

ABSTRACT

THE EFFECT OF TITANIUM DIOXIDE NANOPARTICLES ON THE PHASE DIAGRAMS AND THERMOPHYSICAL PROPERTIES OF NITRATE MOLTEN SALTS

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Due to their desirable thermophysical properties, nitrate molten salts are the main reason for studying the high-temperature storage medium in concentrated solar power plants. Low freezing point temperatures allow for safe operation of the power plant and for thermal energy storage fluids to be in a liquid state over an extended temperature range. Using portions of the obtained thermal energy to maintain the molten salt in its liquid state reduces the overall thermal efficiency of the power plant. Previous studies reveal that the addition of nanoparticles to the 60% NaNO_3 -40% KNO_3 composition of molten salt decreases its freezing point temperature. The main objective of this study is to see how the freezing point temperatures of varying compositions of nitrate molten salts (30% NaNO_3 -70% KNO_3 |40% NaNO_3 -60% KNO_3 | 50% NaNO_3 -50% KNO_3 | 60% NaNO_3 -40% KNO_3 |70% NaNO_3 -30% KNO_3) are effected when titanium dioxide nanoparticles of anatase phase of different volume fractions are added to it. In this study, nitrate molten salts are prepared and then tested using the differential scanning calorimeter (DSC) and scanning electron microscopy (SEM). The DSC tests allow for obtaining the thermal properties such as freezing point temperatures, specific heat capacities, and latent heat of fusion. Observations using the SEM provide an opportunity to quantify the morphological properties like size, the microstructure, and the dispersion of the nanoparticles in the molten salt.

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NITRATE MOLTEN SALTS**

BY

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PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
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TABLE OF CONTENTS

LIST OF FIGURES	v
LIST OF TABLES	vi
Chapter	
1.INTRODUCTION	1
1.1 Molten Salt.....	2
1.2 Molten Salt with Nanoparticles	3
1.3 Molten Salt with Different Compositions.....	6
1.4 Thesis Objective.....	7
2.EXPERIMENTAL PROCEDURE	8
2.1 Materials Used	8
2.2 Equipment Used.....	8
2.3 Synthesis of Molten Salt with Nanoparticles.....	11
3.RESULTS AND DISCUSSION	16
3.1 DSC Results for Melting Point	16
3.2 DSC Results for Latent Heat of Fusion	18
3.3 DSC Results for Specific Heat.....	20
3.4 DSC Curves.....	21
3.5 Scanning Electron Microscope Images and Discussion:	25
4.CONCLUSION	27
4.1 Conclusion	27

4.2 Future Work	27
REFERENCES	28
APPENDIX: MATLAB CODE	30

LIST OF FIGURES

	Page
Figure 1: PHASE DIAGRAMS FOR NaNO_3 AND KNO_3	6
Figure 2: ANALYTICAL BALANCE.....	8
Figure 3: SONICATOR	9
Figure 4: HOT PLATE	9
Figure 5: FURNACE	10
Figure 6: DIFFERENTIAL SCANNING CALORIMETER	10
Figure 7: SCANNING ELECTRON MICROSCOPE	11
Figure 8: DSC PROGRAM	13
Figure 9: SAMPLE DSC CURVE.....	14
Figure 10: MELTING POINT VS NaNO_3 MOL%(WITH REFERENCE)	15
Figure 11: MELTING POINT VS NaNO_3 MOL%	16
Figure 12: MELTING POINT VS TiO_2 CONCENTRATION	16
Figure 13: ENTHALPY VS NaNO_3 MOL%(WITH REFERENCE).....	17
Figure 14: ENTHALPY VS NaNO_3 MOL%	17
Figure 15: ENTHALPY VS TiO_2 CONCENTRATION.....	18
Figure 16: SPECIFIC HEAT VS NaNO_3 MOL%	19
Figure 17: SPECIFIC HEAT VS TiO_2 CONCENTRATION	19
Figure 18: 30-70 HEATING.....	20
Figure 19: 40-60 HEATING	20
Figure 20: 50-50 HEATING	21

	Page
Figure 21: 60-40 HEATING	21
Figure 22: 70-30 HEATING	21
Figure 23: 30-70 COOLING	22
Figure 24: 40-60 COOLING	22
Figure 25: 50-50 COOLING	23
Figure 26: 60-40 COOLING	23
Figure 27: 70-30 COOLING	23
Figure 28: MOLTEN SALT 60-40 TIO2 5%	24
Figure 29: MOLTEN SALT 50-50 TIO2 5%	24

LIST OF TABLES

Table 1: CURRENT RESEARCH IN MOLTEN SALTS..... 2

Table 2: CURRENT RESEARCH IN MOLTEN SALTS WITH NANOPARTICLES..... 5

1. INTRODUCTION

In the past decade, with the exacerbation of energy shortage around the world and the continuous increase in the level of greenhouse gas emissions, the use of various sources of renewable energy was increasingly important for sustainable development. Solar energy is becoming one of the most promising sources of energy. Among various technologies of solar energy, the solar thermal power plant has been considered as the most potential way to massively utilize the solar energy in the future. Thermal energy storage (TES) system plays a key role in solar thermal power plants by providing the ability to match the electrical output for peak and off- peak demands. Heat transfer fluids play a vital role in the TES system and solar thermal power plants. A huge amount of heat transfer fluids is usually required for carrying thermal energy in solar power plants and hence entails high capital investment cost. Therefore, the criterion of minimizing the cost while maximizing the heat transfer performance is a major pursuit for the selection of heat transfer fluids. The main reason behind the reduction in usage of solar energy is the availability of the solar power during the night or a cloudy day. This problem can be easily solved by the implementation of the thermal energy storage (TES) systems. Many TES systems have been tested and implemented since 1985. The main characteristics that a material used in a Thermal energy storage system should possess are high thermal conductivity, low melting point, high latent heat of fusion and high specific heat. For medium-temperature applications, solids can be used as thermal energy storage materials. In some solar applications, liquids are used as storage materials. For sensible heat storage systems, a mixture of rocks and therminol are used. And the latent heat storage system use the phase change materials (PCM) from solid to liquid. Generally, thermal energy storage materials are paraffin waxes, fatty acids, metal alloys and salts that contains fluorides, chlorides, hydroxides,

nitrates and carbonates.

1.1 Molten Salt

Of all the thermal energy storage materials used, the nitrate salts show the best thermal properties. Sodium nitrate and potassium nitrate eutectic mixture is more efficient, cost effective and has better thermal properties such as specific heat, melting point, heat of fusion, etc. Some researchers have done work on the lithium nitrate and calcium nitrate. Of all the nitrate, eutectic mixtures tested till now, the 60% NaNO₃ and 40% KNO₃ showed better thermal characteristics than any other salt mixture is observed in Table 1.

