

DETERMINATION OF TIME CHARACTERISTICS OF SOLIDIFICATION OF SUPERCOOLED HALIDE MELT FROM MEASUREMENTS OF ITS ELECTRICAL CONDUCTIVITY

P. Demo^{1,2}, A. M. Sveshnikov¹, K. Nitsch¹, M. Rodová¹ and Z. Kožíšek¹

¹Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 53 Praha, 6, Czech Republic

²Czech Technical University in Prague, Faculty of Civil Engineering, Dept. of Physics, Thákurova 7, 166 29 Praha 6, Czech Republic

Received: December 20, 2002

Abstract. Origin of supercoolability in metallic and halide melts is discussed. While the level of supercooling in metals is closely connected with the structural incompatibilities between the molten state and product crystal, respectively, the supercoolability of halide melts is caused by their strong complex-forming nature. The investigation of processes in supercooled melts is important, because the supercooling of melt strongly influences the nucleation and growth of crystals from the melt and their final quality. Electrical resistance is a suitable quantity to study the solidification of melts, since it can be measured both in liquid state (including supercooled melt) and during the solidification. The early stage of solidification of PbBr_2 melt was analyzed within the context of nonstationary nucleation theory. The proposed model describes the time dependence of electrical conductivity of the melt. The time lag of nucleation is calculated and compared with the experimental value.

1. INTRODUCTION

One of the principal aims of materials science and technology is to produce macroscopic crystals of required chemical and physical properties under a limited number of conditions controllable from the outside. (For example, temperature field imposed on a solidifying system or composition of a starting material may play the role of such controlling parameters). Main effort of crystal growers is oriented therefore to the problem how to minimize the appearance of undesirable faults in crystals (such as dislocations, cracks or tendency of the solid to be polycrystalline). In practice, the produced crystals usually exhibit a relatively high number of such defects, however carefully the growth procedure is performed. Due to the complexity of this problem, rather semiempirical techniques (based on long-term experience of technologists) have been frequently applied to improve the needed global quality of the final phase.

Nevertheless, it is broadly accepted that the properties of grown crystals are essentially affected (beside technological growth conditions) by the thermal history of the molten state itself. One of the basic characteristics of the melt is its tendency to be supercooled. The question is, why the macroscopic solidification does not start immediately, when the molten system is cooled down to the temperature very slightly below the equilibrium liquidus temperature T_M – as it may be concluded from the standard thermodynamics – but the melt can be deeply supercooled in some cases. (For example, as it follows from the series of electron diffraction measurements [1], the water may be supercooled to temperatures as low as 203K). The answer is not trivial at all and it connects such heterogeneous problems as formation of hadron bubbles in quark–gluon plasma [2], alternative description of dislocations in solids [3], aerosol formation in higher layers of atmosphere [4], traffic jams [5] or creation of new phases from the melts or solutions [6].

Corresponding author: P.Demo, e-mail: demo@fzu.cz

Table 1. Surface tension for some metallic and halide melts [18, 19].

Matter	γ [$N \cdot m^{-1}$]	Matter	γ [$N \cdot m^{-1}$]
Ir	2.1	KBr	0.08
Nb	1.8	CsBr	0.08
Zr	1.4	NaBr	0.09
FeB	1.2	KCl	0.09
Al	1.1	NaCl	0.10

2. ORIGIN OF SUPERCOOLING

In the fifties Frank [7] proposed hypothesis that a relatively high supercooling of metallic melts is probably connected with the structural properties of the liquid state itself. Frank suggested that within the melt a certain short-range ordering exists and that such configuration exhibits fivefold rotational symmetry which is, of course, incompatible with the translational symmetry of the final metal crystal (as it was already proved by Johannes Kepler in 1619 [8]). This hypothesis has been confirmed later by sophisticated experiments using EXAFS techniques [9-13] where the local symmetry of the melt can be determined from intergration of measured radial distribution function.

As a consequence of such incompatibility with the translational invariance of a product metallic crystal, such systems exhibit relatively high values of surface energy between melt and solid [11] (see Table 1). Then, with these high values of surface energies, to lower ΔG (and, thus, to increase probability of the nucleation of a new solid phase) means to increase supercooling of a melt under consideration.

