

Specific-heat Study of Low-energy Vibrational State in Vitreous Samarium Phosphates

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Received 5 September 1994

ABSTRAK

Pengukuran haba tentu dalam julat suhu 1.5K ke 30K telah dilakukan untuk dua sampel kaca samarium fosfat. Satu sumbangan yang besar terhadap haba tentu, melebihi dari apa yang diramalkan dari fonon akustik (dalam penghampiran Debye), telah dibincangkan dalam sebutan jangkaan teori pendekatan lampau silang fonon-frakton. Ketumpatan keadaan fonon-frakton digunakan untuk memadankan lebihan haba tentu bagi menghasilkan parameter model yang mempunyai magnitud yang sama dengan yang telah diperolehi sebelum ini untuk sejumlah besar kaca-kaca.

ABSTRACT

Measurements of specific heat in the temperature range 1.5K to 30K were made for two samples of vitreous samarium phosphates. A large contribution to the specific heat, well above what is expected from acoustic phonons (in the Debye approximation), is discussed in terms of the theoretical predictions of a phonon-fracton cross-over approach. The phonon-fracton density of states used to fit the excess specific heat gives rise to model parameters with the same magnitudes as those found previously for a wide range of glasses.

Keywords: phosphate glasses, specific heat, phonon-fracton

INTRODUCTION

Anomalies in a wide range of physical properties at low temperatures due to frozen-in supplementary degrees of freedom are a dominant feature of glasses. The most characteristic features are the linear behaviour of the specific heat and the T^2 dependence of the thermal conductivity in the

temperature region below 1K, which are well accounted for by the phenomenological tunnelling model of two-level systems (Anderson *et al.* 1972; Phillips 1972).

The same effect of the topological disorder in amorphous structures is observed by the introduction of supplementary degrees of freedom, giving rise to anomalies in the thermal (Pohl 1981), acoustic, dielectric (Hunklinger and Schickfus 1981) and optical (Jäckle 1981) properties. This excess of degrees of freedom is normally attributed to the localized structural defects or particles which have a different mobility from the rest of the host structure and which are subjected to thermally activated local motion at high temperatures and to tunnelling motions at very low temperatures. Besides the acoustic phonons, the existence of additional vibrational states must be included in order to explain the anomalous excess of specific heat and the plateau in the thermal conductivity in the region between 1 and 30K.

It is likely that there is a common origin for these effects together with those observed in low-frequency Raman (Nemanich 1977) and inelastic neutron scattering spectra (Buchenau *et al.* 1988; Malinovsky *et al.* 1990). Several models have been proposed to account for the universal form of the excess of density-of-vibrational states; the two most attractive and general are the phonon-fracton cross-over model (Alexander and Orbach 1982; Orbach 1986) and the soft-potential model (Karpov *et al.* 1983; Parshin 1994).

Neutron scattering measurements support a common interpretation of the low-frequency vibrational states in vitreous SiO_2 arising from local motions of coupled SiO_4 tetrahedra (Buchenau *et al.* 1988). The objective of the present work is to determine whether this finding extends to samarium phosphate glasses. Since the addition of modifier ions to phosphate glasses alters the coupling constant between the PO_4 tetrahedra, it can be expected to influence the density of relaxing particles, a major source of ultrasonic attenuation. It is possible that eventual identification of the microscopic groups involved in local motions could come from study of the glassy systems in which the number or the kind of structural units present in the network is altered by varying the composition and the type of modified ion.

EXPERIMENTAL TECHNIQUES

The glasses were prepared by heating a high-purity stoichiometric mixture of Sm_2O_3 and P_2O_5 to a temperature of 1400°C in a programmable electric furnace (Senin 1994). The heat capacity of each small sample (~ 221.0 mg) of samarium phosphate glass was measured using a standard heat-pulse technique over the temperature range 1.5 to 30K.

The procedures used to measure the specific heat are detailed elsewhere (Avogadro *et al.* 1986).

