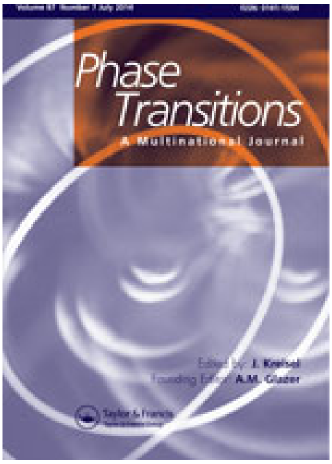
This article was downloaded by: [University of Phoenix]
On: 30 January 2015, At: 01:34
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Click for updates

Phase Transitions: A Multinational Journal
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpht20

Phase transitions and energy storage properties of some compositions in the (1-x)Li_2SO_4-xNa_2SO_4 system

Bo Chen[ab], Tian-Hui Liu[ab], Huan Jiao[a] & Xi-Ping Jing[b]
[a] Key Laboratory of Macromolecular Science of Shaanxi Province, College of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, People's Republic of China
[b] Beijing National Laboratory for Molecular Sciences, The State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, People's Republic of China

Published online: 31 Jan 2014.

To cite this article: Bo Chen, Tian-Hui Liu, Huan Jiao & Xi-Ping Jing (2014) Phase transitions and energy storage properties of some compositions in the (1-x)Li_2SO_4-xNa_2SO_4 system, Phase Transitions: A Multinational Journal, 87:7, 629-640, DOI: 10.1080/01411594.2013.873436

To link to this article: http://dx.doi.org/10.1080/01411594.2013.873436

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Phase Transitions, 2014
Vol. 87, No. 7, 629–640, http://dx.doi.org/10.1080/01411594.2013.873436

Phase transitions and energy storage properties of some compositions in the $(1-x)Li_2SO_4$–xNa_2SO_4 system

Bo Chen[a,b†], Tian-Hui Liu[a,b†], Huan Jiao[a] and Xi-Ping Jing[b*]

[a] *Key Laboratory of Macromolecular Science of Shaanxi Province, College of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, People's Republic of China;* [b] *Beijing National Laboratory for Molecular Sciences, The State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing, People's Republic of China*

(*Received 6 November 2013; accepted 4 December 2013*)

In the binary system $(1-x)Li_2SO_4$–xNa_2SO_4, the solid–solid phase transitions and energy storage properties of Li_2SO_4, Na_2SO_4, the binary compound $LiNaSO_4$ and two eutectoids (E_1: $0.726Li_2SO_4$–$0.274Na_2SO_4$; E_2: $0.03Li_2SO_4$–$0.97Na_2SO_4$) were investigated by X-ray diffraction and differential scanning calorimetry. Li_2SO_4 has a solid–solid phase transition at 578 °C with the transition enthalpy 252 J g^{-1}. The binary compound $LiNaSO_4$ gives a slightly lower enthalpy value, 214 J g^{-1} and its transition temperature is clearly reduced to 514 °C. The transition enthalpy of the eutectoid E_1 is maintained to 177 J g^{-1} and its transition temperature is further reduced to 474 °C. Li_2SO_4, $LiNaSO_4$ and the eutectoid E_1 are applicable phase transition materials because of their large transition enthalpies. The enthalpies of Na_2SO_4 and the eutectoid E_2 are not very high (~45 J g^{-1}), but their transition temperatures are quite low (~250 °C); thus their transition properties may be applied at such low temperatures.

Keywords: phase transition; energy storage; $(1-x)Li_2SO_4$–xNa_2SO_4 system; eutectoid

1. Introduction

With the development of the global economy, demand for energy has increased rapidly. Consequently the energy crisis has been a serious problem for the human society. Inventing all possible high-techs to improve energy utilization is of great significance for sustainable development. Phase transition materials are one kind of energy materials, which can be used to reserve thermal energy by their large transition enthalpies.[1] The phase transition materials are widely applied in the thermal storage of solar energy,[2] passive storage in bioclimatic building,[3] clothing [4] and so on. In the present work, solid–solid phase transition materials are considered due to their advantages over solid–liquid phase transition materials, such as less stringent requirements for containers and more flexible designing.[5] Na_2MoO_4 is one of the solid–solid phase transition materials. Within the temperature range 450–650 °C, this material undergoes three solid–solid phase transitions with total transition enthalpy $\Delta H = 201$ J g^{-1}.[6] By screening several tens of inorganic compounds, we found that Li_2SO_4 and Na_2SO_4 have the solid–solid phase transitions at

---

[†] Joint first authors.
*Corresponding author. Email: xpjing@pku.edu.cn

578 and 243 °C with relatively large transition enthalpies of 252 and 49 J g^{-1}, respectively.

For different applications, the phase transition materials with various transition temperatures are demanded. One approach to change the transition temperature for a given material is to modify its composition in the solid solution range; for example, by replacing WO_4^{2-} for MoO_4^{2-} in the binary system $Na_2Mo_{1-x}W_xO_4$, the transition temperature increased, while by replacing SO_4^{2-} for MoO_4^{2-} in the binary system $Na_2Mo_{1-x}S_xO_4$, the transition temperature decreased. In the $Na_2Mo_{1-x}W_xO_4$ and $Na_2Mo_{1-x}S_xO_4$ systems, the transition enthalpies were reasonably maintained.[7] The phase diagram of $(1-x)Li_2SO_4$–xNa_2SO_4 system was first determined by Nacken [8] and revised later by other authors,[9–11] which is represented in Figure 1. In this system, one binary compound ($LiNaSO_4$) and two eutectoids (E_1: $0.726Li_2SO_4$–$0.274Na_2SO_4$; E_2: $0.03Li_2SO_4$–$0.97Na_2SO_4$) are formed. These three compositions show different solid–solid phase transition temperatures. If these three compositions have large transition enthalpies, they may be applied as new phase transition materials. In this work, the solid–solid transition behaviors of Li_2SO_4, Na_2SO_4, $LiNaSO_4$ as well as two eutectoids are investigated. Additionally, the structure changes during the phase transitions for the three compounds were discussed.