Table 1. Current research in molten salts

Author	Melting Temperature(°C)	Latent Heat of Fusion(kJ/kg)	Specific Heat Capacity(kJ/kg-°C)
Rogers and Janz (1982)	216	109.96	-
Chieruzzi et al. (2013)	219.8	110.01	1.604
Dudda and Shin (2013)	222	-	1.21
Lasfargues et al. (2015)	221.3	97.59	1.415
Gabisa and Aman (2016)	225.3	120.91	6
Luo et al. (2017)	220.4	107.99	1.37

Molten salt is the eutectic mixture of 60% sodium nitrate (NaNO₃) and 40% potassium nitrate (KNO₃). The most desirable properties of molten salt are non-flammable, inert, non-toxic, high density, high heat transfer coefficient, cost effective, flexible and efficient. The melting point and the freezing point of the molten salt are 222°C and 238°C respectively. The specific heat of the molten salt is 1.5 kJ/kg. K and it can operate in low pressure conditions. Many people have

analyzed the 60% NaNO₃ and 40% KNO₃ of molten salt. According to Michael Schuller [1], the specific heat of the 60-40 combination of molten salt is 1.59 kJ/kg. K, whereas Dudda and Shin [2] has its values as 1.21 kJ/kg. K and 1.47 kJ/kg. K for the solid and liquid phases respectively. Chieruzzi [3] got the specific heat capacity of molten salt as 1.604 kJ/kg. K and 1.648 kJ/kg. K for the solid and liquid phases respectively. The melting point of the solar salt mixture was found to be 222°C according to Bergman [4] and 220°C according to Kramer [5] and 221°C according to Koller [6]. From literature the latent heat of fusion of the molten salt, according to Rogers (1982) [7] is 109.96 J/g, its value is 120.91 J/g according to Gabisa and Aman [8] and 114.98 J/g according to Cordaro [9].

1.2 Molten Salt with Nanoparticles

In the past few decades, lot of research has been done in the field of molten salt doped with nanoparticles as shown in Table 2. From the literature, it has known that the addition of nanoparticles enhances the properties of molten salt. There are many nanoparticles doped with molten salt; they are aluminum oxide (Al₂O₃), titanium oxide (TiO₂), silicon dioxide (SiO₂), copper oxide (CuO), etc.

Chieruzzi, et al [3] have found that by addition of Al₂O₃ to the solar salt showed a maximum enhancement in specific heat of 57.7% by addition of 1.0% of mixture of SiO₂-Al₂O₃. Addition of TiO₂ showed a decrease in specific heat. DSC showed that the addition of nanoparticles to base salt increased the heat of fusion of the nanofluid. The melting and the freezing points are lowered by addition of all nanoparticles.

Andreu-Cabedo et al. [12] has found maximum enhancement in specific heat of 25.03% by addition of 0.5% SiO₂ to solar salt and increment of under 5% for remaining combinations varying from 0.5% to 2.0%. The authors have carried out TGA analysis to find changes in

decomposition temperatures of mixture. SEM has been carried out find average sizes of NP and their distribution in mixture.

Lu and Huang [13] have reported somewhat contrasting results to Andreu-Cabedo et al [13]. and Chieruzzi, et al [3]. Lu and Huang [12] have shown reduction in specific heat capacity values by adding different concentrations of alumina NP. They have also studied effect of changing size of NP and have found similar trend of reduction in Cp values.

Researchers like Dudda and Shin [1], Ho and Pan [14] and Zhang et al. [15] have done similar research but with different molten salts and various types of NP. Dudda and Shin [2] have shown increase in specific heat, whereas Ho and Pan [14] and Zhang et al. [15] have shown increase in Cp value for some concentrations of NP while decrease for some concentrations. Cp value calculations by far have been done on a DSC and surface characterization using SEM.

Table 2: Current research in molten salts with nanoparticles

Author	Nano particle	Nanoparticle concentration	Melting Temperature(°C)	Latent Heat of Fusion (kJ/kg)	Specific Heat Capacity (kJ/kg-°C)
Chieruzzi et al. (2013) [3]	SiO ₂ , Al ₂ O ₃ , TiO ₂ , SiO ₂ /Al ₂ O ₃	0.5, 1, 1.5(weight %)	Little change except for SiO ₂ /Al ₂ O ₃ (~10 °C decrease)	All concentrations had an increase with 1% having the highest increase	0.5% and 1.5% had decreases; 1.0% had an increase
Dudda and Shin (2013) [2]	SiO ₂	1% (5, 10, 30,60 nm)	Little change	-	General increase with 1% 60 nm having 28% increase
Lasfargues et al. (2015) [10]	CuO, TiO ₂	0.1, 0.5, 1,1.5(weight %)	Little change	Increase at 0.1% with subsequent decrease at higher concentrations	Increase at 0.1% with subsequent decrease at higher concentrations (CuO)
Luo et al. (2017) [11]	CuO	0.1, 0.5, 1, 2, 3(weight %)	General decrease (3% had ~8 °C decrease)	General decrease (3% had a ~11 kJ/kg decrease)	Increase up to 0.5% with subsequent decrease

1.3 Molten Salt with Different Compositions

The 60-40 combination of molten salt is only a part of the $\text{NaNO}_3\text{-KNO}_3$ eutectic diagram. There is very little research done with different compositions of molten salts, of which Rogers and Janz (1982) [7] have clearly shown that the characteristics of molten salt depends on the compositions of nitrate mixtures in it, In this research, the melting point of the eutectic mixture is initially high, then decreases when it reaches 10 mol% of NaNO_3 then remains almost constant till it reaches 90 mol % of NaNO_3 , Similarly the latent heat of fusion decreases initially and then increases till it reaches pure KNO_3 which can be explained in the figure1.

