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Kinetics of non-isothermal crystallization process and activation energy for crystal growth in amorphous materials

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An equation expressing the volume fraction, x, of crystals precipitating in a glass heated at a constant rate, α, was derived. When crystal particles grow m-dimensionally, x is expressed as

$$\ln[-\ln(1-x)] = -n\ln\alpha - 1.052m\frac{E}{RT} + \text{Constant}$$

where E is the activation energy for crystal growth and n is a numerical factor depending on the nucleation process. When the nuclei formed during the heating at the constant rate, α, are dominant, n is equal to $m+1$, and when the nuclei formed in the previous heat-treatment before thermal analysis run are dominant, n is equal to m. The validity and usefulness of this equation was ascertained by applying it to a $Li_2O\cdot 2SiO_2$ glass. A method for determining the values of n and m from DSC curves was proposed and it was concluded that the modified Ozawa-type plot is very useful and convenient to obtain the activation energy for crystal growth.

1. Introduction

Thermal analysis is a very useful tool for studying the kinetics of chemical reactions and crystallization of glass as it is a rapid and convenient means. Many authors used the so-called Kissinger plot [1] or Ozawa plot [2] directly to examine the kinetics of crystallization of amorphous materials. These methods, however, cannot be directly applied to the crystallization of amorphous materials and the physical meaning of the activation energies thus obtained are obscure because the crystallization is advanced not by the n-th order reaction but by the nucleation and growth process. On the other hand, some authors applied the Johnson–Mehl–Avrami (JMA) equation to the non-isothermal crystallization process [3–10]. Although sometimes they appeared to get reasonable activation energies, this procedure is not appropriate because the JMA equation was derived for isothermal crystallization [11].

Matusita and Sakka [12–14] have proposed a method for analysing the non-isothermal crystallization kinetics on the basis of nucleation and growth process, and emphasized that the crystallization mechanism such as bulk crystallization or surface crystallization, should be taken into account for obtaining the meaningful activation energy. In the present study, the equation expressing the non-isothermal crystallization was derived more rigorously than the equation reported previously [12–14], and the method for determining the activation energy for crystal growth from DSC curves of various heating rates was proposed.

2. Theoretical analysis

Usually, the rate of crystal nucleation in glass reaches the maximum at a temperature somewhat higher than the glass transition temperature and then decreases rapidly with increasing temperature, while the rate of crystal growth reaches the

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maximum at a temperature much higher than the temperature at which the nucleation rate is highest [15]. When a glass is heated at a constant rate, crystal nuclei are formed only at lower temperatures and crystal particles grow in size at higher temperatures without any increase in number [16, 17].

In the case of a quenched glass containing no nuclei, the number, N, of nuclei formed per unit volume in the course of heating from room temperature, T_r, to a temperature, T, is inversely proportional to the heating rate, $\alpha = \mathrm{d}T/\mathrm{d}t$.

$$N = \int_0^t I(T)\mathrm{d}t = \frac{1}{\alpha}\int_{T_r}^{T} I(T)\mathrm{d}T = \frac{N_0}{\alpha}. \quad (1)$$

In the case of a glass which was heated previously at the temperature of maximum nucleation rate for sufficiently long time, a large number of nuclei already exist and N is not dependent on α.

The rate of crystal growth, U, is expressed by [15]

$$U = U_0 \exp(-E/RT) \quad (2)$$

where E is the activation energy for crystal growth. The radius, r, of a crystal particle is expressed as

$$r = \int_0^t U(T)\mathrm{d}t = \frac{U_0}{\alpha}\int_{T_r}^{T}\exp(-E/RT)\mathrm{d}T. \quad (3)$$

This integral cannot be expressed by an elementary function, and a rough approximation was made in previous reports [12–14]. In the present study, this integral is evaluated to a closer approximation by using the Doyle's p-function [18, 19].

