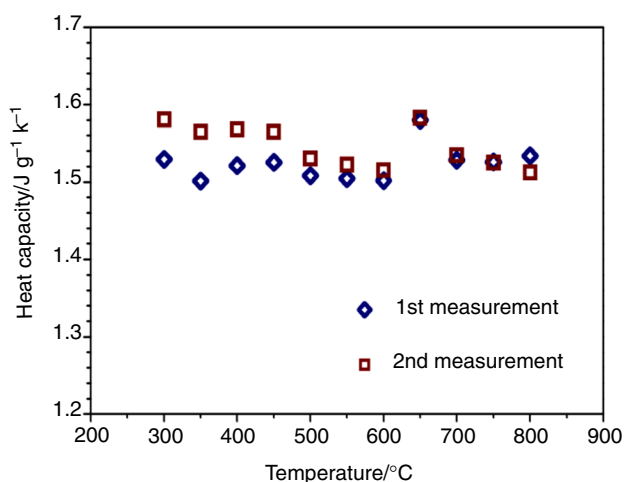
**Table 1** Melting point of different mixtures of ternary Na-K-Li-PO<sub>3</sub> system

N°	LiPO <sub>3</sub> /mol%	NaPO <sub>3</sub> /mol%	KPO <sub>3</sub> /mol%	Melting points/°C
1	33.3	33.3	33.4	398
2	30.0	50.0	20.1	402
3	19.0	19.0	61.9	411
4	37.3	35.9	26.9	425
5	30.0	40.0	30.0	425
6	10.0	10.0	80.0	429
7	40.0	50.0	10.0	436
8	40.0	20.0	39.9	438
9	20.0	30.0	49.9	438
10	60.0	20.0	20.0	445
11	19.9	50.0	30.0	450
12	19.0	37.7	43.3	455
13	30.5	59.4	10.1	474
14	10.0	40.0	50.0	475
15	20.0	60.0	20.0	480
16	10.0	30.0	60.0	490
17	49.9	9.9	40.2	493
18	9.9	49.8	40.3	493
19	30.0	30.0	40.0	521
20	10.0	80.0	10.0	556
21	80.0	10.0	10.0	556
22	50.0	40.1	10.0	X
23	60.0	30.0	10.0	X
24	40.0	39.9	20.1	X
25	40.0	30.0	30.0	X
26	49.9	30.1	20.0	X

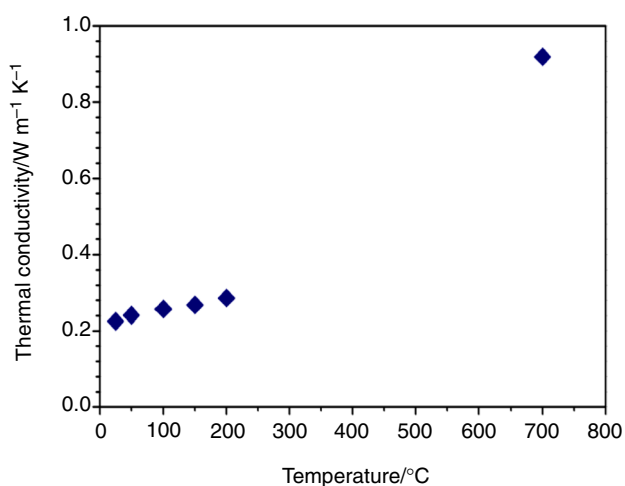
X: the melting point of the mixture could not be observed by TG–DTA method used in this work



**Fig. 8** TG analysis of the mixture Li-Na-K-PO<sub>3</sub> with the molar composition of 33.3% for each alkali under air atmosphere



**Fig. 9** Specific heat capacity of the mixture Li-Na-K-PO<sub>3</sub> with the molar composition of 33.3% for each alkali under air atmosphere



**Fig. 10** Thermal conductivity of synthesized ternary Na-K-Li-PO<sub>3</sub> (33.33 mol% Na, 33.33 mol% K and 33.33 mol% Li)

Figure 9 presents the evolution of the specific heat capacity ( $C_p$ ) of the mixture containing 33.3% of moles of each alkali as a function of the temperature (mixture N<sup>o</sup>1 in Table 1). The measurement has been repeated twice, and the value of  $C_p$  was very close to each other for each heating cycle, which was relatively stable between 1.5 and 1.6 J g<sup>-1</sup> K<sup>-1</sup> within 300 and 800 °C. These values are comparable with the heat capacity value of the commercial solar salt (1.6 J g<sup>-1</sup> K<sup>-1</sup> at 350 °C) [34].

The thermal conductivity of the ternary Na-K-Li-PO<sub>3</sub> containing 33.33 mol% Na, 33.33 mol% K, and 33.33 mol% Li was also investigated. Figure 10 shows the results obtained. Before the melting point, the thermal conductivity increased with the temperature and reached 0.29 W m<sup>-1</sup> K<sup>-1</sup> at 200 °C. After the melting point at 700 °C, the thermal

conductivity increased to 0.92 W m<sup>-1</sup> K<sup>-1</sup>. This jump of the thermal conductivity could be explained by the absence of porosity inside the liquid material. We recall that the thermal conductivity of the commercial Solar Salt<sup>®</sup> was of 0.55 W m<sup>-1</sup> K<sup>-1</sup> at 400 °C, which is relatively low and is considered as the main drawback [35]. So, the high thermal conductivity of the ternary Na-K-Li-PO<sub>3</sub> makes it more flexible for the design of thermal energy storage tanks, compared to the commercial Solar Salt<sup>®</sup>.

## Conclusions

For the first time, binary and ternary alkali polyphosphates have been investigated as media for thermal energy storage (TES) applications. The composition of alkali polyphosphate mixtures was identified as the decisive parameter to control the melting point of these mixtures. The ternary Na-K-Li-PO<sub>3</sub> (33.33 mol% Na, 33.33 mol% K and 33.33 mol% Li) was identified as the best mixture, which showed the lowest melting point around 398 °C. This mixture was thermally stable up to 900 °C without notable mass loss as demonstrated by TG analysis. Its specific heat capacity was comparable with that of the commercial solar salt<sup>®</sup>, while its thermal conductivity was of 0.92 W m<sup>-1</sup> K<sup>-1</sup> at 700 °C. So, this new liquid material is highly promising for high-temperature TES applications. Further work would be conducted on the evaluation of this material in a demonstration TES unit.

**Acknowledgements** The authors thank also the colleagues at RAPSO-DEE Research Center for technical help.

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