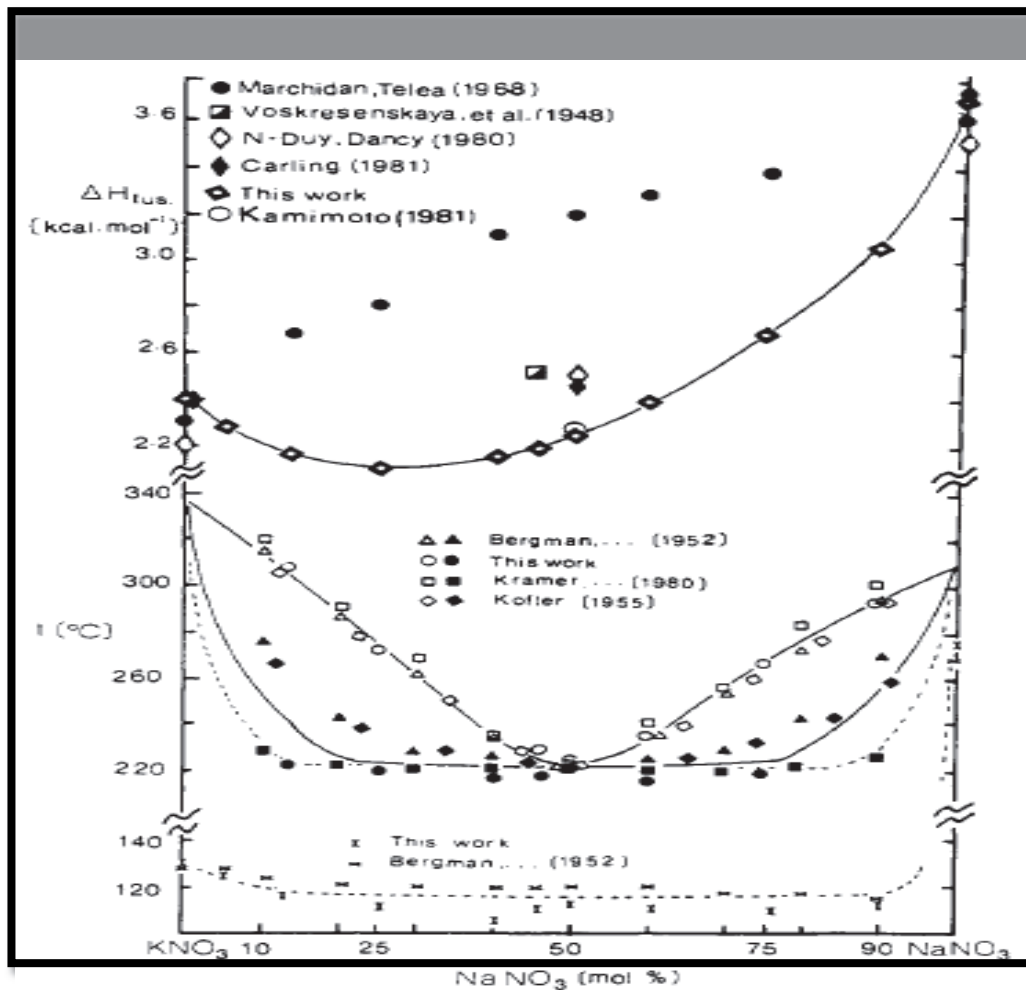


Figure 1: Phase diagram of NaNO_3 and KNO_3 [3]

According to Gabisa and Aman [8], the maximum enthalpy is 120.91 J/g at 60% NaNO₃ and 40% KNO₃, and the minimum is 44.83 J/g at 30% NaNO₃ and 70% KNO₃. The maximum melting point is 225.38°C at 60% NaNO₃ and 40% KNO₃ and the minimum is 224.3°C at 70% NaNO₃ and 30% KNO₃.

Till now everyone who has done work on the molten salt and molten salt with nanoparticles have told that there is increase or decrease in the values of specific heat, the melting temperature, and the latent heat of fusion, but no one said the exact reason behind it. Some people have told that the surface area of the nanoparticles plays a major role in enhancing the thermal properties of molten salt, which leads us to find the appropriate cause to enhance the properties of molten salt by the addition of nanoparticles.

1.4 Thesis Objective

The objective of this study is to investigate the effect of addition of titanium dioxide nanoparticles in different volume fractions (1%,5%, 10%) to molten salt at 60% NaNO₃ - 40% KNO₃ is same when nitrate molten salt is 50% NaNO₃ - 50% KNO₃| 70% NaNO₃ - 30% KNO₃| 40% NaNO₃ - 60% KNO₃|30% NaNO₃-70% KNO₃. I evaluate how the addition of nanoparticles affect specific heat capacity, melting temperature and the latent heat of fusion of the molten salts. I investigate microstructural characteristics of each molten salt nanoparticle system and look at the surface characteristics of molten salts.

2.EXPERIMENTAL PROCEDURE

2.1 Materials Used

- Sodium nitrate bought from Sigma-Aldrich which is 99.99% pure.
- Potassium nitrate bought from Sigma-Aldrich which is 99.99% pure.
- Titanium dioxide nanoparticles from US Research Nanomaterials, Inc.
 - Anatase phase
 - 20nm average diameter
- Deionized water

2.2 Equipment Used

Analytical balance:

The analytical balance used to measure the mass of sample, reference material and the pans, a digital analytical balance USS-DBS5 of US Solid Lab

Equipment. The characteristics of the balance are:

- 1.It can measure from10mg to120g.
2. It has a precision of 0.1mg.

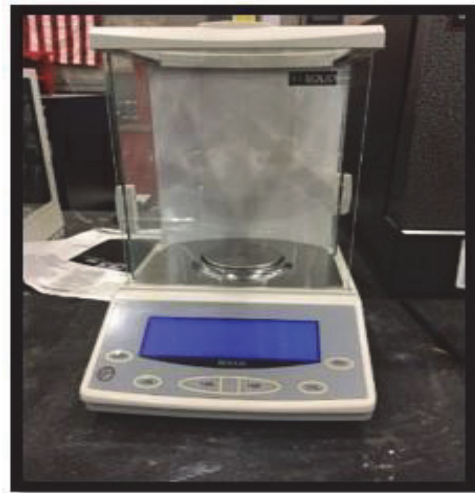


Figure 2: Analytical balance

Sonicator:

Sonication is a process in which sound waves are used to agitate particles in solution. Such disruptions can be used to mix solutions, speed the dissolution of a solid into a liquid (like sugar into water), and remove dissolved gas from liquids. The sonicator used in this work is Branson M1800.



Figure 3: sonicator

Hot plate:

The hot plate is used to maintain the constant heat supply. The hot plate used in this work is Fisher Scientific hot plate. A magnetic stirrer is used on the hot plate to ensure the proper mixture of the sample. The characteristics of the hot plate are:

1. Temperature range: 150° to 590°C
2. The speed of stirrer: 100 to 1200 rpm



Figure 4: Hot plate



Figure 5: Furnace

Furnace:

Furnace used in this work is Omega lux, LMF-3550. It can operate up to a maximum temperature of 1100°C.



