# Infrared thermography method for fast estimation of phase diagrams

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## ABSTRACT

Phase change materials (PCM) are widely used today in thermal energy storage applications. Pure PCMs are rarely used because of non adapted melting points. Instead of them, mixtures are preferred. The search of suitable mixtures, preferably eutectics, is often a tedious and time consuming task which requires the determination of phase diagrams. In order to accelerate this screening step, a new method for estimating phase diagrams in record time (1–3 h) has been established and validated. A sample composed by small droplets of mixtures with different compositions (as many as necessary to have a good coverage of the phase diagram) deposited on a flat substrate is first prepared and cooled down to ambient temperature so that all droplets crystallize. The plate is then heated at constant heating rate up to a sufficiently high temperature for melting all the small crystals. The heating process is imaged by using an infrared camera. An appropriate method based on singular values decomposition technique has been developed to analyze the recorded images and to determine the transition lines of the phase diagram. The method has been applied to determine several simple eutectic phase diagrams and the reached results have been validated by comparison with the phase diagrams obtained by Differential Scanning Calorimeter measurements and by thermodynamic modelling.

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## 1. Introduction

Thermal energy storage (TES) has been recognized as a key component of renewable thermal energy-based systems due to the unpredictable availability of the energy source (e.g. solar radiation, geothermal energy). The most significant applications are heating/cooling and thermal comfort in dwellings and workspaces. Moreover, thermal energy is also rejected by a great number of man-made energy conversion systems, industrial processes, propulsion/transportation systems, etc. Intercepting/recovery, storing and later utilization of thermal energy might be intended as an approach to increase thermal efficiency of a process or an industrial plant. Alternately, storage of thermal energy can be utilized for energy conservation, improving operational life of electronic devices, food transportation, etc.

For the last two decades, there has been a growing interest in the development and the study of phase change materials (PCMs) for thermal energy storage applications. PCMs store (release) thermal energy by undergoing solid to liquid (liquid to solid) phase transition during the energy transfer process. Compared to conventional

materials for sensible heat storage, PCMs are particularly attractive due to their ability to provide high-energy storage density, thus leading to compact storage units. Moreover, PCMs absorb and release heat at a nearly constant temperature. Extensive work has been reported in the literature on the selection, characterization and applications of PCMs. For comprehensive details, readers are referred to recent review articles [1–6]. PCMs for TES should have a large latent heat, a melting temperature lying within the practical range of operation, melt congruently with minimum subcooling and be chemically stable, low in cost, non-toxic and non-corrosive. Organic PCMs (e.g. alkanes, fatty acids, esters, polyols, etc.) and salt hydrates dominate in applications at low and medium temperatures, whilst anhydrous salts and metals are investigated for high temperature applications. However, single compounds are rarely used because there is often a mismatch between their melting point and the storage temperature range needed in the application. A common approach to cope with this problem consists in searching new binary or ternary eutectic mixtures, which will reduce the melting point of the single components while still melting congruently. The search of suitable eutectic mixtures is often a tedious and time consuming task that requires the determination of phase diagrams.

There are two general categories of methods for the determination of phase diagrams [7]. The first category of methods (dynamic

## Nomenclature

*Roman letters*

| | |
|---|---|
| $n$ | total number of pixels per IR image |
| $n_p$ | number of pixels per droplet |
| $n_t$ | number of sampling times |
| $R$ | ideal gas constant |
| $s(i,t)$ | DL-signals |
| $\mathbf{S}$ | matrix $[n_p \times n_t]$ containing $s(i,t)$ data |
| $T$ | temperature |
| $t$ | time |
| $\mathbf{V}$ | left-side matrix $[n_p \times n_p]$ from SVD of $\mathbf{S}$ |
| $x$ | mole fraction |
| $z_m(t)$ | $m$th time-eigenfunction |
| $\mathbf{Z}$ | matrix $[n_p \times n_t]$ containing $z_m(t)$ data |

*Greek letters*

| | |
|---|---|
| $\alpha_m$ | vontribution of $z_m(t)$ to the total energy of DL-signals |
| $\Delta H$ | enthalpy of fusion |
| $\varepsilon$ | infrared emissivity |
| $\sigma_m$ | $m$th singular value |