2. Experimental

Li_2SO_4 (AR) ('AR' stands for 'analytical reagent') and Na_2SO_4 (AR) were used as raw materials, which were dried in an oven at 150 °C for 2 h to remove absorbed H_2O. Initially the binary compound $LiNaSO_4$ were prepared by using conventional solid reactions.

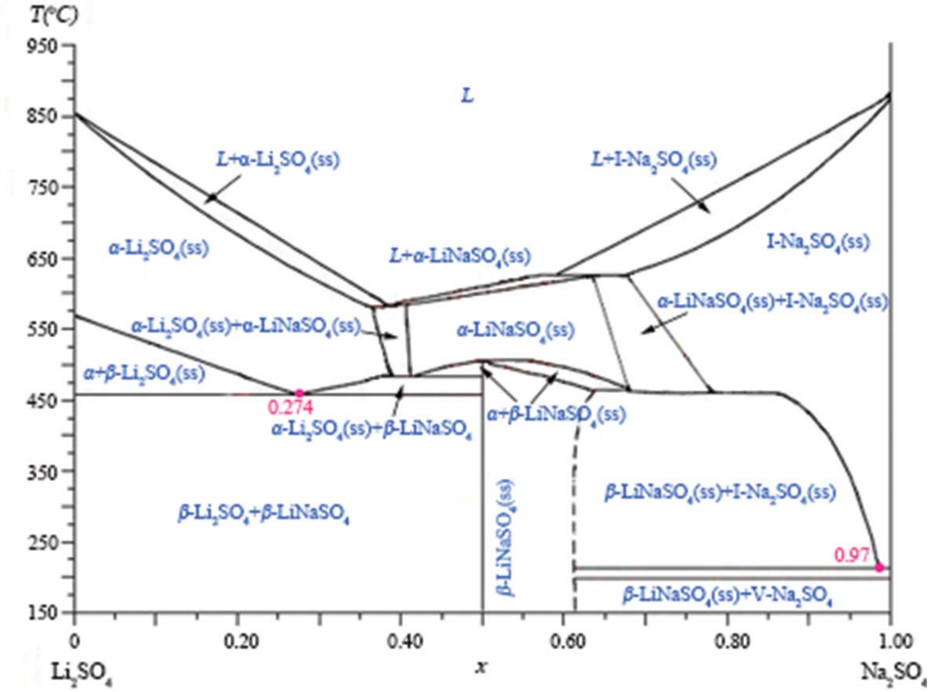


Figure 1. Phase diagram of the binary system $(1-x)Li_2SO_4$–xNa_2SO_4, [8] where 'ss' is the abbreviation of 'solid solution'.

The raw materials Li_2SO_4 and Na_2SO_4 were weighed in 1:1 (mole ratio) and then thoroughly mixed by grinding using an agate mortar and pestle. The mixture was calcined at 550 °C for 12 h in alumina crucibles. After cooling and re-grindings, the powder samples of $LiNaSO_4$ were obtained. The two eutectoid samples were prepared by mixing Li_2SO_4/$LiNaSO_4$ (for E_1) and $LiNaSO_4$/Na_2SO_4 (for E_2) in appropriate amounts and the two samples were also thoroughly ground.

In this work, it was found that the thermal history affects the structure of Na_2SO_4 at room temperature. To understand this effect, two samples of Na_2SO_4(cr) ('cr' stands for 'crystallized') and Na_2SO_4(co) ('co' stands for 'cooling') were prepared. The raw material Na_2SO_4 ($\sim$1 g) was dissolved in $\sim$30 mL H_2O. After evaporation and drying on a hot plate, Na_2SO_4(cr) was crystallized. Na_2SO_4(co) was acquired by heating Na_2SO_4 ($\sim$1 g, raw material) at 300 °C for 30 min, and then by cooling to room temperature.

The sample phases were analyzed by using a Rigaku D/max-2000 X-ray diffractometer (XRD) operating at 40 kV and 100 mA in the reflection mode with Cu Kα radiation ($\lambda = 1.5418$ Å). Diffraction data were collected in the 2θ range 10°–60° with a scanning rate of 6° min^{-1}. The phase transition temperatures and enthalpies of all prepared samples as well as raw materials Li_2SO_4 and Na_2SO_4 were measured by using a differential scanning calorimeter (DSC 131, Setaram instrument, France) in argon atmosphere (99.999%) with a flow rate 30 mL min^{-1}. The measurements were conducted in heating and cooling cycles with the rate 5 °C min^{-1}. The temperature and heat flow rate of the instrument are calibrated by In, Bi and Zn standards to ensure the accuracy and repeatability of data. During the measurements, the samples were placed in aluminum microcells and an empty aluminum microcell was used as reference.

3. Results and discussion

3.1. Phase characterizations

For understanding the phase transition process well, the phases of the prepared samples $LiNaSO_4$, Na_2SO_4 (raw material, abbreviated as rm), Na_2SO_4(cr) and Na_2SO_4(co) were analyzed. Figure 2 represents the XRD pattern of the binary compound $LiNaSO_4$, which

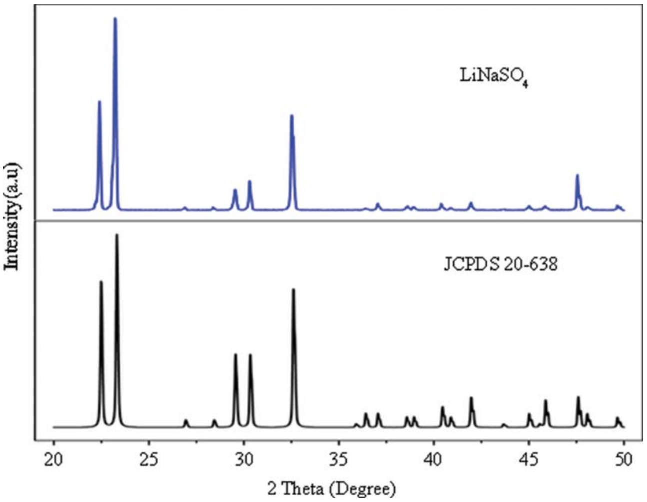


Figure 2. XRD patterns of as-prepared $LiNaSO_4$ and JCPDS file 20-638.