Figure 6: Differential scanning calorimeter

Differential scanning calorimeter:

DSC was used to perform analysis and testing of nanofluid to determine thermophysical properties. DSC is a Perkin Elmer DSC7 with Thermal Analysis Controller TAC7/DX used for heating and temperature control of samples. It has two furnaces, one for the reference and the sample. Reference furnace always has an empty pan in it. The DSC measures the difference of heat flow between the two pans.

Scanning electron microscope (SEM):

SEM is used to understand the surface characteristics and the microstructure of the molten salt along with the nanoparticles.



Figure 7: Scanning electron microscope

2.3 Synthesis of Molten Salt with Nanoparticles

The method used to prepare the nanoparticle-based molten salt is adopted by Lu and Huang [13]. The nanofluids were synthesized by introducing various concentrations of the titanium oxide nanoparticles into the molten salt consisting of different compositions of sodium nitrate and potassium nitrate such as 30-wt.% NaNO_3 and 70-wt.% KNO_3 ; 40-wt.% NaNO_3 and 60-wt.% KNO_3 ; 50-wt.% NaNO_3 and 50-wt.% KNO_3 ; 60-wt.% NaNO_3 and 40-wt.% KNO_3 and

70-wt.% NaNO_3 and 30-wt.% KNO_3 . Initially different concentrations of the titanium oxide nanoparticles are measured by volume fractions. There are four different concentrations of the samples prepared they are 0%, 1%, 5% and 10%. Then these %volume fractions are converted into % mass fractions using a MATLAB code based on simple density calculations. The total mass of each sample prepared is 4 g. The Deionized water is added to the beaker in 1:100 ratio. Then this mixture is sonicated using the sonicator for about 100 minutes to get a well-mixed solution. This solution is then heated on the hot plate at 180°C for about 1 hour till the water in the mixture is totally evaporated. A magnetic stirrer is used while heating on the hot plate to prevent nanoparticle agglomeration. As most of this salt mixtures melt around the temperature range of 220°C - 250°C , this salt mixture is then kept in the furnace at 300°C for 1 hour to accomplish proper melting of mixture. Then this salt is transferred into vials. Then a sample of about 30mg (ASTM Standard) is taken into Aluminum pans for testing on the DSC. And the surface characterization is done using the Joel JSM -7500 F Scanning Electron Microscopy(SEM)

Thermal characterization of the molten salt is done by using the DSC to find the properties like specific heat, melting point, freezing point and latent heat of fusion. Then the heat capacity calculations are done using the heat flow of empty pan, reference pan and the sample pan. The program used for the DSC is initially heating from 120°C to 300°C at $20^\circ\text{C}/\text{min}$, then holding for 2.0 min at 300.00°C and then cooling from 300°C to 120°C at $20^\circ\text{C}/\text{min}$. then repeating the above three steps for three times. This repetition is to get the results accurately. The program explained above is used for two empty pans loaded in DSC.

The schematic sketch of the DSC program is shown in Figure 8

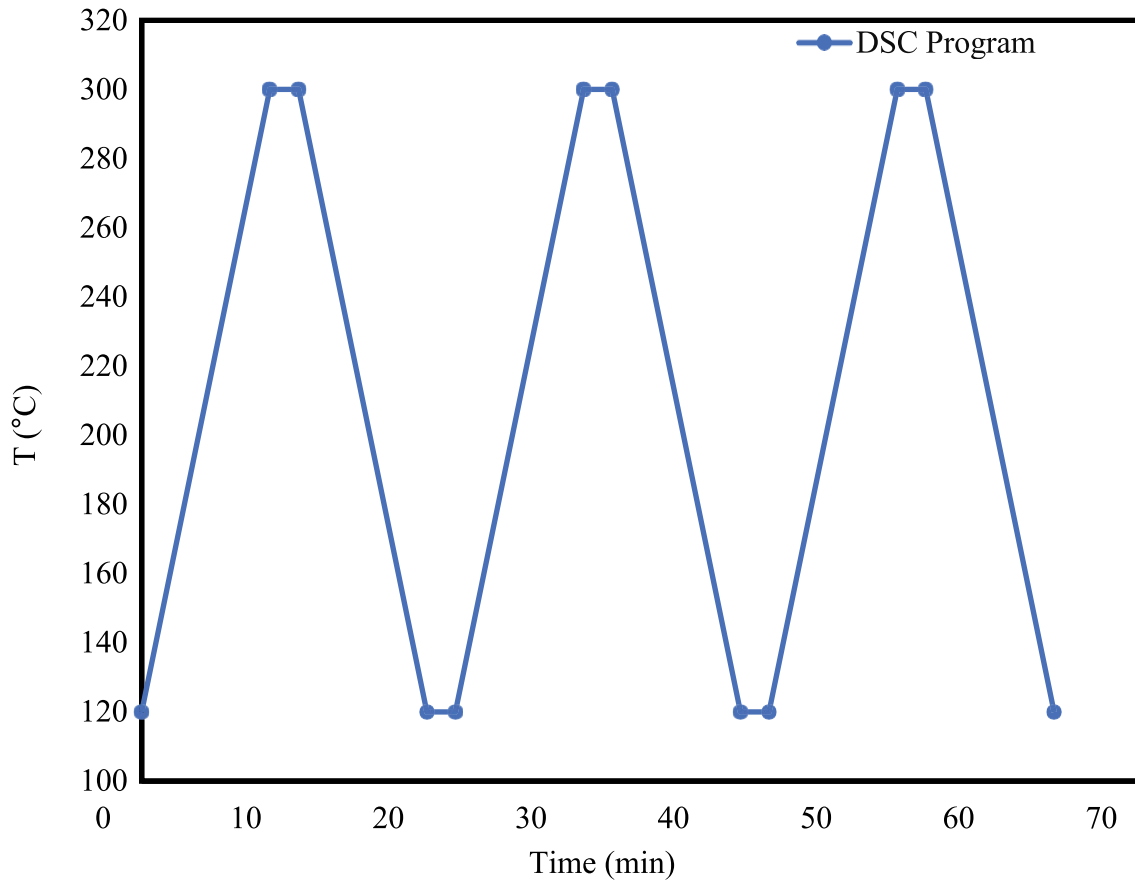


Figure 8: DSC program

The baseline heat flow with respect to temperature change is observed during this run and denoted by Q_0 which is shown in Figure 9 and the second step is to get the heat flow of the reference material which is denoted by Q_{ref} . The masses of all the pans, reference material and sample are measured using the analytical balance. The mass of the sample and reference material is about 30mg (ASTM Standard). Specific heat of the reference material $C_{p,ref}$ (Indium) is 0.262 J/g°C. The heat flow for the samples are measured as Q_{sample} .