$$p(y) = \int_y^{\infty}\frac{\exp(-y)}{y^2}\,\mathrm{d}y. \quad (4)$$

This function was tabulated numerically and if y is larger than 20, this function is expressed to a close approximation as [18, 19]

$$\log p(y) = -2.315 - 0.4567y. \quad (5)$$

Rewriting the variable, $y = E/RT$, Equation 4 can be rewritten as

$$p\left(\frac{E}{RT}\right) = \frac{R}{E}\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T. \quad (6)$$

From Equations 3, 5 and 6,

$$r = \frac{C}{\alpha}\exp\left(-1.052\frac{E}{RT}\right). \quad (7)$$

When crystal particles grow three-dimensionally, the variation of crystal volume fraction, x, is expressed by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = (1-x)N4\pi r^2\frac{\mathrm{d}r}{\mathrm{d}t} \quad (8)$$

where $(1-x)$ is the correction factor for the impingement of crystal particles and reduction of glass phase. This factor was also used to derive the JMA equation [11]. Integration of Equation 8 leads to $-\ln(1-x) = (4\pi/3)Nr^3$ and replacing with Equation 7 leads to

$$-\ln(1-x) = C_0N\alpha^{-3}\exp\left(-1.052\times 3\frac{E}{RT}\right). \quad (9)$$

In the case of a quenched glass containing no nuclei, N is inversely proportional to α as is the case of equation 1, this is converted to

$$-\ln(1-x) = C_0N_0\alpha^{-4}\exp\left(-1.052\times 3\frac{E}{RT}\right). \quad (10)$$

In more general expressions, these are expected as

$$-\ln(1-x) = K_1\alpha^{-n}\exp\left(-1.052m\frac{E}{RT}\right). \quad (11)$$

Similarly, the variation of crystal volume fraction is derived as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = K_2(1-x)\alpha^{-(n-1)}\exp\left(-1.052m\frac{E}{RT}\right). \quad (12)$$

Here, $n = m + 1$ for a quenched glass containing no nuclei and $n = m$ for a glass containing a sufficiently large number of nuclei. Also, $m = 3$ for three-dimensional growth of crystal particles, $m = 2$ for two-dimensional growth, for example, in a thin film glass, and $m = 1$ for one-dimensional growth, for example, in a fibre glass or surface crystallization. These are shown schematically in Fig. 1. The n-value can be obtained from the plot of ln $[-\ln(1-x)]$ against ln α at a specific temperature. Theoretically, the maximum value of n is 4 and minimum value is 1, and in these cases,

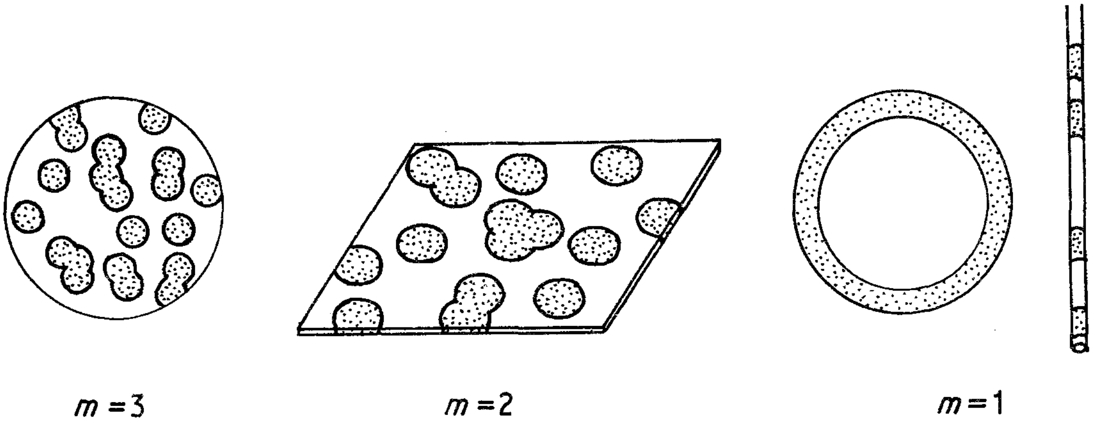

Figure 1 Schematic representation of the growth mechanism of crystal particles.