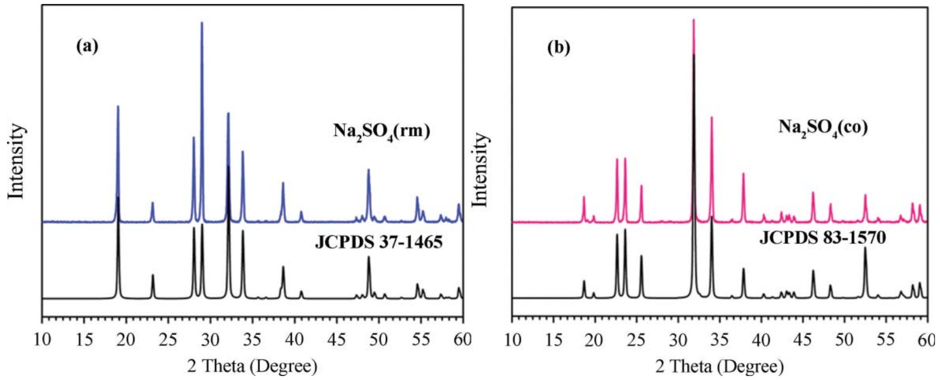


Figure 3. XRD patterns of (a) Na_2SO_4(rm), (b) Na_2SO_4(co) and related JCPDS files.

is consistent with Joint Committee on Powder Diffraction Standards (JCPDS) file 20-638 (β-$LiNaSO_4$, low temperature phase). No impurity peaks are observed in the pattern, which indicates that the obtained sample is the pure-phase β-$LiNaSO_4$. This phase has a trigonal unit cell (space group $P3_1c$) with cell parameters $a = b = 7.6190$Å, $c = 9.849$Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$.[11]

XRD patterns of Na_2SO_4(rm) and Na_2SO_4(co) were represented in Figure 3. The pattern of Na_2SO_4(rm) agrees with the JCPDS file 37-1465, indicating that Na_2SO_4(rm) has the orthorhombic unit cell (space group *Fddd*) with the cell parameters $a = 5.8582$ Å, $b = 12.2990$ Å and $c = 7.98138$ Å. This orthorhombic phase was named as Phase V in reference.[12] The pattern of Na_2SO_4(co) is the same as that of JCPDS file 83-1570, which was named as Phase III [12] and this phase also has the orthorhombic unit cell (space group *Cmcm*) with the cell parameters $a = 5.63041$ Å, $b = 9.04343$ Å and $c = 7.03771$ Å. Although the XRD patterns of both Na_2SO_4(rm) and Na_2SO_4(co) were measured at room temperature, they clearly show different structures. After being heated over the solid–solid phase transition temperature (above 239 °C), Phase V of Na_2SO_4(rm) transforms to Phase III of Na_2SO_4 (co). The pattern of Na_2SO_4(cr) (not shown) is identical to that of Na_2SO_4(rm), which means that Na_2SO_4 crystallized from aqueous solution takes the structure of Phase V and Na_2SO_4(rm) may be produced by the crystallization from aqueous solution. Up to now we have not found any way to transform Phase III to Phase V.

3.2. Phase transitions of Li_2SO_4, $LiNaSO_4$ and the eutectoid E_1

The phase transition temperatures and enthalpies of Li_2SO_4, $LiNaSO_4$ and the eutectoid E_1 ($0.726Li_2SO_4$–$0.274Na_2SO_4$) were measured by DSC. The typical DSC curves with heating and cooling cycles are represented in Figure 4. Actually, the measurements with the heating–cooling cycles were repeated several times and all the DSC curves for each sample were almost identical, which means that the phase transition characters of the materials studied are thermally stable.

The phase transition character of Li_2SO_4 was shown in Figure 4(a). In the heating process, an endothermic peak appears at 578 °C, corresponding to a solid–solid phase transition with the transition enthalpy $\Delta H = 252$ J g^{-1}, which agrees well with the reported value ($\Delta H = 28.84$ kJ mol^{-1} $= 262.3$ J g^{-1}).[13] In the cooling process, an exothermic peak appears at 571 °C with the enthalpy value $\Delta H = -247$ J g^{-1}. The absolute value of