The specific heat of the sample is measured by using the below formula which is adopted from

O'Hanley[16]

$$C_{p_{\text{sample}}} = \frac{Q_{\text{sample}} - Q_0}{Q_{\text{ref}} - Q_0} * \frac{m_{\text{ref}}}{m_{\text{sample}}} * C_{p_{\text{ref}}}$$

where,

$C_{p_{\text{sample}}}$ = Cp value(required)

Q_{sample} , Q_{ref} = heat flow of reference material:

Indium Q_0 = heat flow of empty pan

m_{ref} and m_{sample} are masses of samples in mg

$C_{p_{\text{ref}}}$ is C_p of reference: Indium ($C_p=0.262$

J/g°C)

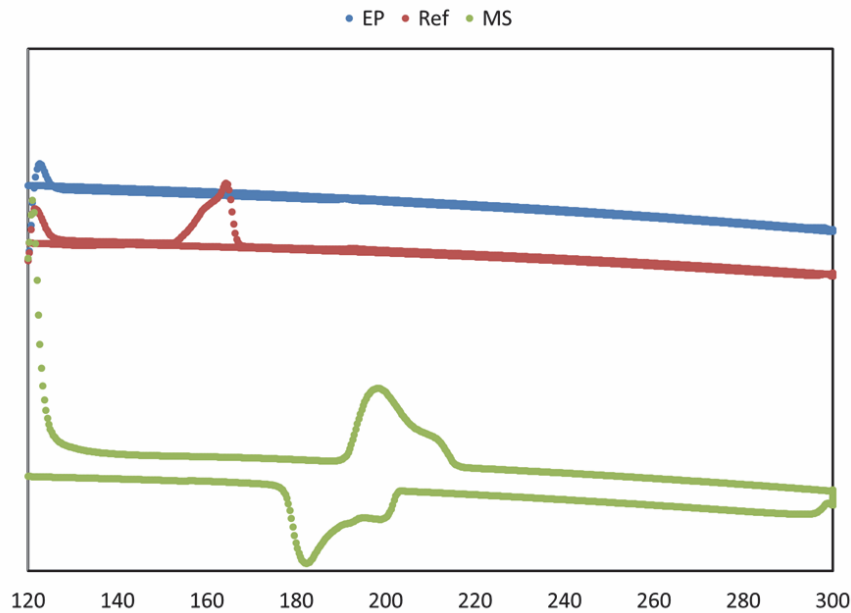


Figure 9: Sample DSC curve

3.RESULTS AND DISCUSSION

3.1 DSC Results for Melting Point

Figure.10 tells us variation of melting temperature of the molten salt with respect to mol% of NaNO_3 follows the same trend as discussed in the literature. It shows us that from 30 mol% NaNO_3 of to 70 mol% NaNO_3 the melting temperature is linearly dependent on the mol% of NaNO_3 .

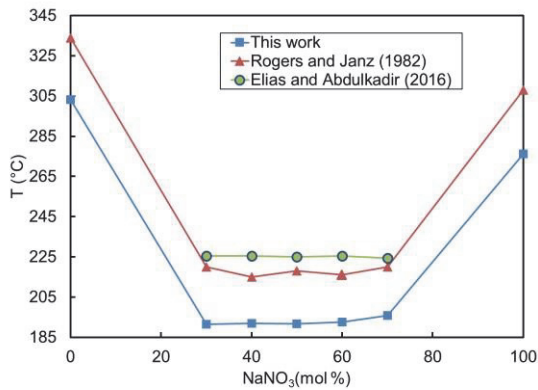


Figure 10: Melting point vs NaNO_3 mol% (with reference)

The variation of melting temperature with respect to mol% of NaNO_3 as a function of TiO_2 is shown in Figure 11 which tells us that there are set of phases of a single solid or the solid solution created. This makes the molten salt to behave differently when the nanoparticles are added to it. Almost every line in the plot shows us that the melting point linearly varies with composition of molten salt as a function of TiO_2 concentration except the 10% TiO_2 which varies parabolically

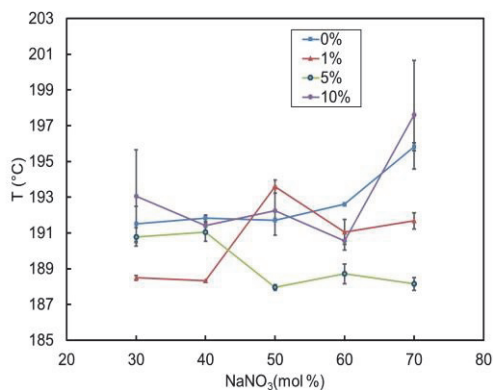


Figure 11: Melting point vs NaNO₃ mol%

The Figure 12 shows us how the melting temperature of molten salt varies with TiO₂ concentration as a function of mol% of NaNO₃ which indicates that there is transition occurring in each composition either in an increasing way or decreasing way. It also indicates that the 30-70 and 40-60 compositions enhanced the melting point at 1% TiO₂ by 4° C, whereas 70-30,60-40 and 50-50 enhance melting point by 8,4 and 3°C, all at 5% TiO₂ respectively.

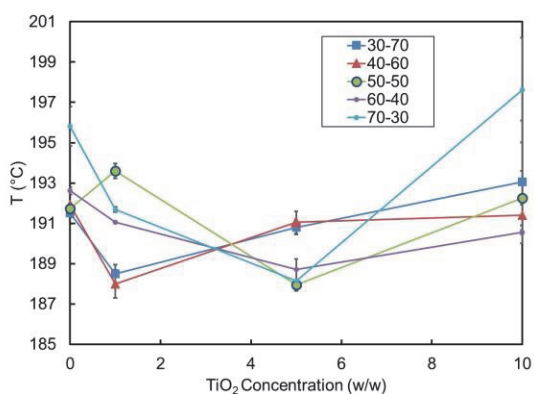


Figure 12: Melting point vs TiO₂ concentration

3.2 DSC Results for Latent Heat of Fusion

Figure 13 Reveals the variation of enthalpy with respect to mol % of NaNO_3 which tells us that the latent heat of fusion curve is linear as discussed in the literature. The shift down in this work is due to the error in the DSC equipment.