RESULTS AND DISCUSSION

The experimental results obtained for the specific heat C_p of $(Sm_2O_3)_{0.190}(P_2O_5)_{0.810}$ and $(Sm_2O_3)_{0.248}(P_2O_5)_{0.752}$ glasses between 1.5K and 30K are shown in Fig. 1. At low temperatures the difference between C_p and C_v is negligible, especially for these glasses in which the thermal expansion is very small (Wang *et al.* 1990). These specific heat results, when plotted as $C(T)/T^3$ (Fig. 2), show behaviour very different from the Debye theory of heat capacities calculated using ultrasound velocities (Reese 1966). The anomalies appear in the same temperature region that the thermal conductivity should display a plateau; however this property has not yet been examined for these glasses. As the temperature is reduced below 2K, there is a steep rise; this is due to the paramagnetic contribution to the specific heat. The present concern is mainly the peak centred at about 10K. Such feature has been observed in many glasses, including vitreous SiO_2 (Zeller and Pohl 1971), Se (Avogadro *et al.* 1987), As (Jones *et al.* 1978) and $AgI-Ag_2O-B_2O_3$ glasses (Avogadro *et al.* 1987) and has been analysed in terms of the phonon-fracton cross-over model (Orbach 1986), which predicts (Avogadro *et al.* 1986) .

$$\frac{C}{kA} = 9n \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{[e^x - 1]^2} dx + \left(\frac{T}{\Theta_D} \right) Q \int_{\Theta_{CO}/T}^{\Theta_M/T} \frac{x^2 e^x}{[e^x - 1]^2} dx \quad (1)$$

where θ_D is the Debye temperature, $\Theta_{CO} = \eta\omega_{CO}/k$, $\theta\eta\omega_M = M/k$ and a dimensionless constant

$$Q = \frac{D_{fr}(\omega)k\Theta_D}{9An}$$

The Debye temperature is relevant to the understanding of the lattice vibrational properties of glasses when describing the specific heat. The Debye temperature has been calculated from room temperature ultrasound velocities and densities. The Debye mean sound velocity $\overline{v_D}$ has been calculated using the expression

$$\overline{v_D} = \left[\frac{1/v_L^3 + 2/v_S^3}{3} \right]^{-\frac{1}{3}} \quad (2)$$

and the Debye temperature Θ_D obtained from

$$\Theta_D = \frac{h}{k} \left(\frac{3 \rho A n}{4 \pi M} \right)^{\frac{1}{3}} \frac{1}{v_D} \quad (3)$$

where A is the Avogadro's number, n is the number of atoms in unit formula, ρ is the density and M is the molecular weight. In Table 1 the Debye temperatures for samarium phosphate glasses calculated using Eq. 3 are given.

