Giant Heat Release in Glass-like Materials

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Abstract. The heat capacity, thermal conductivity and heat release of the glass-like crystalline materials NbTi-D and \((\text{ZrO}_2)_{0.87}(\text{CaO})_{0.13}\) were investigated. Both materials show all typical for structural glasses low temperature anomalies. However, the maximum value of the heat release after a rapid cooling is essentially larger the value observed in other glasses. The analysis of the data within the tunnelling model indicates that this giant heat release is caused by tunnelling systems with unexpected high barrier heights.

1. Introduction

One of the characteristic low temperature anomalies of structural glasses is the long time heat release after rapid cooling the sample from some equilibrium temperature \(T_1\) to a lower phonon temperature \(T_0\) [1], which can be determined in calorimetric experiments from the gradient of phonon temperature \(T\) close to \(T_0\), neglecting the weak time dependence of the heat capacity:

\[ \frac{dQ}{dt} = (C_p + C_{ad}) \dot{T}(t) - (T(t) - T_0)/R_{hl} - \dot{Q}_{par}, \]

where \(C_p\) is the heat capacity of the sample, \(C_{ad}\) the heat capacity of the addenda (thermometer, heater, a copper wire of the mechanical heat switch), \(R_{hl}\) is the thermal resistance between the sample and the sample holder (determined mainly by the electrical wire of the thermometer and heater, and thin nylon threads), \(\dot{Q}_{par}\) is a parasitic heat flow to the sample caused mainly by the power of the thermometer, electrical and mechanical noises. For structural glasses the time and temperature dependences of this heat release are in a good agreement with tunnelling model [2,3] using the standard two-level system (TLS) distribution function \(P(E, \tau) = P_0/\tau\) for long relaxation time, where \(P_0\) is the distribution parameter.

\[ \frac{dQ}{dt} \approx \dot{Q}(T_1, T_0, t) = (\pi^2 k_B^2/24) PV_0(T_1^2 - T_0^2)t^{-1}, \]

where \(V_0\) is the volume of the sample. The \(T_1\) dependence of the heat release is correct for \(T_1 < T^*\), where \(T^*\) is the freezing temperature [4]:

\[ T^* = \frac{V_{eff}}{\ln \left( \frac{k_B T^2}{\tau_0 V_{eff} |R|} \right)}. \]

\(V_{eff}\) is the effective barrier height of TLS causing the heat release at a fixed time \(t_0\), \(R^*\) the cooling rate \(dT/dt\) at the freezing temperature \(T^*\) and \(\tau_0\) is the constant of the thermal activated relaxation time:

\[ \tau^{ta} = \tau_0 \exp V/k_B T, \]
For $T_1 > T^*$ the heat release saturates since all TLS with the corresponding higher energy get the equilibrium during the cooling due to the fast thermal activated relaxation. Thus the maximum value of the heat release at a fixed time $t_0$ is given for $T_0 << T_1$:

$$Q_{\text{max}} = (\pi^2 k_B^2/24)V_0 P_0 T_{\text{eff}}^2/t_0,$$

and is following very sensitive to the absolute value of the effective barrier height of TLS causing the heat release at a given time $t_0$. For the structural glass $a$-$SiO_2$ the heat release experiment yields [5]: $P_0 = 2.10^{+4}/Jm^3, T^* = 4.0K$ and $Q_{\text{max}}t_0/V_0 = 0.26J/m^3$, i.e. 1 h after cooling the sample from some $T_1 > T^*$ down to a temperature $T_0 << T^*$ a heat release $Q_{\text{max}}/V_0 = 0.07\mu W/cm^3$ will be measured - a typical value of structural glasses.

2. Experimental Results and Discussion

In table 1 are given the corresponding parameters obtained in our experiments with different glass-like crystalline solids, where in all investigated properties (heat release, heat capacity, thermal conductivity) the typical low temperature anomalies of structural glasses were found. In the polycrystalline NbTi the TLS are caused by local fluctuations between different structural phases ($\beta$ and $\omega$ phases) [5]. Two percent hydrogen or deuterium stabilizes the $\beta$ phase [6] and the corresponding tunnelling systems disappears. At the same time H ore D produce new TLS. The investigated CaO stabilized ZrO$_2$ sample is a large single crystal ($V_0 = 14.5cm^3$).