The reason of supercooling of halide melts is different. Although by using the X-ray absorption spectroscopy certain local short ordering of molten KBr, RbBr and CuBr has been detected [14, 15], direct proof on existence of the fivefold symmetry fails. In addition, relatively small values of surface energies of most halides [16, 17] (as compared with metallic melts, see Table 1) indirectly favor hypothesis that unmatched structural properties of molten halide salts (if any) play only a minor role in their ability to be supercooled.

In our opinion, supercoolability of ionic (and superionic) systems is closely connected with their strong complex-forming nature above T_M . Indeed, however the initial material is free of impurities resp. inclusions, or the experiments are performed under containerless conditions, massive charged com-

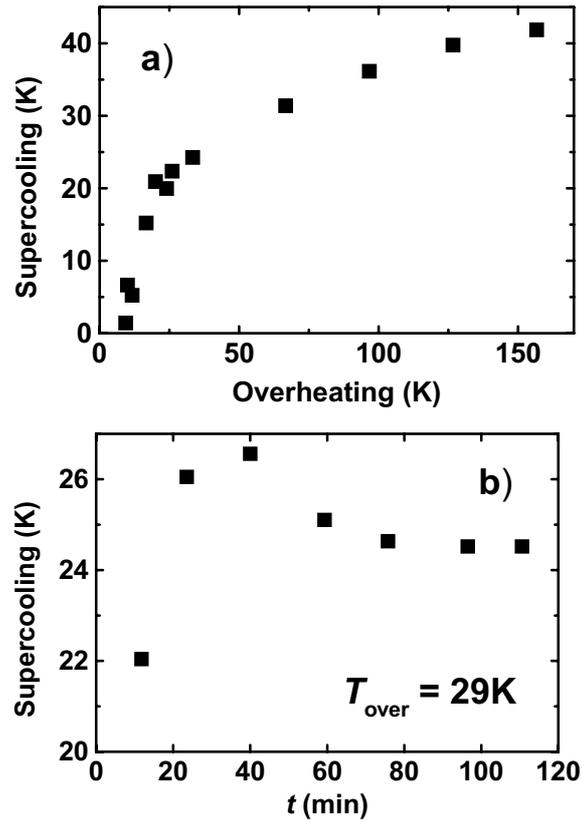


Fig. 1. Dependence of final supercooling of the $PbBr_2$ melt ($T_M = 639K$) on initial overheating (a) and duration of overheating (b).

plexes start to form slightly above T_M . These charge unbalanced objects then serve as active centers for heterogeneous nucleation. Consequently, to maximize supercooling level in complex-forming systems means that the complexes must be broken. One of the easiest way how to decompose these charged particles is to overheat melt to appropriate temperatures above T_M . Then the number density of active sites for heterogeneous nucleation rapidly decreases and the phase transition itself starts homogeneously.

Hence, the larger is the overheating of melt, the larger supercooling is reached. This situation is demonstrated in Fig. 1a for the melt of $PbBr_2$. Moreover, in order to give a chance for decay of large ions, the melt must be exposed to overheating for a sufficiently long period; duration of overheating then also influences the level of final supercooling (see Fig. 1b). Thus, a thermal history of the melt, especially its initial overheating above T_M , may essentially influence degree of its final supercooling.

3. EXPERIMENTAL RESULTS FOR $PbBr_2$ MELT

In department of Optical Crystals of the Institute of Physics of the Academy of Sciences of the Czech

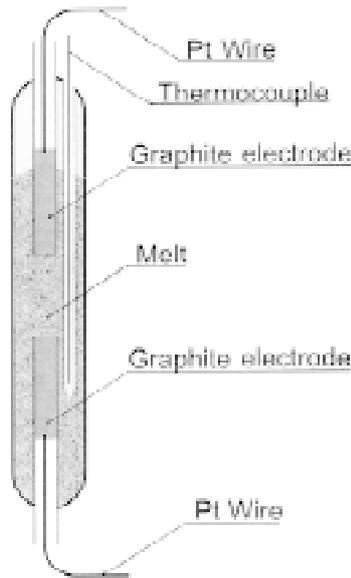


Fig. 2. Scheme of the experimental setup. The melt is placed into the closed quartz tube cell. Alternate voltage of frequency 10 kHz is applied to carbon electrodes and the current is measured. Temperature is measured by a thermocouple in the place with the lowest temperature.