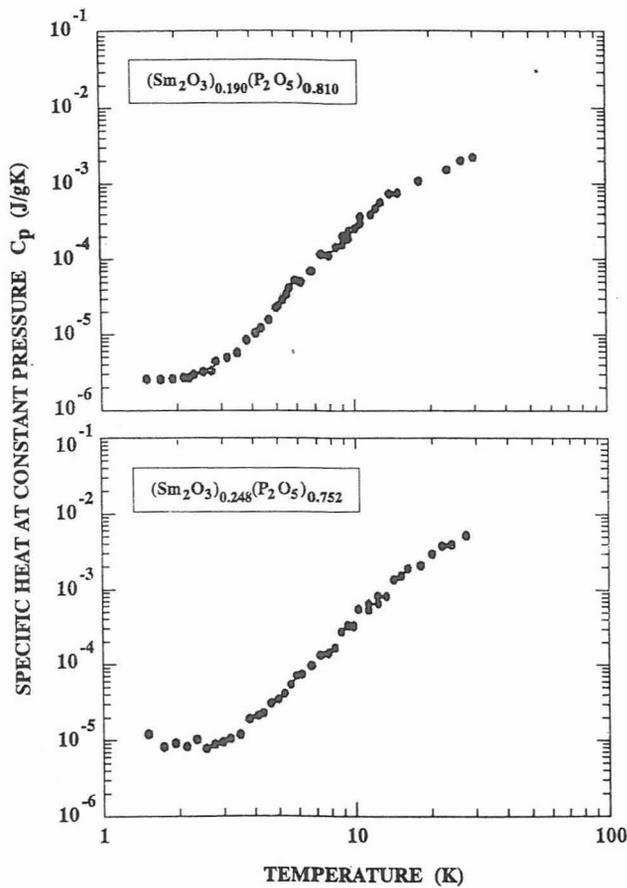


Fig. 1 Specific heat C_p for samarium phosphate glasses measured between 1.5K and 30K

TABLE 1
Main physical quantities of samarium phosphate glasses

x	n	M (g/ mole)	V (cm ³ / mole)	N/V	$\overline{v_D}$ (ms ⁻¹)	θ_D (K)
(Sm ₂ O ₃) _x	0.190	6.62	181.2	56.3	7.08	3128
x(P ₂ O ₅) _{1-x}	0.248	6.50	193.2	55.0	7.12	2796

x is the mole fraction, n the number of atoms per molecular formula, M the molecular weight, V the molar volume, N/V the number of atoms per unit volume in units of 10²⁸ atoms/m³, $\overline{v_D}$ the mean Debye sound velocity and θ_D the Debye temperature.

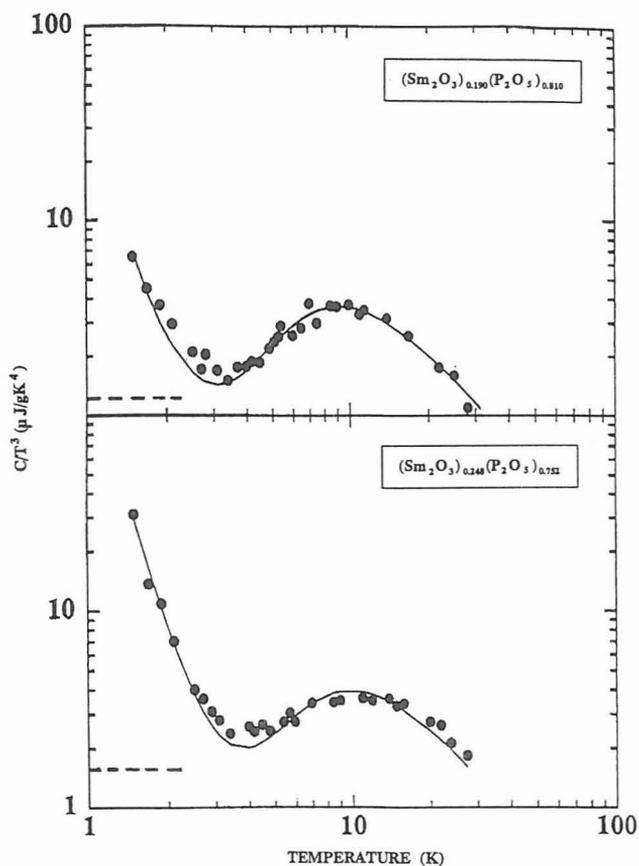


Fig. 2. Temperature dependence of C_v/T^3 for samarium phosphate glasses. The dotted line corresponds to the Debye elastic contribution calculated from ultrasonic wave velocities. The solid line is the best fit of the magnetic and phonon-fracton contributions to the excess specific heat.