Table 1. Parameters of $a$-$SiO_2$ and different glasslike crystalline materials.

| material          | $P_{0C}$  | $P_{0Q}$  | $P_{0C}/P_{0Q}$ | $T^*$ | $Q_{\text{max}}t_0/V_0$ | remarks |
|-------------------|----------|----------|-----------------|------|------------------------|---------|
| $a$-$SiO_2$       | 8.0      | 2.0      | 4.0             | 4.0  | 0.26                   | $t_{\text{amax}} < t_0$ |
| NbTi              | 43.2     | 5.2      | 8.3             | 4.8  | 0.98                   | $t_{\text{amax}} < t_0$ |
| NbTiH$_{9\%}$     | 43.2     | 5.2      | 8.3             | 4.8  | 0.98                   | $t_{\text{amax}} < t_0$ |
| ($ZrO_2)_{0.87}(CaO)_{0.13}$ | 18.5   | 5.7      | 3.2             | 7    | 2.2                    | $t_{\text{amax}} < t_0$ |
| ($ZrO_2)_{0.87}(CaO)_{0.13}$ | 18.5   | 19.2     | 0.96            | $> 50$ | $> 300$               | $t_{\text{amax}} > t_0$ |
| NbTiD$_{10\%}$    | 74.0     | 79       | 0.94            | 50   | 1260                   | $t_{\text{amax}} > t_0$ |

The distribution parameters deduced from the heat capacity $P_{0C}$ and heat release $P_{0Q}$ and also the freezing temperatures $T^*$ for NbTi and NbTiH are close to that of $a$-$SiO_2$. Note, that for both materials $P_{0C}$ is remarkable larger than $P_{0Q}$. But the same discrepancy was found for $a-SiO_2$ too. The heat release data of NbTiD$_{10\%}$ and ($ZrO_2)_{0.87}(CaO)_{0.13}$ are given in Fig. 1 and 2. Fig. 3 shows the heat release of NbTiD$_{10\%}$ measured 30 min after cooling begin as a function of $T_1^2 - T_0^2$ ($T_0 = 1.34K$). The heat release saturates at very high $T_1$ only and as the consequence a giant maximum heat release was observed. This result is very surprising, since this giant heat release was not observed for NbTiH, i.e. a strong isotopic effect in the freezing temperature was found. If we assume that the distribution of the barrier heights is given by the NbTi matrix and following is the same for H and D, the same time $t_0$ corresponds to the same tunnelling parameter $\lambda_0$:

$$\lambda_0 = (2\pi/h)d(2mV_{eff})^{0.5}$$

Assuming in addition that the tunnelling distances $d$ are the same for H and D, we expect from Eq. (5) that the effective barrier height for the larger mass of deuterium must be lower and
following according to Eq. (3) one expects a lower freezing temperature for D in comparison to H:

$$V_{effD} = (m_H/m_D)V_{effH} = 0.5V_{effH}$$  \hspace{1cm} (7)

Instead of the expected reduction of $T^*$ we found a drastic increase and as the consequence a giant heat release.

The heat release of $(ZrO_2)_{0.87}(CaO)_{0.13}$ shows an untypical time dependence. A good fit of the data gives the equation (see solid curves in Fig. 2):

$$\dot{Q} = Q_s t^{-1} \exp(-t/\tau_{amax}) + Qt^{-1}$$  \hspace{1cm} (8)