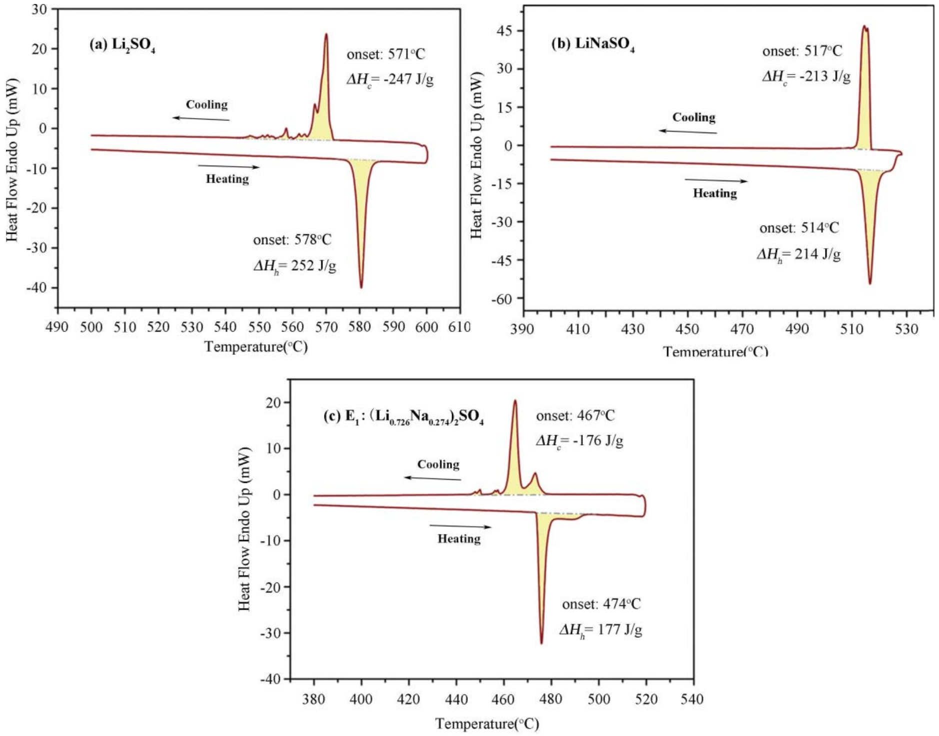


Figure 4. DSC curves of (a) Li_2SO_4, (b) $LiNaSO_4$ and (c) the eutectoid E_1.

ΔH for the cooling process is in accordance with that for the heating process, but compared with the heating process, the transition temperature has 7 °C overcooling.

The low-temperature phase of Li_2SO_4 named as β-Li_2SO_4 takes the monoclinic unit cell (space group $P12_1/a1$) with the cell parameters $a = 8.2390$ Å, $b = 4.9536$ Å, $c = 8.4737$ Å, $\beta = 107.98°$,[14] while the high-temperature phase named as α-Li_2SO_4 takes a face-centered cubic unit cell (space group $Fm\,3\,m$) with the cell parameter $a = 7.07$ Å.[15] The structures of β-Li_2SO_4 and α-Li_2SO_4 are shown in Figure 5. In the low-temperature phase, ${SO_4}^{2-}$ tetrahedron groups take tetrahedron structure in fixed direction, but in the high-temperature phase, the ${SO_4}^{2-}$ tetrahedron groups take two directions, each of which has 50% probability; thus the ${SO_4}^{2-}$ groups are represented as cubes. It is considered that in α-Li_2SO_4, the ${SO_4}^{2-}$ tetrahedron groups can rotate between two directions; thus the phase contains more inner energy, which benefits the large ΔH value of the phase transition.

$LiNaSO_4$ is considered as a fast ionic conductor that has attracted a lot of attentions.[16] In this work, the phase transition properties of $LiNaSO_4$ are mainly concerned. In the heating process, $LiNaSO_4$undergoes a solid–solid phase transition at 514 °C with the transition enthalpy $\Delta H = 214$ J g^{-1} [Figure 4(b)]. In the cooling process, the exothermic peak of the phase transition appears at 517 °C with the enthalpy value $\Delta H = -213$ J g^{-1}, which indicates that in the phase transition, almost no overcooling occurs and the absolute values of ΔH are almost identical for both of the heating and cooling processes. The ΔH value was also reported by Rojas ($\Delta H = 130$ J g^{-1}) [17] and Freiheit ($\Delta H = 20.8$ kJ mol^{-1} = 165.1 J g^{-1}).[18] The value reported in this work is larger than the above reference data. This difference possibly came from the measuring error in different labs.

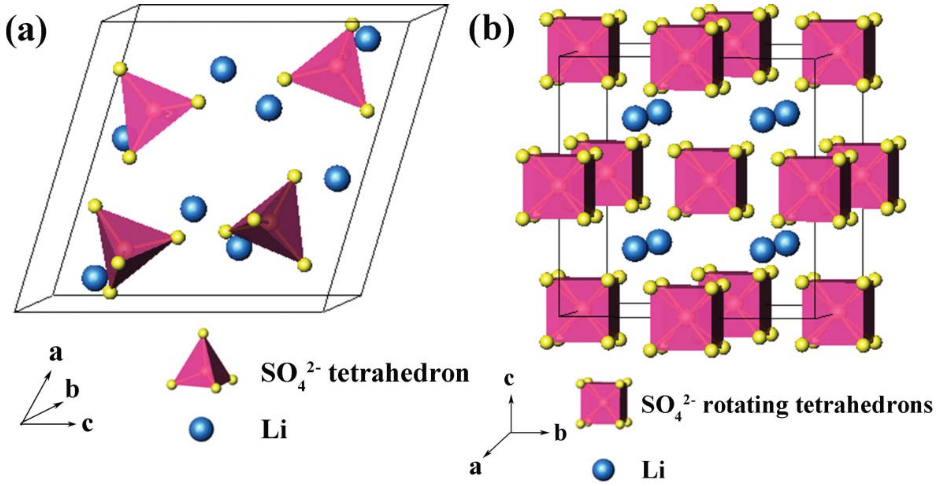


Figure 5. Structures of (a) β-Li_2SO_4 (low-temperature phase) and (b) α-Li_2SO_4 (high-temperature phase).