The high frequency cut-off of the spectrum, ω_M , is determined by the normalization condition

$$\int_0^{\omega_M} D(\omega) d\omega = 3An \quad (4)$$

According to phonon-fracton cross-over model (Orbach 1986), the density of states increases as ω^2 up to a cross-over frequency ω_{CO} , corresponding to a wavelength for the Debye-type elastic modes comparable to the characteristic size of structural units in the disordered system. For frequency higher than ω_{CO} , the density of fracton states $D_{fr}(\omega)$, has a frequency dependence ω^{p-1} , $p < 3$, with a sudden increase at ω_{CO} (Orbach 1986). In the present theoretical fit, it has been assumed that $p=1$, so that $D_{fr}(\omega)$ is frequency-independent:

$$D_{fr}(\omega) = \frac{9AnQ}{k\Theta_D} \quad (5)$$

The best fit to the experimental data obtained by considering the addition of the magnetic and phonon-fracton contributions to the specific heat of the $(Sm_2O_3)_x(P_2O_5)_{1-x}$ glasses is shown by the continuous line in Fig. 2. It can be seen that the shape of the experimental peak as a function of temperature is closely defined by the theory. Table 2 summarizes the parameters used to fit the experimental data according to Eq. 1. The value of the characteristic length L in Table 2 has been obtained from the relationship

$$L = \left(\frac{\Theta_D}{\Theta_{CO}} \right) a \quad (6)$$

predicted by the phonon-fracton cross-over model, where a is an atomic distance which sets the shortest length scale in the model, and is approximated here by the average interatomic distance. The cross-over temperature Θ_{CO} , corresponding to the cross-over frequency ω_{CO} , is higher for the $(Sm_2O_3)_{0.248}(P_2O_5)_{0.752}$ glass, and in consequence the characteristic length L is shorter than found for the $(Sm_2O_3)_{0.190}(P_2O_5)_{0.810}$ glass. This is consistent with the structure of phosphate glasses (Senin 1994). The $(Sm_2O_3)_{0.190}(P_2O_5)_{0.810}$ glass should have a higher degree of three-dimensional network connectivity, in consequence having a larger network coherence and longer characteristic length L than that with the metaphosphate composition.

There is a strong correlation between the temperature T_{\max} , which defines the maximum in the peak in the excess specific heat and the Debye temperature θ_D for a wide range of glasses (Fig. 3). This can be seen as a consequence of the link between T_{\max} and θ_{CO} , implying that the characteristic length L should be similar for all oxide glasses. In Table 2 the model parameters θ_{CO} , θ_M , L and Q determined for the samarium phosphate glasses are compared with data of glasses in other systems, such as the covalent network glass ($Ag_2O.B_2O_3$), the superionic glasses $(AgI)_x(Ag_2O.B_2O_3)_{1-x}$ (Avogadro *et al.* 1986), the amorphous chalcogenide alloys $Se_{1-x}Te_x$ (Avogadro *et al.* 1987) and the polymeric Se types (Avogadro *et al.* 1987). The close similarity between the model parameters shows that this model fits the peak in the excess specific heat of the samarium phosphate in the same way as it does for the other glasses. It is also possible to make an estimate of the cross-over temperature θ_{CO} from phonon to fracton behaviour from the low-frequency region of the Raman scattering where the light scattering is determined by the acoustic vibrational modes.

Recently low-frequency Raman-scattering measurements have been made from 8K to room temperature on the samples of samarium phosphate glasses used for the present study (Carini *et al.* 1993). It was found that there is a reduction in slope of the reduced Raman intensity $I\omega/$

