Supplementary Information For

Predicting Solid-Solid Phase Transition of Quaternary Ammonium Salts by Machine Learning

Xiao Li [a,b,c], Ruonan Li [d], Luoming Hu [d], Lianjing Mao [a,b,c], Tianyu Zheng [a,b,c], Chunsen Ye [a,b,c], Wei Sun [a,b], Pengrui Zhang [a,b], Jinhe Sun [a,b*]

a *Key Laboratory of Green and High-end Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China*

b *Qinghai Engineering and Technology Research Center of Comprehensive Utilization of Salt Lake Resources, Xining 810008, China*

c *University of Chinese Academy of Sciences, Beijing 100049, China*

d *Dalian University of Technology, Dalian 116024, China*

Abstract: Solid-solid phase change is the key to energy storage technology. As important solid-solid phase change materials (SS-PCMs), quaternary ammonium salts, provide a variety of options for the development of SS-PCMs with different properties due to their diverse molecular structures. However, the relationship between the molecular structure of quaternary ammonium salts and their solid-solid phase change behavior is unclear. This study investigates the effect of three structural factors: type of anion, length and number of alkyl chains on the solid-solid phase transition behavior of quaternary ammonium salts. It is found that the ability of quaternary ammonium salts to undergo solid-solid phase transition is not determined by a single structural factor, but is influenced by a synergistic effect of multiple factors, which makes the prediction of their phase-transition behavior extremely difficult In order to accurately predict the solid-solid phase transition behavior of quaternary ammonium salts, a prediction model based on a machine learning algorithm was constructed. Three different machine learning models: Support Vector Machine (SVM), Random Forest (RF) and Deep Neural Network (DNN) were used to analyze the dataset. By comparing the performances of the models, SVM was finally identified as the optimal solution with an accuracy of 0.9524 in predicting whether solid-solid

phase transition can occur in quaternary ammonium salts. This study provides an efficient and accurate method to predict whether unknown quaternary ammonium salts possess solid-solid phase change capability. This is valuable in guiding the design and development of new high-performance SS-PCMs.