Republic several series of measurements of supercoolability of halide melts have been carried out. To extend information on properties of the supercooled molten state, its electrical conductivity has been measured until macroscopic solidification starts. Due to its promising acoustooptical properties, we restrict our attention to PbBr_2 melt.

During the first stage of the typical crystal preparation the original material is heated usually from the room temperature T_R above its melting (liquidus) temperature T_M until entire charge is molten. In order to exclude transition to glassy state, the system is then carefully cooled down below T_M . Within this nucleation region, supercooled metastable melt survives until sufficiently large fluctuations (internal thermal, or artificially imposed from the outside — e.g., vibrations) provoke formation of microscopic domains (clusters) of a new, product crystal growable to macroscopic sizes.

Since halide melts have a strong complex-forming nature, the supercooled melt is not homogeneous, but contains complexes, which are in general electrically charged. Appearance of charged complexes within molten halide salt may be related to its electrical current and, thus, to its electrical resistance. We have measured this quantity in a special closed quartz tube cell with carbon electrodes using a method of constant alternate current with a frequency of 10 kHz (see Fig. 2).

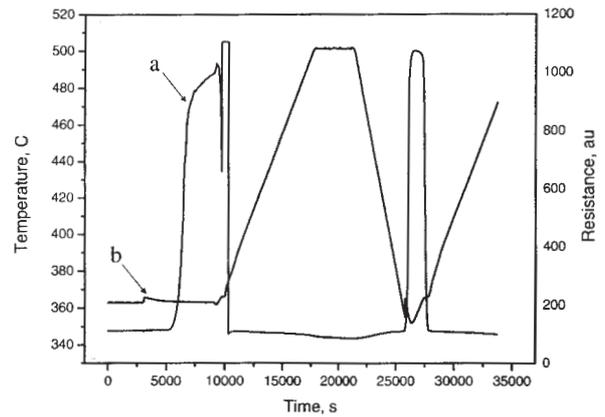


Fig. 3. Measured dependence of electrical resistance (a) and temperature (b) on time for PbBr_2 . At moment 25490 s the temperature of the cooled melt is equal to $T_M = 365^\circ\text{C}$ and after that moment the melt is in supercooled state. At moment 25791 s the temperature jumps to T_M , which indicates that the active nucleation process begins. The jump of the temperature is followed by the rapid growth of resistance.

Typical result of experiment is shown in Fig. 3. In this case, sample of PbBr_2 (with T_M of 639K) was overheated up to temperature 773K and then — after a certain time delay — melt has been controllably cooled down with rate of 1 C/min. As it can be seen, during whole cooling process resistivity of melt remains almost constant until solidification begins. At this moment, temperature jumps to value close to T_M (due to release of latent heat of the phase transition) and electrical resistance starts to grow. The behavior of the temperature and the electrical resistance can be seen in more details in Fig. 4. In

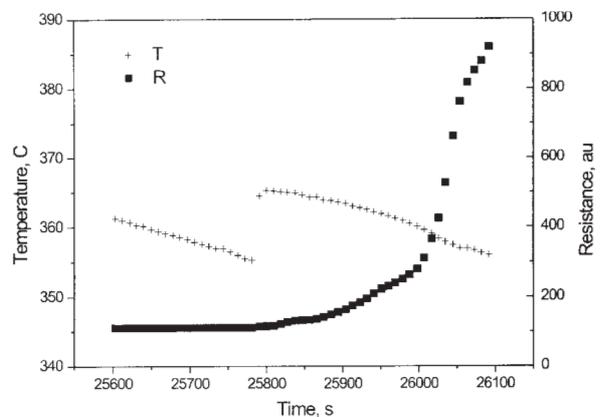


Fig. 4. Detailed picture of the first stage of the phase transition. Data on this figure represent a magnified part of the Fig. 3.