The structures of $LiNaSO_4$ (both high-temperature and low-temperature phases) are shown in Figure 6. The low-temperature phase has the trigonal unit cell (space group $P3_1c$) with the cell parameters $a = 7.6190$ Å and $c = 9.849$ Å,[11] and the high-temperature phase belongs to the body-centered cubic structure with the cell parameter $a = 5.77$ Å.[19] Since we do not have detailed data for the high-temperature phase, in Figure 6(b), only unit cell rather than the detailed structure is illustrated and the structure change during the phase transition cannot be well discussed. In the low-temperature phase, Li^+ or Na^{2+} takes its own site. In the high-temperature phase, it is assumed that if the balls represent the SO_4^{2-} tetrahedrons, Li^+ and Na^+ randomly occupy the interstitial sites. The

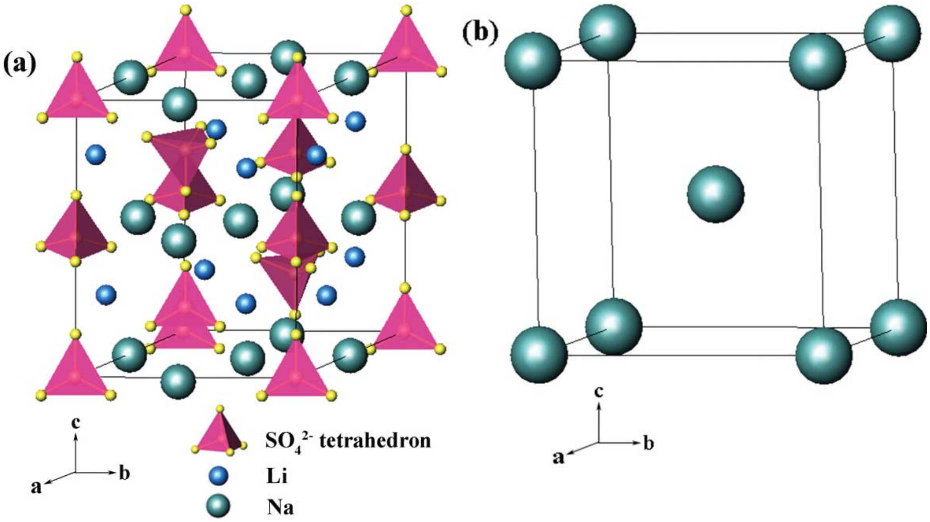


Figure 6. Structures of (a) β-$LiNaSO_4$ (low-temperature phase) and (b) α-$LiNaSO_4$ (high-temperature phase, only unit cell).

transition from the ordered distribution to the disorder distribution of the cations and the possible rotation of the SO_4^{2-} tetrahedrons may supply the inner energy of the high-temperature phase.

It is deduced that in the binary eutectic system, the melting enthalpy for the sample with the composition at the eutectic point should not be larger than that of the end compound with larger melting enthalpy.[20] Similar rule should be applied for the eutectoid system. The data in Figure 4(c) indicate that the E_1 sample has transition enthalpy $\Delta H = 177$ J g^{-1}, less than the transition enthalpy of Li_2SO_4 of 252 J g^{-1}, but similar to the largest transition enthalpy $\Delta H = 186.5$ J g^{-1}with the lowest temperature (462 °C) in the three solid–solid phase transitions of $NaMoO_4$.[7] The data also show that the transition temperature (~474 °C) is clearly lower than those of both Li_2SO_4 and $LiNaSO_4$, indicating that the eutectoid compositions may contribute new phase transition materials applied in different temperatures from the end compositions. Below 474 °C, the E_1 sample is the mixture of Li_2SO_4 and $LiNaSO_4$ with their low-temperature structures. However, above this temperature it takes the high-temperature structure of Li_2SO_4. In both heating and cooling processes, more than one peak was observed, possibly because the sample composition slightly deviated from the eutectoid point.

3.3. Phase transitions of Na_2SO_4 and eutectoid E_2

Figure 7 represents the DSC curves of Na_2SO_4 in the different heating and cooling cycles. In the heating process for the first cycle [Figure 7(a)], the exothermic peak appears at 242 °C with $\Delta H = 78$ J g^{-1}. However, in the cooling process, two exothermic peaks are observed at 241 °C with $\Delta H = -32$ J g^{-1} and at 234 °C with $\Delta H = -17$ J g^{-1}. The total enthalpy (in absolute value) in the cooling process is clearly smaller than that in the heating process. In the second as well as subsequent cycles, the absolute values of the transition enthalpy for both of the heating and cooling processes are almost identical. Although the phase transition enthalpy of Na_2SO_4 is not very large, its transition temperature is quite low; thus as the phase transition material, it may be used at relatively low temperature.

The XRD results indicated that the raw material Na_2SO_4(rm, Phase V), which may be crystallized from aqueous solution, has a different structure from that of the Na_2SO_4(co, Phase III); thus it is understandable that in the first cycle, the transition enthalpy in the heating process is different from that in the cooling process. Brodale and Giauque have

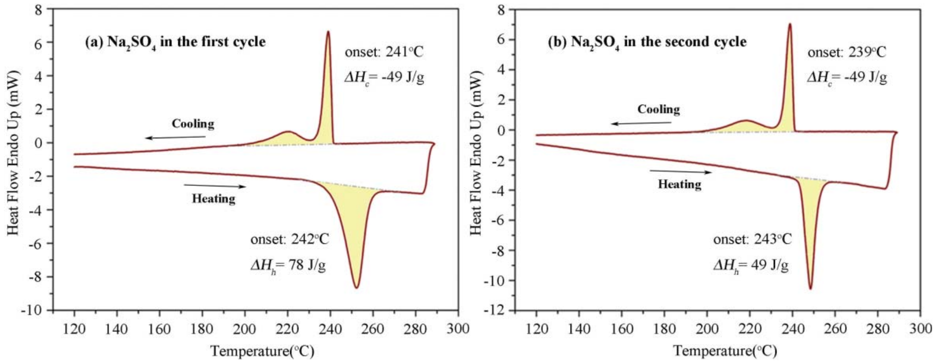


Figure 7. DSC curves of Na_2SO_4: (a) first heating and cooling cycle and (b) the second cycle.

reported that Na_2SO_4 had five different crystal structures, named as Phase I to Phase V.[21] During the first heating process, only one DSC peak appears, indicating that Na_2SO_4 transforms directly from Phase V to Phase I (high-temperature phase) above 240 °C and in the cooling process, two peaks are observed, indicating that two phase transitions occur, corresponding to the transitions in the sequence Phase I → Phase II → Phase III. Phase II is an intermediate phase with a narrow temperature range. In the re-heating process, Phase III directly transforms to Phase I without appearance of Phase II. Normally Phase IV cannot be observed.[20,22]