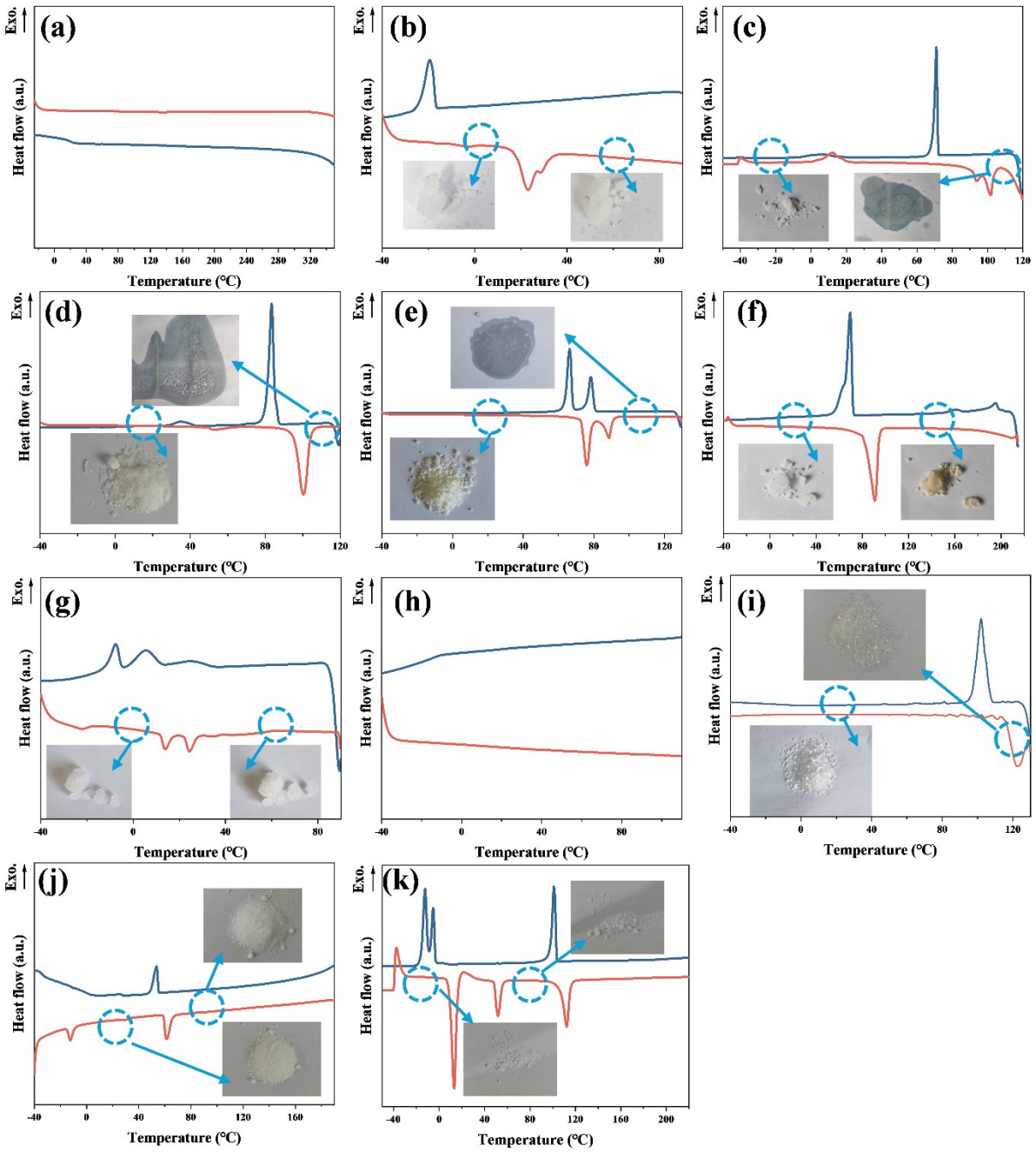

Fig. S1. DSC curves: (a) Tetramethyl ammonium bromide. (b) Tetraethyl ammonium bromide. (c) Tetrabutyl ammonium bromide. (d) Tetraoctyl ammonium bromide. (e) Tetra(decyl) ammonium bromide. (f) Octyl trimethyl ammonium bromide. (g) Dioctyl dimethyl ammonium bromide. (h) Tetrabutyl ammonium chloride. (i) Tetrabutyl ammonium iodide. (j) Tetrabutyl ammonium perchlorate. (k) Tetrabutyl ammonium trifluoromethane sulfonate. The inserted figures showed the physical figures of quaternary ammonium salts before and after the phase