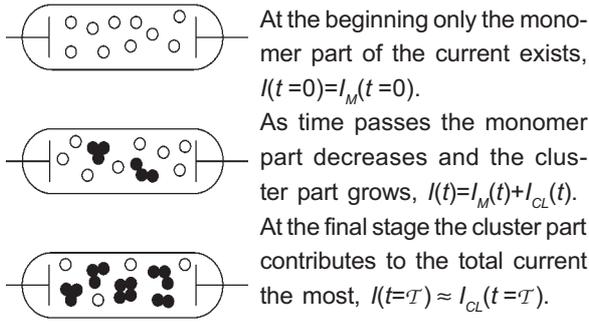


Fig. 5. Composition of the total electrical current at different moments.

order to explain such behavior we must determine total electrical current remembering that beside charged complexes also the clusters of a new solid phase as potential current carriers are formed within molten matter by nucleation.

4. THEORETICAL MODEL

Taking into account the complex-forming nature of halide melts we suppose that there are two types of charge carriers in the supercooled melt: charged complexes and clusters of a new solid phase. Consequently, total electric current $I(t)$ consists of two components:

$$I(t) = I_M(t) + I_{CL}(t). \quad (1)$$

Origin of the first one, $I_M(t)$, corresponds to charged elemental building units (monomers) of melt arising by decomposition of massive complexes during overheating; second part, $I_{CL}(t)$, of total current is made by nucleating clusters.

When nucleation starts, there are only monomers in the system and the total current is determined by $I_M(0)$, while at the end of the nucleation stage ($t = T$) the clusters part of the current prevails (see Fig. 5).

Within the framework of nonstationary nucleation theory we obtain for the total electrical current (for details see [20]):

$$I(t) = I(0) \left[1 - \frac{y^4(t) - 1}{y^4(T) - 1} \right] + I(T) \left[\frac{y^6(t) - 1}{y^6(T) - 1} \right]. \quad (2)$$

Here, $y(t)$ is a linear function of time, $y(t) = 1 + at$, where parameter a depends on rate of cluster growth and the critical cluster's size. First term on r.h.s. is formed by charged complexes and second one by charge carriers corresponding to nucleating clusters.

Having computed $I(t)$, the resistance of nucleating halide melt may be easily expressed to be:

$$I(t) = \left\{ \frac{1}{R(0)} \left[1 - \frac{y^4(t) - 1}{y^4(T) - 1} \right] + \frac{1}{R(T)} \left[\frac{y^6(t) - 1}{y^6(T) - 1} \right] \right\}, \quad (3)$$

where $R(0)$ (resp. $R(T)$) represents resistance of the melt (resp. of the solid state). Fig. 6 shows the comparison of experimental data with the theoretical dependencies (2) and (3).

5. TIME LAG

Time characteristics of nucleation can be represented by a time lag. There exist, however, different definitions of time lag. The widely used definition of the time lag determines the time, which is need for the system to achieve a state of steady growth [21]. Fig. 7 shows the typical time dependence of the integrated flux. At the beginning of the nucleation, the integrated flux is zero, then it starts to increase and after a certain delay changes linearly with time. The definition of the time lag τ itself is clear from the Fig. 7: τ is determined by the intersection of the tangent to the linear part of the integrated flux temporal dependence with the time axis.

From the theoretical model described in the previous section it follows that in our case the integrated flux $Z(t)$ is proportional to the electrical current $I(t)$. Consequently, we can determine the time lag τ of nucleation from the following relation (see Fig. 8):

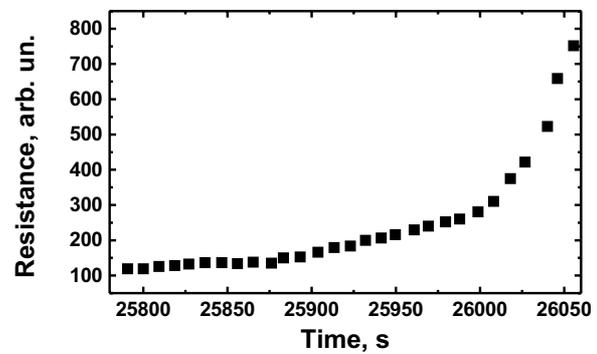


Fig. 6. Resistance of PbBr_2 melt as functions of time. Squares are experimental data, solid line represents the theoretical dependence (3) ($a = 0.1$).