i.e. at short time an additional contribution of TLS with a for glasses anomalous short maximum relaxation time $\tau_{amax}$ exist. In the long time range the results are similar to that of $a-SiO_2$ including the discrepancy between $P_{0C}$ and $P_{0Q}$ (see Table 1). At short time the heat release does not saturate up to the highest $T_1 = 50K$, i.e. the freezing temperature is even larger. This leads again to an giant heat release. If we calculate $P_{0Q}$ from the heat release data at short time ($Q_s$) we get a value, which is in an excellent agreement with $P_{0C}$. Therefore, a simple explanation of the heat release in $(ZrO_2)_{0.87}(CaO)_{0.13}$ can be given: at short time $t_0 < \tau_{amax}$ additional (anomalous) TLS contribute to the heat capacity and the heat release. At long time one group of TLS contributes to the heat release only and the absolute value is reduced. Due to the high freezing temperature the additional TLS at short time exhibit anomalous high barrier heights together with anomalous short relaxation time, since $\tau_{amax}$ is much shorter than for the second (normal group). Thus, we observe this additional contribution in NbTiD and in $(ZrO_2)_{0.87}(CaO)_{0.13}$, and for both materials $P_{0C} = P_{0Q}$. The unexpected isotopic effect in NbTiH/D find now a simple explanation: the larger mass of D increases $\tau_{amax}$. For NbTiH $\tau_{amax}$ is shorter the time necessary for cooling the sample and the giant heat release was not observed. Since the step in the distribution function exists at shorter time, the heat capacity yields a larger value $P_{0C}$ than $P_{0Q}$. If we again assume that barrier heights are determined by the matrix NbTi (i.e. the distribution of barrier heights is the same for H and D) the increase of $\lambda_{amax}$ and consequently $\tau_{amax}$ follows directly from Eq. (6):

$$\lambda_{Dmax} = (m_D/m_H)\lambda_{Hmax} = 2\lambda_{Hmax}$$  \hspace{1cm} (9)

Since the giant heat release is caused by TLS with very high barrier heights it is not so surprising that we observe in the heat release the upper limit of the relaxation time spectrum of $(ZrO_2)_{0.87}(CaO)_{0.13}$, where the measuring time becomes longer $\tau_{amax}$. In fact, the estimation of the effective barrier heights with Eq. (3) yields for $(ZrO_2)_{0.87}(CaO)_{0.13}$ $V_{eff}/k_B > 1700K$, while the absorption peak in internal friction measurements of this sample gives $V_{max}/k_B = 1800K$ [7]. Formal we could introduce an anomalous large zero point energy $E_{0a}$ for the additional TLS to explain the giant heat release and also the unexpected time dependence observed for $(ZrO_2)_{0.87}(CaO)_{0.13}$. However, together with the open question, why a part of TLS exhibit a much larger $E_0$, this assumption cannot explain the observed $T_1$ dependence of $\tau_{amax}$. Within the standard tunnelling model $\tau_{amax}$ is proportional to $1/E$ for a constant $\lambda_{amax} = V_{max}/E_{0a}$, while in the experiment $\tau_{amax}$ increases with the average energy $E/k_B = T_0 + T_1$ of TLS causing the heat release (see Fig. 5).

An interesting question is also: do exist anomalous TLS in structural glasses too? At least this could explain the large discrepancy between $P_{0C}$ and $P_{0Q}$ in a-SiO$_2$. Notice that the physical nature of the measured effects is still an open problem. As a possible reason, we have considered the role of random thermally-induced internal stresses appearing due to fast cooling. As is known, the random internal thermal stresses can change the barrier heights and asymmetry of
TLS and, as a consequence, the character of both tunnelling and activation relaxation of these systems [8]. Within this scenario a redistribution of TLS occurs towards the shorter relaxation times. Actually, these TLS would contribute to the heat release and short time heat release. Unfortunately, our calculations show that the typical thermal stresses at low temperatures are too small for a quantitative explanation of the observed effect. Therefore this problem calls for further theoretical investigations.

Figure 1. The heat release in $10cm^3$ $NbTiD_{10\%}$ after cooling from different $T_1$.

Figure 2. The heat release in $14.5cm^3 (ZrO_2)_{0.87}(CaO)_{0.13}$.

Figure 3. The heat release observed 30 min after cooling.

Figure 4. The parameter $Q_s$ used in the fit curves in Fig. 2.

Figure 5. The parameter $\tau_{max}$ used in the fit curves in Fig. 2.

3. References

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This work was supported by the Landau-Heisenberg program.