transition

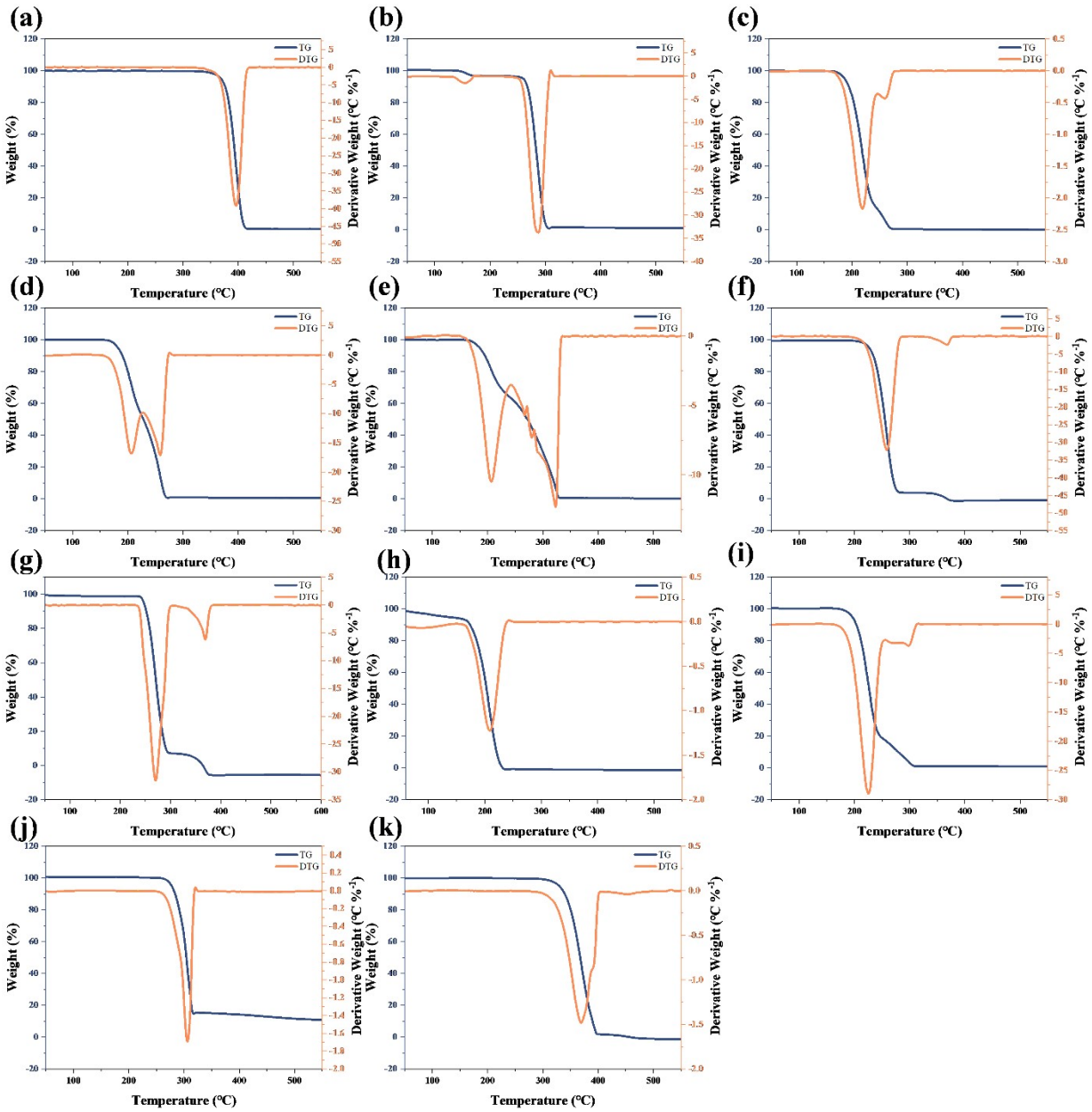

Fig. S2. TG-DTG curves: (a) Tetramethyl ammonium bromide. (b) Tetraethyl ammonium bromide. (c) Tetrabutyl ammonium bromide. (d) Tetraoctyl ammonium bromide. (e) Tetra(decyl) ammonium bromide. (f) Octyl trimethyl ammonium bromide. (g) Dioctyl dimethyl ammonium bromide. (h) Tetrabutyl ammonium chloride. (i) Tetrabutyl ammonium iodide. (j) Tetrabutyl ammonium perchlorate. (k) Tetrabutyl ammonium trifluoromethane sulfonate.

Table S1 Solid-solid phase transition behavior of different quaternary ammonium salts

Samples	Solid-Solid phase transition
$C_{11}H_{21}NO_8$	No
$C_7H_5O_3C_5H_{14}NO$	No
$C_{16}H_{38}NO_4P$	No
$C_6H_{16}ClNO$	Yes
$C_7H_{16}ClNO_2$	Yes
$C_6H_{16}ClNO_2$	No
$C_5H_{15}NO_4PCl$	No
$C_6H_{16}ClNO_2$	Yes
$C_{12}H_{28}ClN$	No
$C_{16}H_{36}IN$	Yes
$C_{16}H_{36}N_2NO_3$	No
$C_{18}H_{39}NO_2$	No
$C_{16}H_{36}NClO_4$	Yes
$C_{18}H_{36}F_3NO$	Yes
$C_{16}H_{36}BrN$	No
$C_8H_{20}BrN$	Yes
$C_{16}H_{36}ClN$	No
$C_{32}H_{68}BrN$	No
$C_{34}H_{72}BrN$	Yes
$C_{18}H_{40}BrN$	Yes
$C_{26}H_{56}BrN$	No
$C_9H_{20}INO_2$	No
$C_{16}H_{38}I_2N_2$	Yes
$C_{38}H_{80}IN$	No
$C_9H_{20}INOS$	No
$C_{25}H_{54}ClN$	No
$C_6H_{16}BrN$	Yes
$C_{30}H_{64}BrN$	Yes
$C_{40}H_{84}BrN$	No