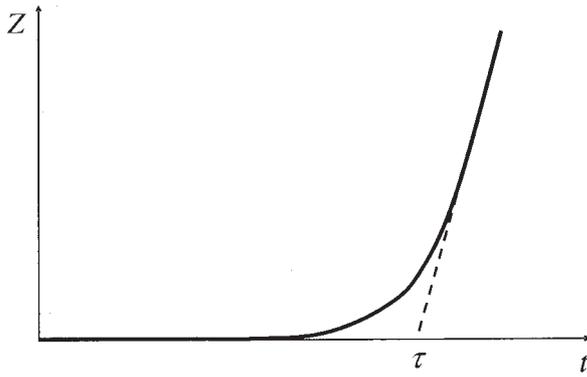


Fig. 7. Time dependence of integrated flux Z .

$$\tau = \mathcal{T} - \frac{I(\mathcal{T}) - I(0)}{\left. \frac{dI(t)}{dt} \right|_{t=\mathcal{T}}} \quad (4)$$

Substitution of (2) into (4) gives:

$$\tau \approx \mathcal{T} \left(1 - \frac{1}{6} \cdot \frac{\mathcal{R} - 1}{2/3\mathcal{R} - 1} \right), \quad (5)$$

where $\mathcal{R} = R(\mathcal{T})/R(0)$ and $y(\mathcal{T}) \gg 1$ is taken into account. One can see from (5) that the relative time lag τ/\mathcal{T} depends only on ratio of final and initial resistance \mathcal{R} . The initial resistance $R(0)$ represents just the resistance of the liquid phase, while $R(\mathcal{T})$ corresponds to resistance of the solid phase. Thus, as usual, $R(\mathcal{T}) \gg R(0)$ and $\mathcal{R} \gg 1$. Performing the limit $\mathcal{R} \rightarrow \infty$ in (5) we obtain:

$$\tau \approx \frac{3}{4} \mathcal{T}. \quad (6)$$

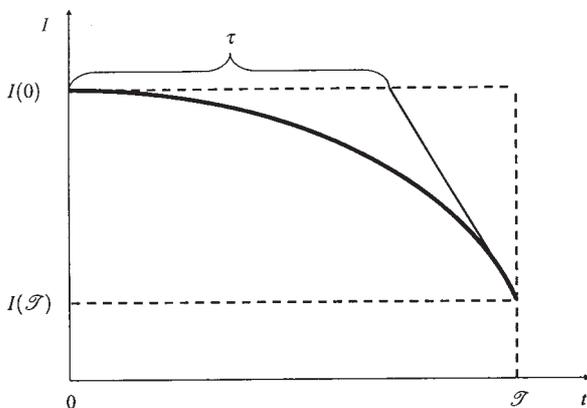


Fig. 8. Time lag of nucleation may be determined from the time dependence of the electrical current $I(t)$.

This means, that the time lag of homogeneous nucleation in supercooled halide melts equals approximately to 75% of the total duration of nucleation process itself. In Fig. 9 we compare the time lag measured experimentally with the theoretical value (6). (The initial overheating of the melt in this experiment was 155 C).

Deviation of the measured time lag from its theoretical value (5) (resp. (6)) allows to estimate the role of heterogeneous nucleation in the phase transition. The smaller is the relative time lag, the more significant is the heterogeneous mechanism of nucleation and the less is the quality of the produced crystal. There is, however, another application of expression (5) which is more important. The time lag τ estimates the time, when small particles of the new phase begin to appear in the ambient phase. After the time τ there is a certain number of embryos for the future crystals in the system, but the process of their growth just begins. If the conditions of the experiment remain constant, the nucleation process will continue, producing more nuclei and deteriorating the quality of the crystal. If, however, after the time τ the experimentalist changes the conditions of the experiment, the process of subsequent nucleation may be suppressed and only a relatively small number of nuclei already existing in the system will continue to grow. In this case, one can expect a better quality of the crystal. The expression (5) contains only parameters, values of which can be found in literature, and estimates the time when the conditions of the experiments are to be changed to improve the quality of the final crystal.