the corresponding m-values must be 3 and 1, respectively. But when $n = 2$, the corresponding m-value is 2 or 1, and when $n = 3$, the corresponding m-value is 3 or 2. One way for determining the m-value is to observe the change of n with reheating at the nucleation temperature. If n does not change with reheating, a large number of nuclei exist already in the specimen and $n = m$. If n decreases with reheating, not so many nuclei exist in the specimen. In this case, $m < n \leqq m + 1$ before reheating and $n = m$ after reheating.

In order to obtain the activation energy, Equation 11 is rewritten as

$$\ln\alpha = -1.052\frac{m}{n}\frac{E}{RT} - \frac{1}{n}\ln[-\ln(1-x)] + \text{constant}. \tag{13}$$

Thus the plot of $\ln\alpha$ against $1/T$, where T is the temperature at which the crystal volume fraction reaches a specific value, gives a straight line and the slope gives the value of $1.052(m/n)E$. This plot is very similar to the so-called Ozawa plot [2] which was derived for chemical reactions, so, we may call this a modified Ozawa-type plot. The activation energy can be obtained when the ratio m/n is known. Since it is known that the volume fraction of crystals at the peak temperature, T_0, in DSC or DTA curves is almost the same irrespective of α [14], this equation should apply for the peak temperature.

The rate of increase of x reaches its maximum at a temperature T_0. Solving Equation 12 for $\mathrm{d}(\mathrm{d}x/\mathrm{d}t)/\mathrm{d}t = 0$, the following equation is derived;

$$\ln\left(\frac{\alpha^n}{T_0^2}\right) = -1.052m\frac{E}{RT_0} + \text{constant}. \tag{14}$$

This is very similar to the so-called Kissinger equation [1] when $n = m = 1$, so we call this a modified Kissinger-type equation. Usually, the change of $\ln T_0^2$ with α is negligibly small compared with the change of $\ln \alpha^n$, and, therefore, the modified Kissinger-type Equation 14 is essentially the same as the modified Ozawa-type Equation 13.

3. Experimental procedures

Glass of the composition $Li_2O\cdot 2SiO_2$ (mole ratio) was used. The mechanism and kinetics of crystallization of this glass are already well known, and the rate of crystal nucleation reaches its maximum at about 460° C [20, 21]. The DSC measurements were made with Rigaku Denki thermal analysis apparatus which has a platinum sample holder of 4 mm inner diameter and 2 mm depth. Bulk glass, instead of powder, was used to avoid the effects of particle radius distribution. To fill the sample holder with glass, a glass melt of 90 mg was poured into it, remelted in an electric furnace at 1400° C for 20 min, and allowed to cool in air. Some of the samples were heated at 462° C for 46 h in order to form a large number of nuclei. It was ascertained by X-ray diffraction that no crystalline peaks were detected after the nucleation treatment. Alumina powder was used as a reference material and the heating rates used were 0.25, 0.5, 1 and 2° C min^{-1}. When the heating rate was higher than 2° C min^{-1}, the specimen temperature increased more rapidly than the settled heating rate due to the latent heat of crystallization.

4. Analysis of experimental results

The volume fraction, x, of crystal was obtained

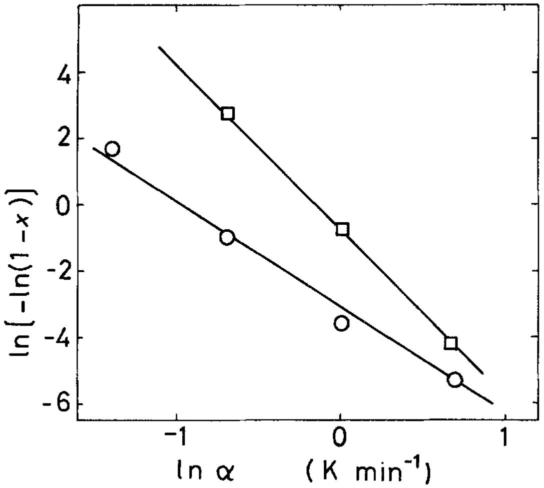

Figure 2 Variation of ln[$-$ln(1 $-x$)] with natural logarithm of heating rate. □: Quenched glass; 600° C. ○: Reheated glass; 560° C.