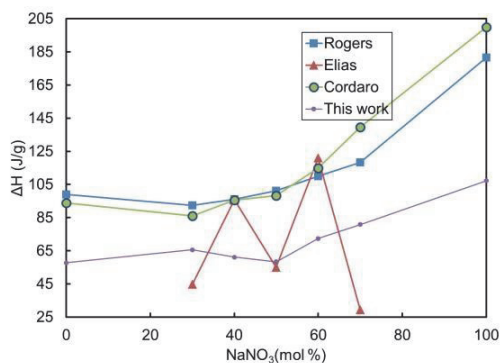


Figure 13: Enthalpy vs NaNO_3 (with reference)

Figure 14 tells us how the enthalpy varies with respect to mol % NaNO_3 as a function of TiO_2 concentration, reveals that adding nanoparticles makes it easy to change phase. But once melting begins crystal structure has nothing to do, whereas the amount of nanoparticle makes difference. Each line in the graph tells us there is an increasing trend of enthalpy with respect to mol % of NaNO_3 .

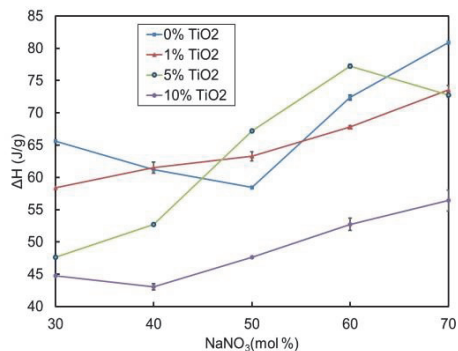


Figure 14: Enthalpy vs NaNO_3 mol%

Figure 15 tells us that the variation of enthalpy with respect to TiO_2 concentration as a function of mol % of NaNO_3 , which reveals that each latent heat of fusion curve has a peak at 5% TiO_2 . But the 30-70 and 40-60 has the decreasing trend whereas the other three has the increasing trend overall.

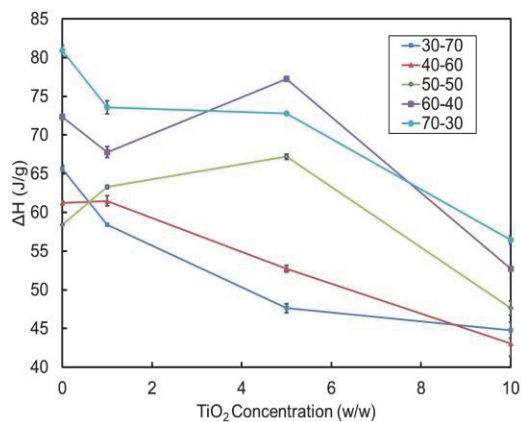


Figure 15: Enthalpy vs TiO_2 concentration

3.3 DSC Results for Specific Heat

Figure 16 tells us how the specific heat varies with respect to mol % NaNO_3 as a function of TiO_2 concentration. It clearly tells us that the nanoparticles have good impact in increasing the specific heat of molten salt in which 40-60 composition has the highest specific heat of 3.4 KJ/Kg-K . Even 5% TiO_2 has enhanced the specific heat.

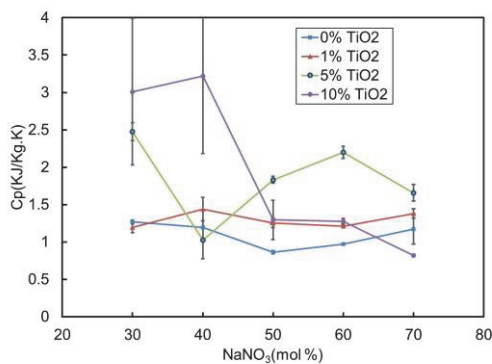


Figure 16: Specific Heat vs NaNO_3 mol%

Figure 17 tells us that the variation of specific heat with respect to TiO_2 concentration as a function of mol % of NaNO_3 , in which 30-70 and 40-60 have the highest specific heat at 10% of TiO_2 .

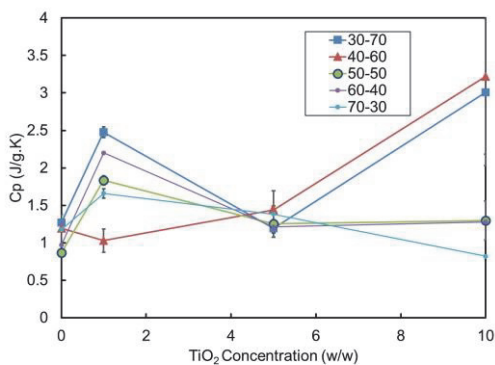


Figure 17: Specific Heat vs TiO_2 concentration

3.4 DSC Curves Heating Curves

Figures 18-22 reveals that how the DSC heating curves look for different compositions of molten salt as a function of TiO₂ nanoparticle concentrations. As we go from right to left, each graph indicates the phase change from solid to liquid. The area of the hump gives us the enthalpy. The shape of the hump purely depends on the crystal structure of molten salt before the phase transition.