Based on the data in the reference [23], the Na_2SO_4 structures of Phase I to Phase V (without Phase IV) are represented in Figure 8 and the unit cell parameters are listed in Table 1. In all the structures, SO_4^{2-} groups are isolated by Na^+ cations. In Phase I, Phase II and Phase III, the arrangement of the Na^+ cations and the SO_4^{2-} groups is similar and the main difference among them is that the SO_4^{2-} groups tilt in different directions and

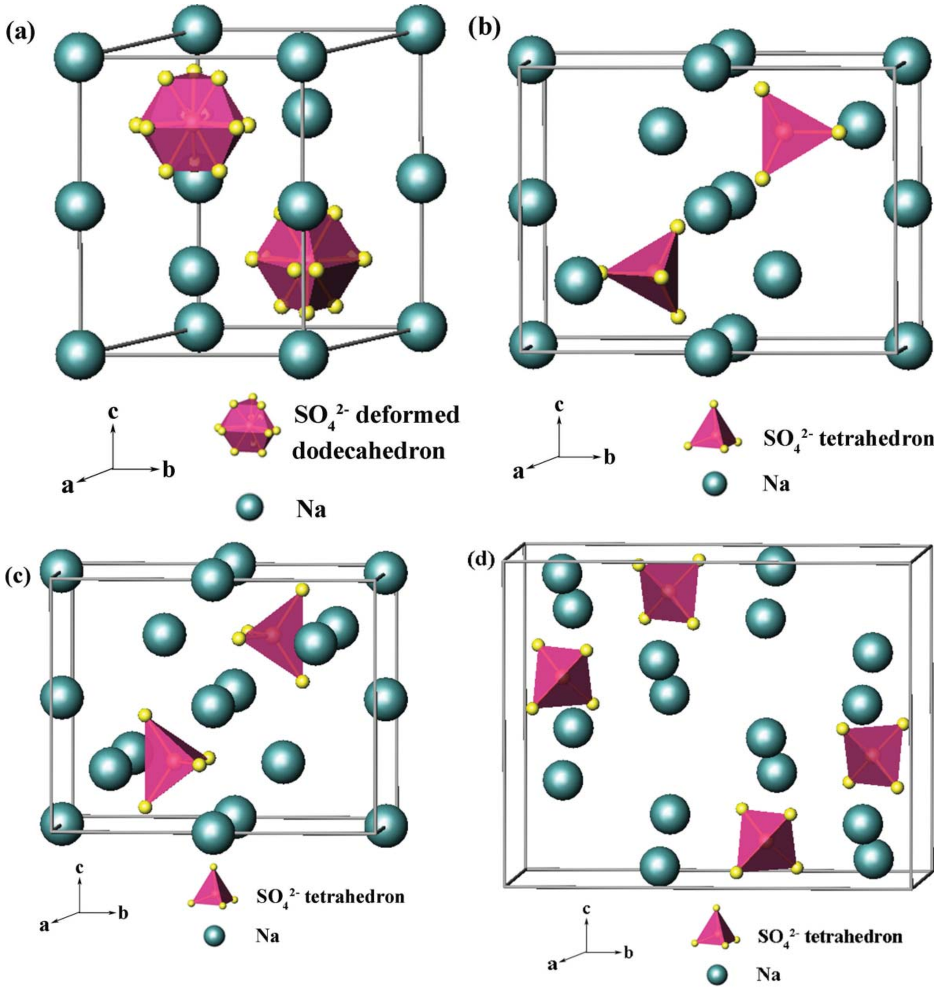


Figure 8. The structures of Na_2SO_4: (a) Phase I (high-temperature phase), (b) Phase II (intermediate phase), (c) Phase III (room temperature stable phase) and (d) Phase V (crystallized phase at room temperature).

Table 1. Unit cell parameters and space groups of various phases of Na_2SO_4.

Phase	Crystal system	Space group	*a* (Å)	*b* (Å)	*c* (Å)
Phase I	hexagonal	$P6_3/mmc$	5.39357	5.39357	7.24651
Phase II	orthorhombic	*Pbnm*	5.30991	9.46928	7.14360
Phase III	orthorhombic	*Cmcm*	5.63041	9.04343	7.03771
Phase V	orthorhombic	*Fddd*	5.8582	12.2990	7.98138

the positions of the Na^+ cations are slightly shifted. In the high-temperature phase (Phase I), the material has more inner energy; thus the tetrahedral SO_4^{2-} groups randomly take three directions in 120° difference, which are represented as deformed dodecahedrons. Since the transitions among Phase I, Phase II and Phase III belong to the displacive phase transitions, their space groups have supergroup and subgroup relations.[19] *Cmcm* (Phase III) is a subgroup of $P6_3/mmc$ (Phase I) and *Pbnm* (Phase II) is a subgroup of *Cmcm*. The structure of Phase V has a relatively large difference from those of the above three phases.

According to our results and the reported data in references,[22] the phase transitions of Na_2SO_4 are illustrated in Figure 9 for the first heating and cooling cycle and Figure 10 for the second and subsequent cycles. The transitions from Phase V to Phase I, from Phase III to Phase I (in heating process) and from Phase I to Phase II (in cooling process) correspond to order/disorder transition; thus the relative large enthalpies are involved, while for the transition between Phase II and Phase III (from Phase II to Phase I and from Phase III to Phase II), only a small direction tilt occurs for the SO_4^{2-} tetrahedrons; as a result, the transition enthalpy is relatively small. Phase V only appears in the first cycle and disappears in the subsequent cycles.