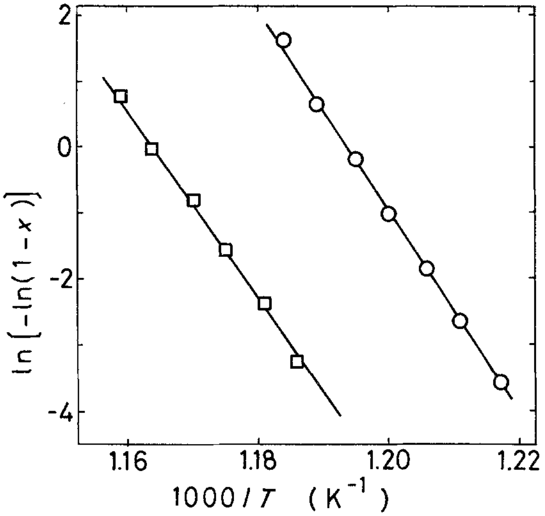

Figure 3 Variation of ln[$-$ln(1 $-x$)] with reciprocal temperature for heating rate of 0.5 K min^{-1}. □: Quenched glass; ○: Reheated glass.

as a function of temperature from the area under DSC curve as described previously [12].

Fig. 2 shows the relation between ln[$-$ln(1 $-$ x)] and ln α for quenched glass at 600° C and reheated glass at 560° C. According to Equation 11, the slope of these lines give the n-value, and it was found that $n = 4.3$ for the quenched glass and $n = 3.1$ for the reheated glass. Allowing for experimental error, these values are close to 4 and 3, respectively. This indicates that $m = 3$, that is the crystal particles grow three-dimensionally. Fig. 3 shows the variation of ln[$-$ln(1 $-$ x)] with the reciprocal temperature, as examples, of quenched and reheated glasses for $\alpha = 0.5°$ C min^{-1}. According to Equation 11, the slopes of these straight lines should give the activation energy for crystal growth. The activation energies thus obtained are shown in Table 1.

Fig. 4 shows the relation between ln α and the reciprocal temperature at which the volume fraction of crystal reaches 0.3 and 0.7. According to Equation 13, this plot should give the $(m/n)E$, namely, $(3/4)E$ for quenched glasses and E for reheated glasses. Fig. 5 shows the relation between lnα and $1/T_0$, where T_0 is the peak temperature in DSC curve. Since the volume fraction of crystal at T_0 is the same irrespective of α, this plot should give the same information as Fig. 4. The activation energies thus obtained are shown in Table II.

5. Discussion

The crystallization kinetics and mechanism of $Li_2O{\cdot}2SiO_2$ glass are already well known, and the activation energy for crystal growth in this glass is equal to that for viscous flow. The viscosity, η(poise), of this glass is expressed by the Fulcher equation [22]:

$$\log\eta = -1.44 + \frac{3.37 \times 10^3}{T - 460}. \qquad (15)$$

TABLE I Activation energy for crystal growth, E, obtained from the plot of ln[$-$ln(1 $-x$)] against $1/T$ and the activation energy for viscous flow, E_η, in the temperature region where exothermic peaks are found

	α(° C min⁻¹)			
	0.25	0.5	1.0	2.0
Quenched glass				
E(kcal mol^{-1})		92	91	84
E_η(kcal mol^{-1})		73	69	66
		(570–595° C)	(585–615° C)	(605–635° C)
Reheated glass				
E(kcal mol^{-1})	110	97	96	73
E_η(kcal mol^{-1})	79	77	75	73
	(540–560° C)	(545–575° C)	(560–585° C)	(565–600° C)