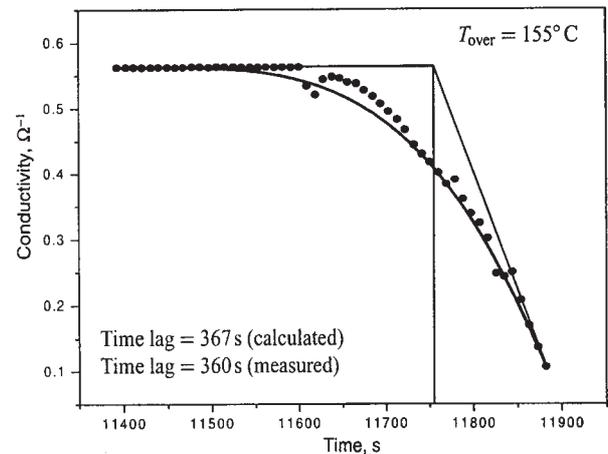


Fig. 9. Conductivity of PbBr_2 melt as a function of time. Circles represent experimental data, solid line is a theoretical curve (2). Initial overheating of the melt is 155 °C.

6. CONCLUSION

Measurements of the electrical resistance can provide additional information about the state of the supercooled halide melt. The theoretical model describing temporal changes of resistance is proposed. The model assumes that there are two contributions to the total electrical current in the supercooled melt: the monomers' component of the current and the clusters' one. From the obtained expressions one can determine the time lag of nucleation, which finds to be equal to 75% of the total duration of nucleation. The theoretical dependences are compared with experimental results for PbBr_2 melt.

ACKNOWLEDGEMENTS

This work was supported by the grant No. 202/03/0428 of the Grant Agency of the Czech Republic. P. Demo acknowledges support from the Ministry of Education, Youth and Sports of the Czech Republic (project J04/98:210000020).

REFERENCES

- [1] J. Huang and L. S. Bartell // *J. Phys. Chem.* **99** (1995) 3924.
- [2] E. Witten // *Phys. Rev. D* **30** (1984) 272.
- [3] C. L. Kelchner *et al.* // *Phys. Rev. B* **58** (1998) 11085.
- [4] J. C. Barrett and T. J. Baldwin // *J. Aerosol Sci.* **32** (2001) 957.
- [5] D. Chowahury *et al.* // *Phys. Rep.* **329** (2000) 199.
- [6] P. Demo and Z. Kožíšek // *Phys. Rev. B* **48** (1993) 3620.
- [7] F. C. Frank // *Proc. R. Soc. London* **A215** (1952) 43.
- [8] C. Kittel, *Introduction to Solid State Physics* (4th edition, J. Wiley and Sons, New York, London, Sydney, Toronto, 1975).
- [9] D. Holland-Moritz, D. M. Herlach and K. Urban // *Phys. Rev. Lett.* **71** (1993) 1196.
- [10] D. M. Herlach, F. Gillessen, T. Volkman, M. Wollgarten and K. Urban // *Phys. Rev. B* **46** (1992) 5203.
- [11] D. Holland-Moritz // *Mater. Sci. Eng. A* **304-306** (2001) 108.
- [12] D. Holland-Moritz, G. Jacobs and I. Egry // *Mater. Sci. Eng. A* **294-296** (2000) 369.
- [13] A. Filipponi, A. DiCicco and S. De Panfilis // *Phys. Rev. Lett.* **83** (1999) 560.
- [14] A. DiCicco, M. J. Rosolen, R. Marassi, R. Tossici, A. Filipponi and J. Rybicki // *J. Phys: Condens. Matter* **8** (1996) 10779.
- [15] A. DiCicco // *J. Phys.: Condens. Matter* **8** (1996) 9341.
- [16] D. R. Rosseinsky and K. Stead // *J. Phys. and Chem of Solids* **60** (1999) 697.
- [17] B. Vinet, J. P. Garandet and L. Cortella // *J. Appl. Phys.* **73** (1993) 3830.
- [18] D. R. Rosseinsky and K. Stead // *J. Phys. and Chem. of Solids* **60** (1999) 697.
- [19] B. Vinet, J. P. Garandet and L. Cortella // *J. Appl. Phys.* **73** (1993) 3830.
- [20] P. Demo, A. Sveshnikov, M. Rodová, K. Nitsch and Z. Kožíšek // submitted to *Phys. Rev. B* for publication.
- [21] D.T. Wu // *Solid State Physics* **50** (1997) 38.