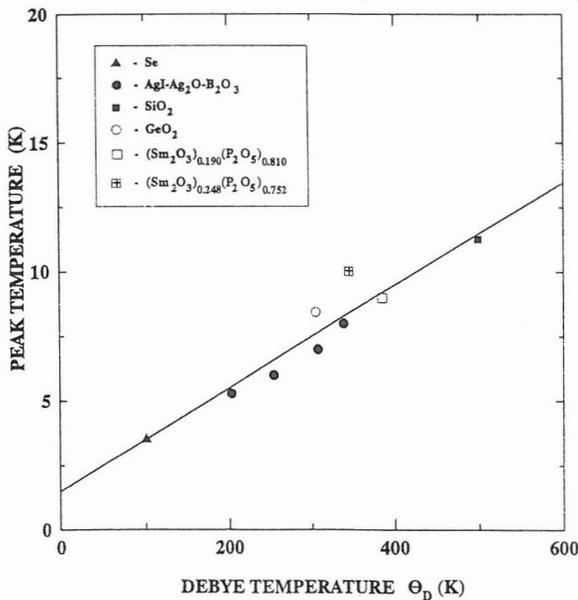


Fig. 3. Plot of the temperature at which the maximum in C_v/T^3 occurs as a function of the Debye temperature θ_D for a range of glasses

$[n(\omega, T) + 1]$ as a function of frequency shift at $\sim 30 \text{ cm}^{-1}$. Below this frequency the slope is 3.8 which corresponds to the value expected from Debye-like density of states where the reduced Raman intensity is given by $C(\omega)g(\omega)$ with both the coupling constant $C(\omega)$ and the phonon density of states being proportional to ω^2 . Above this frequency the slope is markedly lower corresponding to a possible cross-over into the fracton regime (Carini *et al.* 1993). A cross-over frequency of 30 cm^{-1} is equivalent to a characteristic temperature of 43K quite close to that of θ_{CO} determined from the fit to the peak in the normalised specific heat (Table 2). This provides additional confirmation that samarium phosphate glasses show an excitation spectrum which can be explained in terms of a long-wavelength (low-frequency) phonons at low temperatures and of short-wavelength localised vibrations (fracton) at higher temperature. As a conclusion, the thermal and ultrasonic properties of the rare earth phosphate glasses comply with the universal observation now widely recognized for the vibrational properties of glasses.

TABLE 2

Values of the main physical quantities used in the fit of the excess of specific heat by Eq. 1. The results for the samarium phosphate glasses are compared with data of glasses in other systems by reference of work of Avogadro *et al.* (1986, 1987).

Glasses	θ_D (K)	θ_{CO} (K)	Q	$L(\text{\AA})$	Q_M (K)	$a(\text{\AA})$
$(\text{Sm}_2\text{O}_3)_{0.190}(\text{P}_2\text{O}_5)_{0.810}$	387	33.8	0.065	27.7	890	2.42
$(\text{Sm}_2\text{O}_3)_{0.248}(\text{P}_2\text{O}_5)_{0.752}$	345	37.3	0.082	22.5	1050	2.44
Se	99.7	16.0	0.08	24.2	411	3.82
$\text{Se}_{0.933}\text{Te}_{0.067}$	101.4	20.6	0.14	19.2	246	3.90
$\text{Se}_{0.866}\text{Te}_{0.134}$	103.5	23.5	0.18	17.3	206	3.91
$\text{Se}_{0.79}\text{Te}_{0.21}$	105.1	24.6	0.19	16.7	200	3.92
$\text{Ag}_2\text{O}.2\text{B}_2\text{O}_3$	334	27.3	0.11	28	1035	2.27
$(\text{AgI})_{0.2}(\text{Ag}_2\text{O}.2\text{B}_2\text{O}_3)_{0.8}$	313	23.1	0.10	31	993	2.39
$(\text{AgI})_{0.5}(\text{Ag}_2\text{O}.2\text{B}_2\text{O}_3)_{0.5}$	255	20.1	0.12	31	722	2.41
$(\text{AgI})_{0.65}(\text{Ag}_2\text{O}.2\text{B}_2\text{O}_3)_{0.35}$	207	17.5	0.11	30	613	2.53

ACKNOWLEDGEMENTS

HBS is grateful to the Universiti Pertanian Malaysia and the Government of Malaysia for study leave and financial support and also the hospitality of the School of Physics, University of Bath, UK. We are grateful to Johnson Matthey Technology Centre and DRA Maritime Division, UK for support of our programme of work on rare earth phosphate glasses.

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