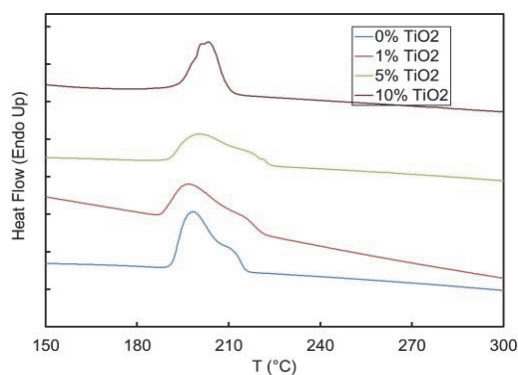


Figure 18: 30-70 heating

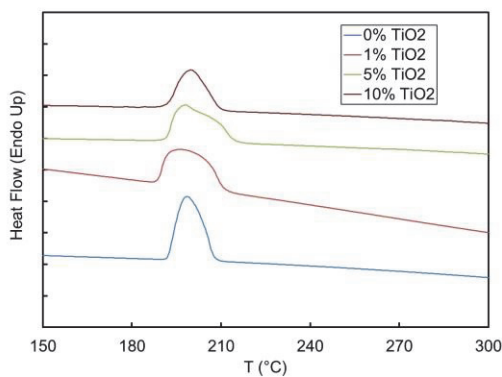


Figure 19: 40-60 heating

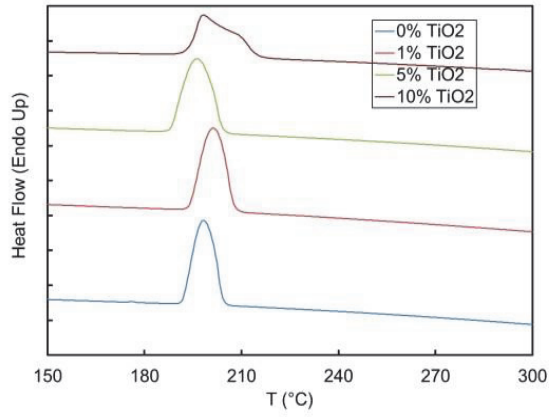


Figure 20: 50-50 heating

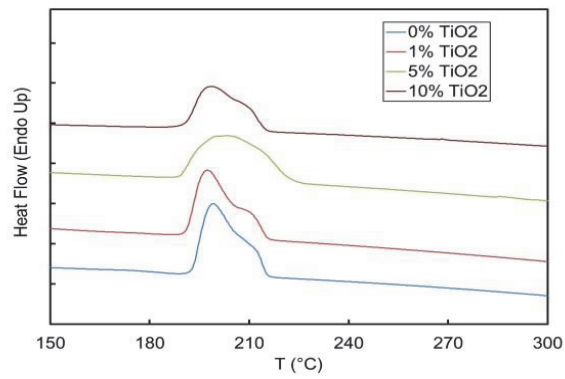


Figure 21: 60-40 heating

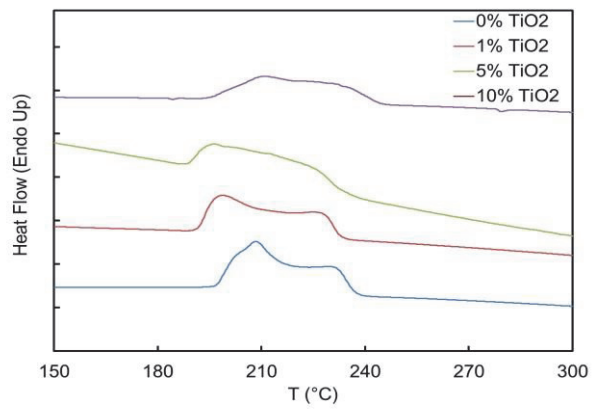


Figure 22: 70-30 heating

Cooling Curves

Figures.23-27 reveal that how the DSC cooling curves look for different compositions of molten salt as a function of TiO₂ nanoparticle concentrations.

As we go from left to right, each graph indicates the phase change from liquid to solid. The area of the hump gives us the enthalpy. The shape of the hump purely depends on the crystal structure of molten salt which is going to form after the phase transition.

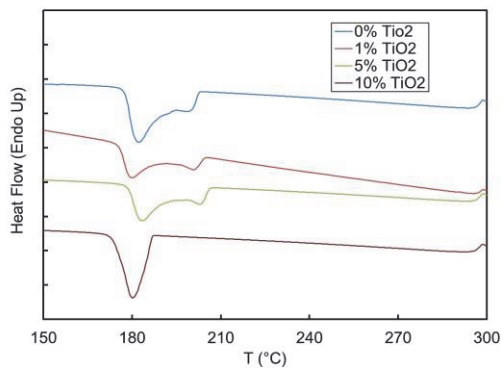


Figure 23: 30-70 cooling

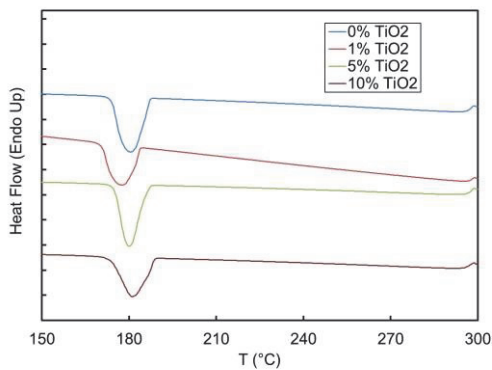


Figure 24: 40-60 cooling

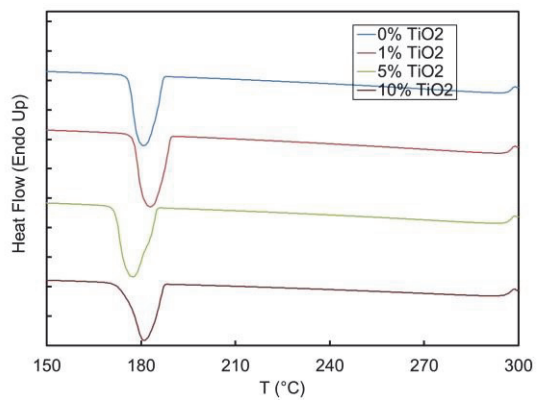


Figure 25: 50-50 cooling

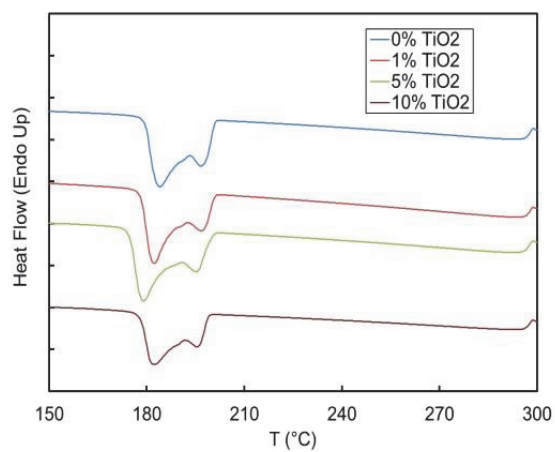


Figure 26: 60-40 cooling

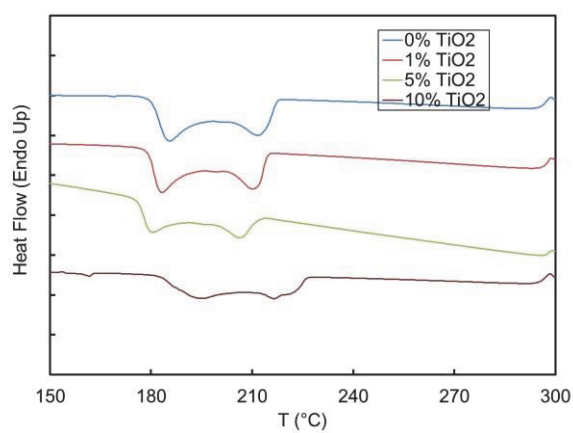


Figure 27: 70-30 cooling

3.5 Scanning Electron Microscope Images and Discussion:

Figures 28 and 29 are the scanning electron microscope images of 60-40 &50-50 composition of molten salt with 5% of TiO₂ nanoparticles.

