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Invited article

Thermodynamic assessment of binary systems Tris(hydroxymethyl) aminomethane-Pentaglycerine (TRIS-PG) and 2-amino-2-methyl-1, 3-propanediol-Pentaglycerine (AMPL-PG) phase diagrams

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ABSTRACT

Solid state phase change materials are considered as potential candidates for thermal energy storage. Among the solid–solid heat storage materials, the most promising heat storage materials are organic polyalcohol globular tetrahedral molecular crystals such as $(CH_3)C(CH_2OH)_3$ for PG, $(NH_2)C(CH_2OH)_3$ for TRIS, and $(CH_3)(NH_2)C(CH_2OH)_2$ for AMPL, which store a large amount of thermal energy in their solid state high temperature phases with orientationally disorder crystal structure. In this study, we obtained the Gibbs energies of pure PG and pure TRIS derived utilizing the available experimental data including temperature-dependency of heat capacity, enthalpy, and transitions temperatures, as well as obtained *optimized* binary phase diagrams of TRIS-PG and AMPL-PG by CALPHAD calculations. The phase boundaries are verified by in-situ X-ray diffraction (XRD). Optimized database of these two binaries will allow exploration of ternary and higher order systems using CALPHAD methodology that will provide a wider selection of materials for practical thermal energy storage applications. Regular and sub-regular solution models are used for calculations in which the excess Gibbs energies are expressed by the Redlich–Kister–Muggianu polynomial. A set of self-consistent interaction parameters formulating the Gibbs energies of various phases in binary systems are obtained. The TRIS-PG binary phase diagram was calculated from room temperature to the liquid phase temperature, the modeled phase diagram and the experimental data from our work are in good agreement. We also used experimental data of TRIS-PG from the literature which shows a good agreement between the two data sets. Our optimized TRIS-PG phase diagrams show a wider solid-state two phase region, where there is de-mixing of phases, whereas the calculations from the literature show a very narrow region. We also present optimized AMPL-PG binary phase diagram using PARROT module in Thermal-Calc software. The calculated phase diagrams for the two systems mentioned above are presented along with the experimental data.

1. Introduction

Thermal energy storage materials are gaining importance in environmental and ecological systems. Thermal energy can be stored as sensible and latent heat in materials in solid–liquid or solid–solid phase change materials; the stored thermal energy may be released later by cooling the material [1]. In addition, thermal energy storage materials can also be used in applications for waste heat recovery, solar energy utilization, energy saving in buildings, and electronic device management [2]. Phase change materials (PCMs) [3] have a great potential for thermal energy storage, absorbing/releasing heat during their phase transitions. PCMs are classified according to the phase transition involved (1) solid–solid phase transition, and (2) solid–liquid phase transition materials. In 1938, Timmermanns [4] proposed a special class of organic materials and classified them as globular molecules. This group of organic molecular crystals exhibit polymorphisms that are characterized by high enthalpies of solid–solid transitions and a low enthalpy of fusion. An important characteristic of these molecules is that they undergo reversible phase transition from a low temperature layered or chain structure (tetragonal, orthorhombic, monoclinic etc.) to a high temperature

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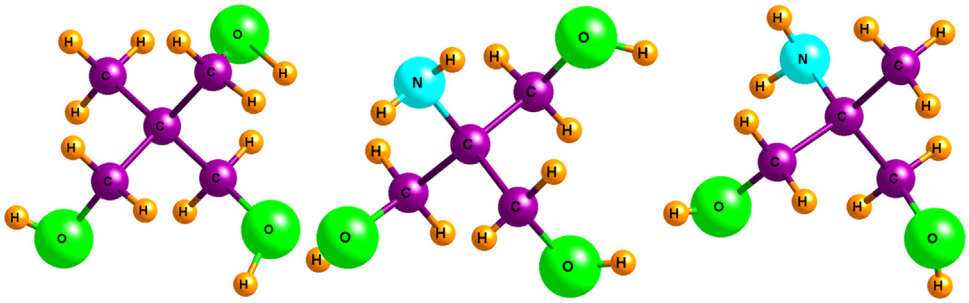

Fig. 1. Molecular structures of PG($C_5H_{12}O_3$), TRIS($C_4H_{11}NO_3$), and AMPL($C_4H_{11}NO_2$).

orientationally disordered phase such as face centered cubic (FCC) and body centered cubic (BCC). This high temperature phase is referred to as orientationally disordered crystal (ODIC) or plastic crystal phase. Alcohol or amine derivatives form these "Plastic Crystals", such as Pentaglycerine (PG), $(CH_3)C(CH_2OH)_3$, 2-hydroxymethyl-2 methyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol (AMPL), $(NH_2)(CH_3)C(CH_2OH)_2$, and Tris(hydroxymethyl) aminomethane (TRIS), $(NH_2)C(CH_2OH)_3$ etc.