The DSC curves of the eutectoid E_2 are represented in Figure 11. The composition of the E_2 sample is very close to the end compound Na_2SO_4; thus its transition properties

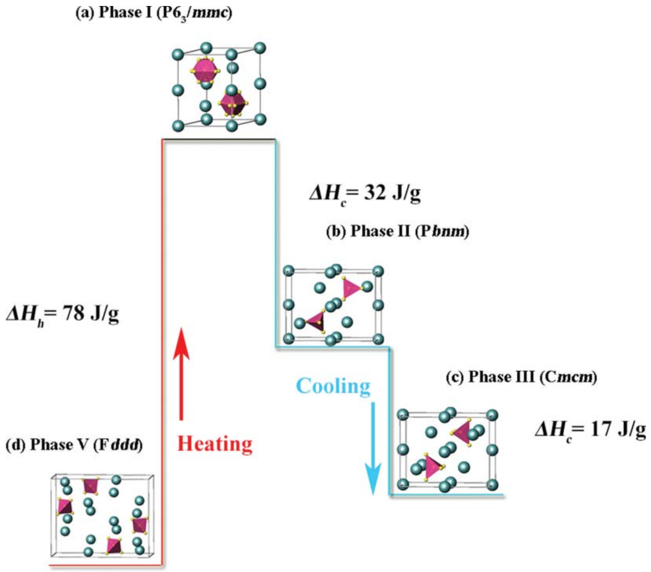


Figure 9. Phase transitions of Na_2SO_4 in the first heating and cooling cycle.

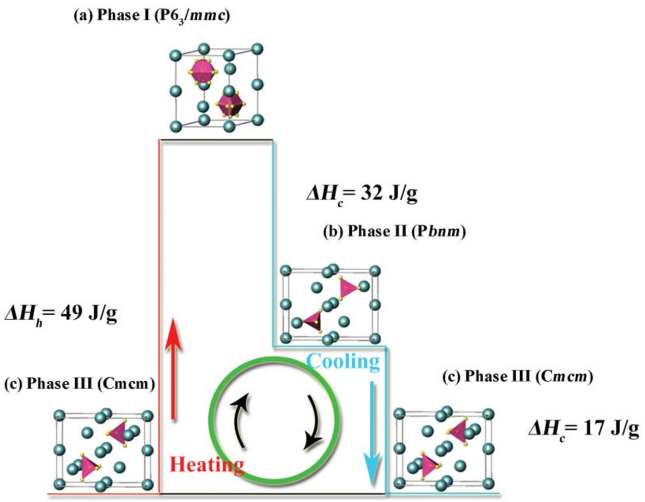


Figure 10. Phase transitions of Na_2SO_4 in the second and subsequent heating and cooling cycles.

are very similar to those of Na_2SO_4. The DSC profile in the first cycle in Figure 11(a) is different from that in the second cycle and consequently circles in Figure 11(b). In the heating process for the first cycle, the transition occurs at 254 °C, very similar to that of Na_2SO_4, with transition enthalpy $\Delta H = 69$ J g^{-1}, slightly smaller than that of Na_2SO_4. In the cooling process, two exothermic peaks with ~20 °C overcooling are observed, with total enthalpy $\Delta H = -46$ J g^{-1}, which is clearly smaller than that in the heating process. In the second and subsequent cycles, the total transition enthalpies for both of the heating and cooling processes are almost identical and slightly smaller than those of Na_2SO_4.

Both Na_2SO_4 and Li_2SO_4 have similar structures, in which the SO_4^{2-} tetrahedrons are isolated by cations (Na^+ or Li^+). However, they have quite different phase transition properties. Li_2SO_4 has much higher transition temperature and enthalpy than Na_2SO_4. We consulted the bond energy (BE) of Li–O and Na–O. It is found that the difference of the phase transition properties between Li_2SO_4 and Na_2SO_4 may be understood by the BE data of Li–O and Na–O. During the phase transition process, the M–O bonds (M = Li or Na) are twisted. Since the Li–O bond (340.5 kJ mol^{-1}) has a larger BE value than the

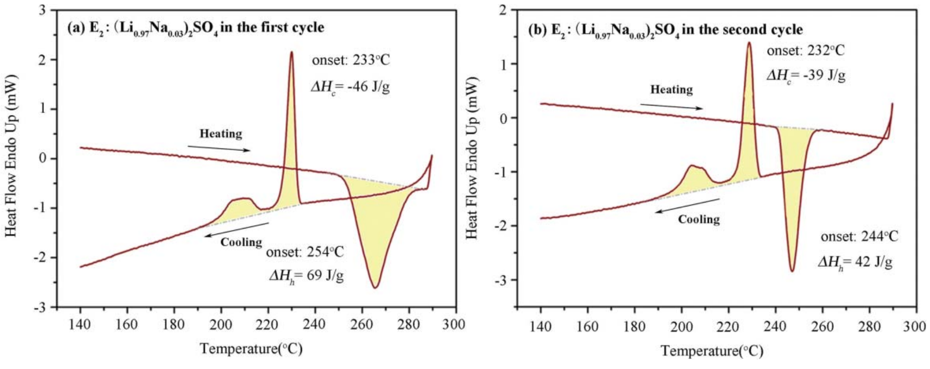


Figure 11. DSC curves of the eutectoid E_2: (a) first heating and cooling cycle and (b) the second cycle.

Na–O bond (270.0 kJ mol^{-1}) in the transition,[24] a relatively high energy barrier has to be overcome for Li_2SO_4.

