

Low temperature thermal properties of amorphous materials

Takasuke Matsuo

*Department of Chemistry, Graduate School of Science, Osaka University
Toyonaka, Osaka 560 Japan*

Abstract : The knowledge derived from thermal measurements are important for non-crystalline materials because the structural disorder severely limits the precision of the information from diffraction and scattering experiments. To show the difference between the crystalline and amorphous substances, the heat capacities of glassy and crystalline potassium meta-phosphate are presented. A large excess heat capacity was found for the glassy sample at temperatures between 10 to 40 K with a maximum value at 25 K and is reproduced well by a distribution of harmonic oscillator frequencies with an excess density of vibrational states at 41 cm^{-1} relative to the crystal. This is identified with low energy excitations and Boson peaks generally known to occur in glassy substances in scattering experiments. For glassy hydrocarbons neutron scattering and calorimetry give the frequency dependence and absolute magnitude of the excess vibrational density of states.

INTRODUCTION

Adiabatic low temperature calorimetry has been used in physical chemistry of condensed matter for more than 80 years in the past. It continues to be useful in solid state science owing to the inherent accuracy and the unique versatility of the calorimetric method: it gives heat capacity data on substances with the same accuracy and precision whatever the physical state the sample is in. Thus, samples in various states (crystals, liquids, powder and amorphous materials) can be studied equally well, resulting in the same quality of data. Discontinuous increase of the enthalpy and entropy can also be determined at melting and other first order transitions. The versatility is not shared by many of the experimental methods. This orthodox use of calorimetry has been further promoted recently by introduction of calorimeters for small samples[1-3]. In a more recent development, time dependent properties are also studied by adiabatic calorimetry[4].

Non-crystalline and glassy substances have been of general interest in recent years for two of their properties that distinguish them from crystalline substances. These are glass transitions and low energy excitations. In the following we describe our recent results on molecular and ionic glass-forming substances obtained with adiabatic calorimeters.

ADIABATIC CALORIMETRY

An adiabatic calorimeter for heat capacity measurement works on the following principle. A sample confined in a vacuum-tight vessel is supplied with a precisely determined amount of electric energy while it is kept in isolation from the surroundings with respect to any other mode of energy exchange. The Joule heating results in an increment of the sample temperature. The heat capacity of the sample and the vessel is given by the ratio of the supplied energy to the temperature rise. With the heat capacity of the vessel determined in a separate measurement, the molar heat capacity of the substance is determined to its absolute value with no need of a calibration experiment. The temperature of the sample is measured with a platinum or rhodium-iron resistance thermometer to a precision of 0.1 mK using an automatic AC resistance bridge. The Joule energy supplied from a precision current source is determined with a digital voltmeter and quartz clock (of a personal computer running the experiment) with high enough accuracy. Thermal isolation of the sample is achieved by adiabatic shields that provides a uniform-temperature environment for the sample with a fast responding electronic mechanism regulating the temperature of the shield to within 5 mK of that of the surface of the sample vessel. The calorimetric experiment can be made automatic with a small personal computer doing all the task of data collection as well as computation leading to the final molar heat capacity. The data obtained with a well-designed calorimeter are precise to within 0.1 % and believed to be accurate to 0.3 % at temperatures between 20

to 300 K. Below 20 K, the relative inaccuracy increases rapidly with decreasing temperature because of the small absolute values of the heat capacity.

A recent innovation in adiabatic calorimetry is an ultra-fast-cooling calorimeter[5]. In this calorimeter, the sample is plunged into liquid nitrogen (or any other coolant) and then set in a pre-cooled cryostat in less than 10 seconds without ever experiencing a temperature above 100 K. This allows metastable and unstable states of substances to be frozen at low temperature and their thermal properties determined with the same accuracy as is done with samples in the stable states. Relaxation of a quenched unstable sample back to equilibrium at a glass transition or crystallization is also a subject of interest to be studied using the new technique. With a calorimeter of the traditional design, an experiment is set up typically in one hour. During this time the sample stays at the room temperature, inevitably undergoing unwanted annealing or recrystallization. Previously, only the quenched unstable states of a substance that can be prepared in the calorimetric cryostat have been studied by heat capacity measurement. This limited the type of substances we could study (and the range of experimental parameters we could vary) to within certain narrow limits. The newly designed calorimeter, also known as a top-loading calorimeter (a name descriptive of the setting-up of an experiment with this calorimeter) has reduced the limitation, enables us to study substances in an extreme non-equilibrium state and will extend the application of the adiabatic calorimetry beyond the equilibrium and near-equilibrium states.