$C_{21}H_{46}ClN$	No
$C_6H_{15}Cl_2NO$	No
$C_6H_{15}Cl_2NO$	No
$C_7H_{16}Cl_2NO3$	Yes
$C_5H_{14}ON^+$	No
$C_5H_{14}ONF$	No
$C_5H_{14}BrNO$	Yes
$C_5H_{14}ClNO$	Yes
$C_5H_{14}INO$	Yes
$C_{13}H_{30}BrN$	Yes
$C_{15}H_{34}BrN$	Yes
$C_{17}H_{38}BrN$	Yes
$C_{19}H_{42}BrN$	Yes
$C_{21}H_{46}BrN$	Yes
$C_8H_{17}N(CH_3)_3Cl$	Yes
$C_9H_{19}N(CH_3)_3Cl$	Yes
$C_{10}H_{21}N(CH_3)_3Cl$	Yes
$C_{11}H_{23}N(CH_3)_3Cl$	Yes
$C_{12}H_{25}N(CH_3)_3Cl$	Yes
$C_{13}H_{27}N(CH_3)_3Cl$	Yes
$C_{14}H_{29}N(CH_3)_3Cl$	Yes
DC_8NO_3	Yes
$DC_8H_2PO_4$	Yes
DC_8Cl	Yes
DC_8Br	Yes
DC_8I	Yes
DC_8HSO_4	Yes
DC_8ClO_3	Yes
DC_8ClO_4	Yes
$DC_{10}NO_3$	Yes
$DC_{10}Cl$	Yes
$DC_{10}Br$	Yes

$DC_{10}ClO_3$	Yes
$DC_{10}H_2PO_4$	Yes
$DC_{12}NO_3$	Yes
$DC_{12}F$	No
DC_8F	No
$DC_{12}Cl$	Yes
$DC_{12}Br$	Yes
$DC_{12}I$	Yes
$DC_{12}HSO_4$	Yes
$DC_{12}ClO_3$	Yes
$DC_{12}ClO_4$	Yes
$DC_{12}H_2PO_4$	Yes
$DC_{12}Ac$	No
$DC_{18}NO_3$	Yes
$DC_{18}F$	No
$DC_{18}Cl$	Yes
$DC_{18}Br$	Yes
$DC_{18}I$	Yes
$DC_{18}HSO_4$	Yes
$DC_{18}ClO_3$	Yes
$DC_{18}ClO_4$	Yes
$CH_3(CH_2)N^+(CH_3)_2CH_2CH_3Br^-$	Yes
$CH_3(CH_2)N^+(CH_3)_2CH_2CH_2CH_3Br^-$	Yes
$CH_3(CH_2)N^+(CH_3)_2CH_2CH_2OHBr^-$	Yes
$CH_3(CH_2)N^+(CH_3)_2CH_2CH_2CH_2OHBr^-$	Yes
$CH_3(CH_2)N^+(CH_3)_2CH_2COOHBr^-$	Yes
$CH_3(CH_2)N^+(CH_3)_2CH_2CH_2COOHBr^-$	Yes
$CH_3(CH_2)N^+(CH_3)_2CH_2CH_2CH_2CNBr^-$	Yes
$CH_3(CH_2)N^+(CH_3)_2CH_2COOCH_3Br^-$	Yes
$CH_3(CH_2)N^+(CH_3)_2CH_2COOCH_2CH_2OHBr^-$	Yes
$CH_3NH_3NO_3$	Yes
$C_{18}H_{37}NH_3Cl$	Yes