4. Conclusions

The solid–solid phase transition properties of Li_2SO_4, Na_2SO_4, the binary compound $LiNaSO_4$ and two eutectoids (E_1: $0.73Li_2SO_4$–$0.27Na_2SO_4$; E_2: $0.03Li_2SO_4$–$0.97Na_2SO_4$) in the binary system $(1-x)Li_2SO_4$–xNa_2SO_4 were investigated by XRD and DSC. Li_2SO_4 is quite a good phase transition material: its solid–solid transition occurs at 578 °C with the transition enthalpy 252 J g^{-1}, comparable to the total value of three transitions of Na_2MoO_4. Although the binary compound $LiNaSO_4$ gives slightly lower enthalpy value (214 J g^{-1}), the transition temperature is clearly reduced to 514 °C. For the eutectoid E_1, the transition enthalpy is maintained to 177 J g^{-1} and its transition temperature is further reduced to 474 °C. Besides Li_2SO_4, $LiNaSO_4$ and the eutectoid E_1 are also applicable phase transition materials that may be used at different temperatures. The results in this work indicate that searching for suitable binary (or even ternary) compounds and eutectoid compositions is an effective way to find satisfied phase transition materials. The composition of the eutectoid E_2 is very close to that of Na_2SO_4; thus these two materials have similar phase transition properties. Although their enthalpy values are not very high (~45 J g^{-1}), their transition temperatures are quite low (~250 °C); thus they may be applied at such low temperature.

Funding

We are thankful for financial support from the National Basic Research Program of China [grant number 2009CB939901].

References

[1] Francis A, Neil H, Philip E, Mervyn S. A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS). Renewable Sustainable Energy Rev. 2010;14:615–628.

[2] Stephanie G, Abdessamad F, Aydar R, Julien L, Emmanuel V, Patrick E, Catherine B, Nicolas C, Xavier P. Corrosion effects between molten salts and thermal storage material for concentrated solar power plants. Appl Energy. 2012;94:174–181.

[3] Atyah N, Afif H. Modeling of greenhouse with PCM energy storage. Energy Conversion Manag. 2008;49:3338–3342.

[4] Mondal S. Phase change materials for smart textiles – an overview. Appl Thermal Eng. 2008;28:1536–1550.

[5] Vakilatojjar SM, Saman W. Analysis and modeling of a phase change storage system for air conditioning application. Appl Thermal Eng. 2001;21:249–263.

[6] Zhao RX. [The determination of Na_2XO_4 (X = Cr, Mo, W) for solid–solid transition phase transition in thermal energy storage]. Chem Eng. 2002;14:30–31. Chinese.

[7] Sun XL, Li WX, Wang XM, Jing XP. Variations of phase transition temperature and enthalpy in the systems $Na_2Mo_{1-x}W_xO_4$ and $Na_2Mo_{1-y}S_yO_4$. Phase Transit. 2010;83:491–500.

[8] Nacken R. On the formation and inversion of mix-crystals and double salts in the binary systems of the dimorphous sulfates of lithium, sodium, potassium, and silver. Neues Jahrb Mineral Geol Palaeontol Beilageband.1907;24:1–68.

[9] Schroeder K, Kvist A. Determination of phase diagram Li_2SO_4-Na_2SO_4 from differential thermal analysis. Z Naturforsch A Astrophys Phys Phys Chem. 1968;23:773–774.

[10] Schroeder K, Kvist A, Ljungmark H. Phase-diagram of binary-systems Li_2SO_4-Na_2SO_4, Li_2SO_4-Rb_2SO_4, and Li_2SO_4-Cs_2SO_4. Z Naturforsch. 1972;27:1252–1256.

[11] Mata J, Solans X, Calvet MT, Molera J, Font-Bardia M. X-ray structural characterization, Raman and thermal analysis of $LiNaSO_4$. The phase diagram of the Li_2SO_4–Na_2SO_4 system. J Phys: Condensed Matter. 2002;14:5211–5220.

[12] Eysel W. Crystal chemistry and structure of Na_2SO_4(I) and its solid solutions. Acta Crystallogr. 1985;B41:5–11.

[13] Zhang RY. Phase change materials and energy storage technology. Beijing: Sci Press; 2009. p. 171.

[14] Mord AG. The crystal structure of the low temperature modification of lithium sulphate Li_2SO_4-alpha. A three-dimensional refinement. Chem Commun. 1973;1:1–20.

[15] Nilsson L, Thomas JO, Tofield BC. The structure of the high temperature solid electrolyte lithium sulphate at 908 K. J Phys C: Solid State Phys. 1980;13:6441–6451.

[16] Chen RH, Tseng CM, Shern CS, Fukami T. Ionic conductivity and dielectric relaxation studies of $LiNaSO_4$ single crystal. Solid State Ionics. 2010;181:877–882.

[17] Rojas RM, Martin De Vidales JL, Delgado A, Sinisterra JV. Microstructural and thermal characterization of basic and stoichiometric lithium phosphates in relation with their catalytic activity. J Solid State Chem. 1993;106:237–252.

[18] Freiheit HC, Kroll H, Putnis A. The trigonal-to-cubic phase transition in $LiNaSO_4$: an X-ray and calorimetric study. Z Kristallogr. 1998;213:575–584.

[19] Fsrland T, Krogh-Moe J. The structure of the high temperature modification of sodium lithium sulfate. Acta Crystallogr. 1958;11:224–225.

[20] Zhang YP, Hong SY, Ge XS. [The theoretical predictions about eutectic melting point and melting enthalpy of phase change materials]. J Uni Sci Technol China. 1999;25:125. Chinese.

[21] Brodale GE, Giauque WE. The relationship of crystalline forms I, III, IV, and V of anhydrous sodium sulfate as determined by the third law of thermodynamics. J Phys Chem. 1972;76:737–743.

[22] Choi BK. Thermal-prehistory dependence of the phase stability in the structural phase transitions of Na_2SO_4 crystal. Physica Status Solidi B. 2008;245:946–949.

[23] Rasmussen SE, Jorgensen JE, Lundtoft B. Structures and phase transitions of Na_2SO_4. J Appl Crystallogr. 1996;29:42–47.

[24] Luo YR. Comprehensive handbook of chemical bond energies. Boca Raton (FL): CRC Press; 2007. p. 498–519.