The Figure 28 has the magnification of 1700 whereas the Figure 29 has 8500 magnifications. Figure 28 clearly reveals that the molten salt and nanoparticles are not thoroughly mixed where as in the Figure 29, we can see both without agglomeration. This is same with each concentration of nanoparticle and in the same way we can clearly differentiate every molten salt prepared in this work using SEM images.

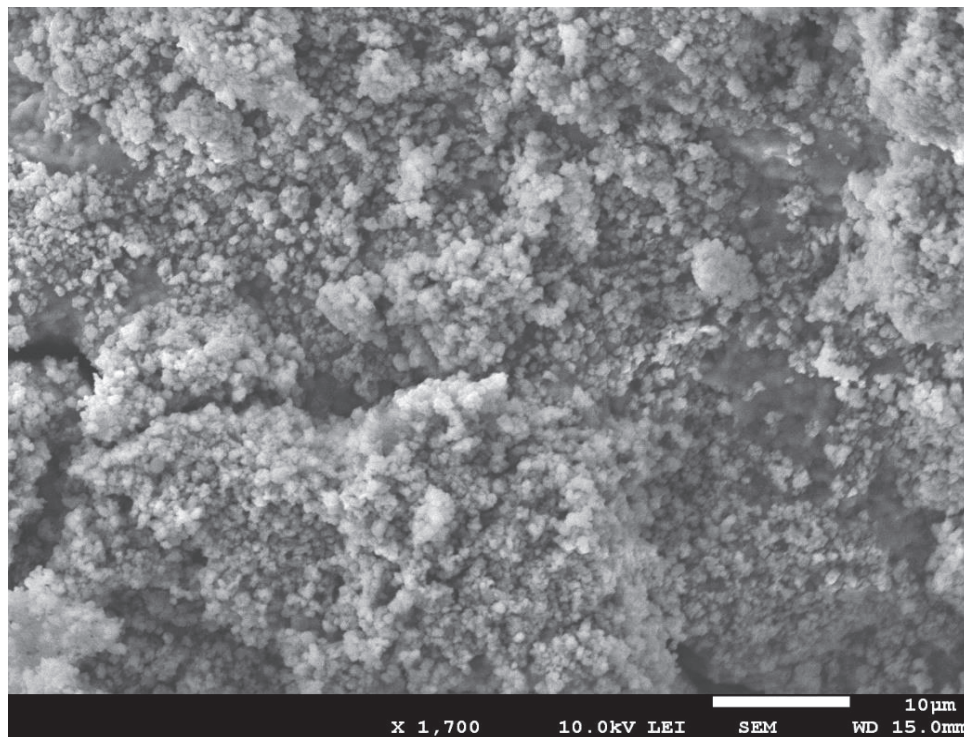


Figure 28: Molten Salt 60-40TiO₂ 5%

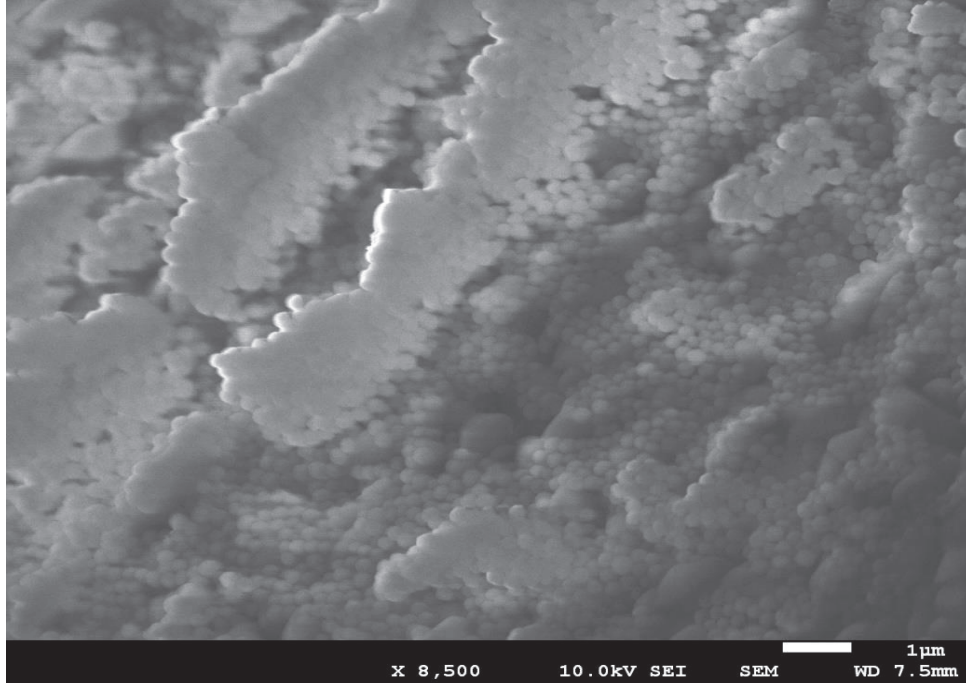


Figure 29: Molten Salt 50-50TiO₂ 5%

4.CONCLUSION

4.1 Conclusion:

When we look at the specific heat,30-70 and 40-60 compositions give us better performance when 10% nanoparticles are added to it. When we look at the latent heat of fusion, 50-50, 60-40 and 70- 30 give us the better results when they are doped with 5% of nanoparticles. When we look at the melting point, 30-70 and 40-60 give us the better results at 1% of nanoparticles and the other three give better results at 5% of nanoparticles.

4.2 Future Work:

This work can be further carried out by conducting the XRD analysis and it is preferable to do the other compositions like 20-80|10-90|90-10|80-20 with addition of nanoparticles and the pure salts can be tested by adding nanoparticles to it.

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APPENDIX

A1. MATLAB code for conversion of % by volume to % by weight for a

mixture. clear all;

$C_v = [0.01, 0.05, 0.1];$ %Volume

concentration% $D_b = 0.83;$ %Density of Base

fluid g/cm³%

$D_p = 4.23;$ %Density of Nano particle g/cm³%

$D_n = (D_p * C_v) - (D_b * C_v) + D_b;$ %Density of Nano fluid%

$A_{Dp} = 4.23 * \text{ones}(1,12);$

$C_m = (A_{Dp} ./ D_n) .* C_v;$ %mass concentration%

$PC_m = C_m .* 100;$ %mass concentration in '%'

%

$PC_v = C_v .* 100;$ %volume concentration in '%'