$C_{22}H_{45}NH_3Cl$	Yes
$C_{10}H_{21}NH_3Br$	Yes
$C_{12}H_{25}NH_3Br$	Yes
$C_{14}H_{29}NH_3Br$	Yes
$C_{18}H_{37}NH_3Br$	Yes
$C_{22}H_{45}NH_3Br$	Yes
$C_{10}H_{21}NH_3I$	Yes
$C_{12}H_{25}NH_3I$	Yes
$C_{14}H_{29}NH_3I$	Yes
$C_{18}H_{37}NH_3I$	Yes
$C_{22}H_{45}NH_3I$	Yes
$(C_{10}H_{21}NH_3)_2MnCl_4$	Yes
$(C_{10}H_{21}NH_3)_2CuCl_4$	Yes
$(C_{10}H_{21}NH_3)_2CoCl_4$	Yes
$(C_{10}H_{21}NH_3)_2FeCl_4$	Yes
$(C_{10}H_{21}NH_3)_2HgCl_4$	Yes
$(C_{10}H_{21}NH_3)_2ZnCl_4$	Yes
$(C_{11}H_{23}NH_3)_2MnCl_4$	Yes
$(C_{11}H_{23}NH_3)_2CuCl_4$	Yes
$(C_{11}H_{23}NH_3)_2CoCl_4$	Yes
$(C_{11}H_{23}NH_3)_2FeCl_4$	Yes
$(C_{11}H_{23}NH_3)_2HgCl_4$	Yes
$(C_{11}H_{23}NH_3)_2ZnCl_4$	Yes
$(C_{12}H_{25}NH_3)_2MnCl_4$	Yes
$(C_{12}H_{25}NH_3)_2CuCl_4$	Yes
$(C_{12}H_{25}NH_3)_2CoCl_4$	Yes
$(C_{12}H_{25}NH_3)_2\ FeCl_4$	Yes
$(C_{12}H_{25}NH_3)_2\ HgCl_4$	Yes
$(C_{12}H_{25}NH_3)_2ZnCl_4$	Yes
$(C_{13}H_{27}NH_3)_2\ MnCl_4$	Yes
$(C_{13}H_{27}NH_3)_2CuCl_4$	Yes
$(C_{13}H_{27}NH_3)_2CoCl_4$	Yes

$(C_{13}H_{27}NH_3)_2\ FeCl_4$	Yes
$(C_{13}H_{27}NH_3)_2\ HgCl_4$	Yes
$(C_{13}H_{27}NH_3)_2ZnCl_4$	Yes
$(C_{14}H_{29}NH_3)_2MnCl_4$	Yes
$(C_{14}H_{29}NH_3)_2CuCl_4$	Yes
$(C_{14}H_{29}NH_3)_2CoCl_4$	Yes
$(C_{14}H_{29}NH_3)_2\ FeCl_4$	Yes
$(C_{14}H_{29}NH_3)_2\ HgCl_4$	Yes
$(C_{14}H_{29}NH_3)_2ZnCl_4$	Yes
$(C_{15}H_{31}NH_3)_2MnCl_4$	Yes
$(C_{15}H_{31}NH_3)_2CuCl_4$	Yes
$(C_{15}H_{31}NH_3)_2CoCl_4$	Yes
$(C_{15}H_{31}NH_3)_2\ FeCl_4$	Yes
$(C_{15}H_{31}NH_3)_2\ HgCl_4$	Yes
$(C_{15}H_{31}NH_3)_2ZnCl_4$	Yes
$(C_{16}H_{33}NH_3)_2MnCl_4$	Yes
$(C_{16}H_{33}NH_3)_2CuCl_4$	Yes
$(C_{16}H_{33}NH_3)_2CoCl_4$	Yes
$(C_{16}H_{33}NH_3)_2\ FeCl_4$	Yes
$(C_{16}H_{33}NH_3)_2\ HgCl_4$	Yes
$(C_{16}H_{33}NH_3)_2ZnCl_4$	Yes
$(NH_4)Al(SO_4)_2\cdot 12H_2O$	No