GLASS TRANSITIONS

Glass transitions are characterized, in a thermodynamic measurement, by a steep increase of the heat capacity as a function of the temperature. At the same time, the sample kept in thermal isolation warms by itself as the glass transition temperature is approached from below. The self-heating occurs as a result of energy transfer from the configurational degrees of freedom to the lattice and molecular vibrations. The heat capacity at temperatures below the glass transition is close to the heat capacity of the crystalline phase, although there is an important difference at low temperature as discussed below. The heat capacity of a glass is essentially of a vibrational origin. Above the glass transition the heat capacity includes the contribution from the intermolecular potential energy that depends on the relative orientation of the molecules and the segments within the molecule. With such contribution from the configurational degrees of freedom, the heat capacity above the glass transition is equal to the heat capacity of the supercooled liquid state. For some substances, the heat capacity of the supercooled liquid states can be measured all through the metastable region from the glass transition temperature to above the normal melting point. For other substances such measurement is disrupted by spontaneous crystallization at some temperature above the glass transition point.

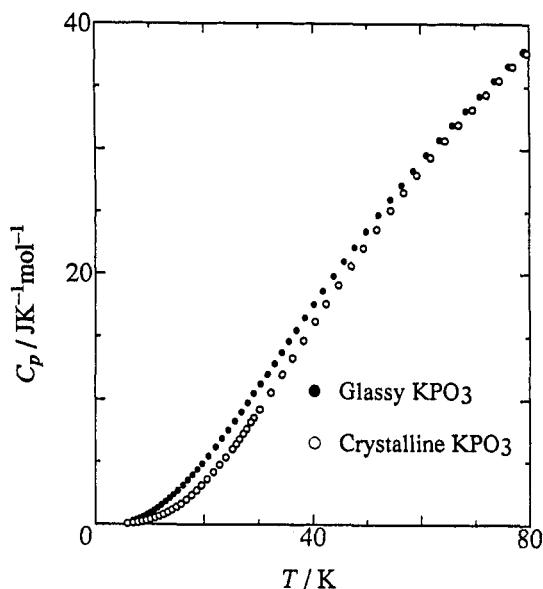


Fig. 1 Heat capacity curves of crystalline and glassy potassium meta-phosphate samples KPO_3 . [8]

The glass transition marks the temperature at which the molecular reorientation becomes as slow as (or as fast as, depending on whether one approaches the temperature from above or from below) the experimental time. One thousand second is normally taken as the relaxation time defining the glass transition temperature. One should recognize the enormous difference between the characteristic time (ca. 1 ps) of the molecular vibration and the configurational relaxation time (1000 s) at the glass transition. Between these two, there can be time scales characterizing other modes of molecular motion. Current discussion on glassy states is often centered around this point.

The concept of the glassy state has been extended to glassy crystals and the glassy state attained from a stable phase (as distinct from a meta-stable phase). C_{60} is a glassy crystal below 87 K. Above this temperature the molecule jumps between equivalent and non-equivalent orientations relative to the crystal axes. The time constant of the reorientation is ca. 1000 s at 87 K and becomes larger at lower temperatures. With such a large time constant, most of the experimental techniques determine the properties of the crystal essentially frozen in one of the configurations. Hence it is glassy. It is also a glassy state of a stable phase, because the partially ordered simple-cubic crystal at 87 K is the stable phase formed by the molecule below 257 K[6,7].

LOW ENERGY EXCITATIONS

It is known experimentally that at low temperatures the heat capacity of an amorphous substance is larger than the heat capacity of the same substance in an ordered crystalline phase. An extra group of vibrational modes is believed to be responsible for the excess heat capacity. The temperature where the extra heat capacity is most evident is below 30 K. At such low temperature, the configurational degree of freedom is frozen and does not contribute to the heat capacity. The heat capacity can be reproduced by assuming excess density of vibrational states at lower frequencies where the density of states $g(\omega)$ for the crystalline modification has the Debye ω^2 frequency dependence. The extra density of states is known as low energy excitations. Because of their low energy, they contribute to the heat capacity at lower temperatures, thus giving rise to the excess heat capacity.