*Acronyms*

| | |
|---|---|
| DL | digital level |
| DSC | differential scanning calorimeter |
| IRT | infrared thermography |
| PCM | phase change material |
| SVD | singular values decomposition |
| TES | thermal energy storage |

methods) detects the phase boundaries by means of thermal, physical, chemical, mechanical, or other property changes during cooling and/or heating of an alloy, and therefore studies the approach of a system to the equilibrium state. The other category of methods (static methods) employs equilibrated alloys, and therefore studies the behavior of a system in an equilibrium or local equilibrium state. The most popular techniques used in dynamic approaches are thermal analysis (TA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The first of them, based on recording of cooling curves, has no significant meaning nowadays; instead, DTA and DSC are widely used. DSC has an advantage over DTA, because in addition to temperature it gives the precise value of enthalpy of thermal effect [8–10]. Along with the static methods, metallography analysis is one of the key tools for determining phase diagrams [11,12]. Microstructure examinations are routinely used to investigate the number of phases (single phase or multiphase) and invariant reaction types (such as the eutectic or peritectic ones). In particular, the characteristics of each phase, such as composition, size, shape, distribution, colour, orientation, and hardness can be examined. Optical metallography is still widely used but has now been expanded to include results from electron microscopy. Electron microscopy offers the capability of greater magnification and, in addition, allows quantitative determination of the compositions of individual grains, provided that the microscope is equipped with suitable attachments for composition analysis like EDS (X-ray Dispersive Spectrometer) or WDS (Wavelenght Dispersive Spectrometer). Another powerful tool for the determination of phase diagrams is diffraction. Initially this was XRD (X-ray diffraction), but during the past century electron and neutron diffraction have been developed.

Each of the aforementioned techniques has its own advantages and limitations (see e.g. [11] for a discussion), so that no phase diagram can be considered fully reliable until the corroborating observations were made by at least two independent methods. A new method based on infrared thermography is proposed in this paper to determine approximate phase diagrams in record time. The method detects the phase boundaries of the studied system by means of infrared emissivity changes during heating of a large population of droplets with different compositions. It is well-known that the infrared spectrum (IR spectrum) of a material is determined largely by the nature and the arrangement of the bonds in the primary molecular structure [13]. Changes in the IR spectrum due to temperature variations can be correlated with structural intermolecular and/or intra-molecular changes. For example, any transition from a crystalline to a liquid phase results in a broadening of bands due to the destruction of long range lattice order on melting. In crystalline materials, a change from a polymorph to another generally causes band shifts and splitting. Sharp changes in the IR-absorption coefficient (or emissivity) of polymers, salt systems, metals and metal alloys during melting have already been reported in the literature [14–17]. As shown later, the signals recorded by an infrared camera during droplets' heating will show a first-order discontinuity when a droplet crosses a transition line. This corresponds to a change in the thermal emissivity of the droplet and represents the basis of the method proposed for phase diagrams construction. It is worth to notice that this method does not replace existing techniques but completes them by providing an efficient way to establish preliminary phase diagrams that can be then refined by more accurate but time-consuming methods. In applications where time is a premium, as those related with the development of new PCMs for TES, the proposed method has great interest because it is able to accelerate the screening step by indicating whether or not the studied systems have suitable eutectic points, providing approximate values for the corresponding eutectic temperature and composition. Although TES motivates our work, the results achieved can also be used in many other areas of application, especially in pharmaceutical field where screening is usually needed.

The proposed method is described in Sections 2 and 3. Experimental issues (materials, samples preparation, experimental set-up and protocols) are presented in Section 2, whereas Section 3 is devoted to data treatment issues. A mathematical method based on singular values decomposition techniques has been proposed to identify transition lines from the recorded data and is detailed in Section 3. The experimental and theoretical methods used for validation are introduced in Section 4, namely differential scanning calorimeter and thermodynamic modelling of solid–liquid equilibrium lines. The method has been applied to determine the phase diagram of six simple eutectic systems. The results achieved are presented and discussed in Section 5.

## 2. Experimental method based on infrared thermography

### 2.1. Materials and binary systems employed

Erythritol, D-mannitol, dulcitol, xylitol and adonitol are the compounds selected for the study. They are all mono-saccharide polyols with linear carbon chain structure. Their respective CAS number, stoichiometric formula, provider and purity grade are given in Table 1. The binary systems investigated are the following: adonitol–dulcitol, adonitol–mannitol, xylitol–dulcitol, xylitol–mannitol, mannitol–dulcitol and eythritol–dulcitol.

### 2.2. Preparation of the samples

Let us consider a binary system with components A and B. A sample of the system is a sufficiently large number of small droplets deposited on a thin plate in a more or less regular manner (Fig. 1).