Crystallographic and thermodynamic parameters of the pure polyalcohol and amines are already established in the literature [5–13]. The low temperature crystal structure of AMPL is reported by Rose et al. [5] as monoclinic with lattice parameters: $a=8.62$ Å, $b=11.00$ Å, $c=6.10$ Å, $\beta=93.32°$, $V=580.3$ Å^3 at 293 K ($Z=4$). The molecular structures of AMPL are shown in Fig. 1. Chandra et al. [7] reported high temperature phase structure of AMPL as body centered cubic (BCC) with $a=6.78$ Å above ~365 K. Eilerman and Rudman [9–10] reported the low temperature structure of TRIS is orthorhombic $Pn2_1a$ (space group 33) with lattice parameters $a=8.844(1)$ Å, $b=7.794(1)$ Å, $c=8.795(1)$ Å, $Z=4$. At low temperature, TRIS forms layered or chain structures where hydroxyl groups are connected by strong hydrogen bonds within each layer and amine groups are connected by relatively weak hydrogen bonds. The molecular structure of TRIS is also shown in Fig. 1. Eilerman and Rudman [9–10] also reported the high temperature phase of TRIS as body centered cubic (BCC), $Im3m$, with $a=6.876$ (6)Å at 423 K ($Z=2$). Low temperature phase of the PG was determined by Eilerman et al. [11] as tetragonal (space group I-4) with $a=6.054$ Å and $c=8.866$ Å; three hydroxyl groups form the connection of strong hydrogen bonds in the layers of ordered crystal structure reported by Barrio et al. [12]. Doshi et al. [13] reported that the PG undergoes a solid state phase transition at 351.3 K to high temperature phase with an orientationally disordered face-centered cubic (FCC) with a lattice parameter, $a=8.86(5)$ Å at 373 K.

For practical applications, solid-state phase transition temperatures (T_{SSTR}) of pure materials range from 353 K (AMPL) to 407 K (TRIS); there are only a few materials with these characteristics. In order to increase the selection of these energy storage materials, we make polyalcohol and amine solid solutions that have different phase transition temperatures (T_{SSTR}) to suit a particular application [14]. To study the effect of solutions/mixtures of polyalcohol and amines on the solid–solid phase transitions, Barrio et al. [12] conducted experimental investigations on binary system such as TRIS-PG. Lopez et al. [15] carried out computational studies of molecular mixed crystals of TRIS-PG. However, there is a significant difference between Barrio's experimental results and Lopez's computational phase diagram about the low temperature phase regions for PG-rich solid solution and TRIS-rich solid solution. Salud et al. [16] established a comparative analysis of crystallography and thermodynamics of AMPL-PG. As part of our ongoing work on creating new binaries for thermal energy storage applications, Gantan [17] conducted the AMPL-PG system experiment work as a part of his M.S thesis. Salud et al. [16] performed further experimental studies on the AMPL-PG system including a calculated phase diagram, but there were slight differences between these two-phase diagrams of Gantan [17] and Salud et al. [16].

In this study, the optimized phase diagrams of TRIS-PG and AMPL-PG are determined, by using available experimental data from our work as well as the literature [12,16,17], which are remarkably important to understand the polymorphism in the binary systems, and further develop ternary or higher order systems to develop more materials for thermal energy storage.

2. Materials and methods

2.1. Materials

Polycrystalline samples of PG (99%), TRIS (99.9%), and AMPL (99.9%) were procured from Sigma-Aldrich; The samples were heated in VWR KIMAX, Culture tubes (20 mm × 125 mm) with sealable screw top. These samples were heated in air using a standard Bunsen burner, once the powders melted; we sealed the tube with the screw top so as to prevent any moisture backstreaming into the sample. The TRIS-PG, and AMPL-PG mixture binary samples were prepared at various compositions, and all compositions were reported as mole% in this paper. We followed a protocol in which the sample powders were premixed and melted in test tubes. Generally, the solidified melt does not give an equilibrium mixture of solid phases due to supercooling, and high temperature phases are retained at room temperature. To avoid this, we used strain induced transformation method in which equilibrium phases were attained. The methodology involves placing the melted and solidified binary mixtures in a freezer (~253 K) for 12 h and then subjected them to a high strain in a small cylinder with a piston. This method worked well to obtain equilibrium crystal structures at room temperature.

2.2. X-ray diffraction analyses

In-situ X-ray diffraction studies were performed, using a θ-θ PANalytical X'Pert PRO diffractometer, to determine the lattice parameters by superimposing the lattice symmetry of the pure PG, TRIS, AMPL, and their binary solid solutions (TRIS-PG, and AMPL-PG). Powder samples of binary solid solutions were prepared by adding an internal standard silicon powder. A PANalytical X-ray diffractometer system was modified to accept sapphire capillaries as sample holders. This home-made device was fabricated using hot air blowing system incorporated with the diffractometer, and the temperature was maintained by using a Watlow temperature controller with a feedback to the hot air blower. A position sensitive detector, which is part of the PANalytical diffractometer, was used to capture the diffraction angles and intensities of the Bragg peaks. The diffraction scans were made using CuKα radiation, and