Figure 1 shows the heat capacities of crystalline and glassy forms of potassium meta-phosphate KPO_3 [8]. The difference between the curves is largest at 25 K reaching 2 J/Kmol which is 30 % of the heat capacity of the glassy state. We have also examined a glassy phase prepared from molten KH_2PO_4 and obtained a similar result[9]. The occurrence of the excess heat capacity is a very general feature of non-crystalline material, and may be related to their inherent atomic disorder. Unlike in crystals, the atoms and molecules in non-crystalline solids are in different surroundings formed by their randomly packed neighbors. When displaced from their stable positions some molecules experience weaker, and others stronger restoring forces acting on them than the same molecule does in the crystal. On the average, the restoring force will be weaker, considering the smaller mass density of a glass than that of the crystal. Assuming that the restoring force is still harmonic, one expects that the frequencies of the normal modes will be lower than in the crystal. This is equivalent to a higher density of states at low energies, thus explaining the experimental result. For KPO_3 the excess heat capacity was reproduced well by a Schottky heat capacity function with an excitation energy of 41 cm^{-1} . This indicates that the density of states is augmented at this energy and reduced around 82 cm^{-1} .

This model of excess density of states has been made quantitative and compared with the heat capacity and neutron scattering data for some glassy hydrocarbons[10,11]. The assumption of the harmonic vibration is supported by the temperature dependence of the scattered neutron intensity obeying the Bose statistics. Thus the low energy excitation is also known as a Boson peak.

The neutron scattering experiment is based on the fact that, for a sample containing hydrogen, the incoherent scattering by protons dominates the scattered intensity and gives a relative harmonic spectrum proportional to the vibrational density of states. By combining this with the molar heat capacity, we determined the absolute value of the excess density of states. For a crystal the absolute number of the vibrational states belonging to the acoustic branch and each of the optical branches are trivial quantities once the substance is specified and the crystal structure known. But this is not the case for an amorphous substance because of the lack of the structural periodicity. The absolute value of the density of states is an essential quantity for quantitative modeling the dynamics of non-crystalline states. At present to combine the spectroscopic and calorimetric experiments is the only way to determine it experimentally. For the phosphate glasses the neutron scattering method is not applicable because of the scattering property of the nuclei involved.

REFERENCES

- [1] Takasuke Matsuo, *Pure & Appl. Chem.*, **67**, 911 (1995).
- [2] T. Matsuo, *Thermochim Acta*, **163**, 57-70 (1990).
- [3] T. Matsuo and H. Suga, *Thermochim. Acta*, **88**, 149 (1985).
- [4] H. Suga and T. Matsuo, *Pure & Appl. Chem.*, **61**, 1123 (1989).
- [5] I. Tsukushi, O. Yamamuro, K. Sadanami, M. Nishizawa and T. Matsuo, *Rev. Sci. Instrum.*, in press, 1997.
- [6] T. Matsuo, H. Suga, W. I. F. David, R. M. Ibberson, P. Bernier, A. Zahab, C. Fabre, A. Rassat and A. Dworkin, *Solid State Commun.*, **83**, 711 (1992).
- [7] W. I. F. David, R. M. Ibberson and T. Matsuo, *Proc. Roy. Soc. Lond.*, **A442**, 129 (1993).
- [8] H. Obara and T. Matsuo, unpublished data.
- [9] H. Obara, O. Yamamuro and T. Matsuo, *Proc. 9th International Meeting on Ferroelectricity*, 26-29, August 1997, Seoul.
- [10] O. Yamamuro, T. Matsuo, K. Takeda, T. Kanaya, T. Kawaguchi and K. Kaji, *J. Chem. Phys.*, **105**, 732 (1996).
- [11] O. Yamamuro, I. Tsukushi, T. Matsuo, K. Takeda, T. Kanaya and K. Kaji, *J. Chem. Phys.*, **106**, 2997 (1997).