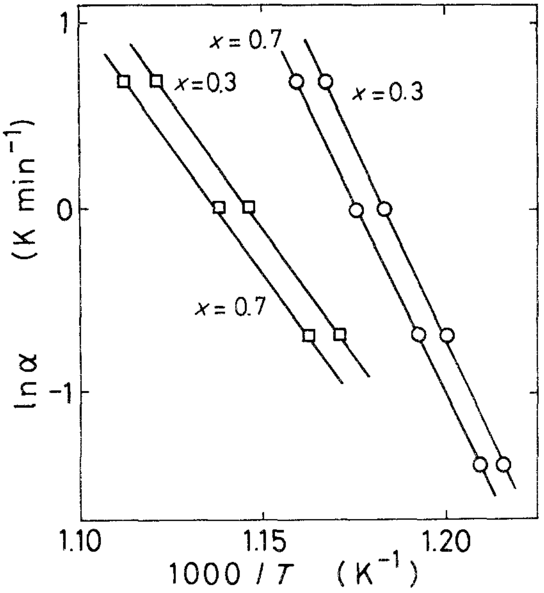

Figure 4 Modified Ozawa-type plot. □: Quenched glass, ○: Reheated glass.

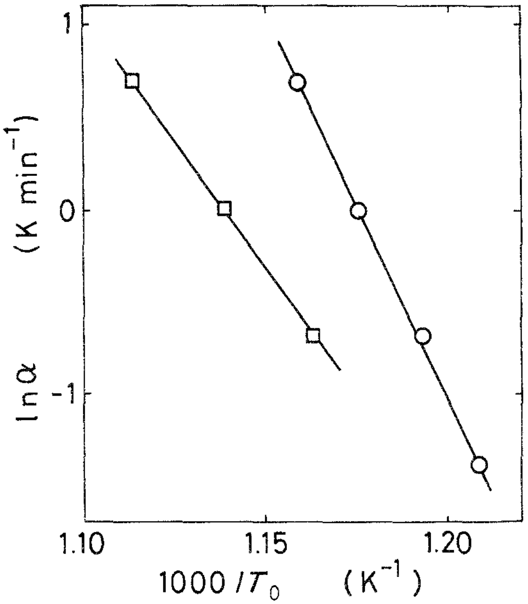

Figure 5 Relation between natural logarithm of heating rate and reciprocal of peak temperature in DSC curve. □: Quenched glass, ○: Reheated glass.

The activation energy for viscous flow, E_η, can be calculated as a function of temperature. The calculated E_η in the corresponding temperature ranges of exothermic peaks in the DSC curves are shown in Tables I and II together with those for crystal growth, E, obtained from DSC curves.

It is seen that the activation energy, E, obtained from the modified Ozawa-type plot, the plot of $\ln \alpha$ against $1/T$, are very close to E_η as shown in Table II, indicating the validity of the Equation 13. However, those obtained from the plot of $\ln[-\ln(1-x)]$ against $1/T$ in Fig. 3 are much higher than corresponding E_η as shown in Table I. The reason of this discrepancy is not clear. The left hand side of Equation 11 is a function of only x. However, the correct function may not be $\ln(1-x)$, in other words, the correction factor in Equation 8 may not be $(1-x)$. Moreover, it is not adequate to obtain the activation energy for crystal growth from a single DSC curve, and the energy should be obtained from several DSC curves of different heating rates by using the modified Ozawa-type plot or modified Kissinger-type plot.

So far, a number of authors have examined the crystallization kinetics of amorphous materials, such as oxide glasses [5–6, 23–25], chalcogenide glasses [26–29] and amorphous metals [3, 7, 30–33] by thermal analysis. Many of them used the so-called Kissinger plot or Ozawa plot without considering the crystallization mechanism thoroughly. Therefore, the physical meaning of the activation energies thus obtained are sometimes obscure and lead to misunderstandings. Even with the same glass, the crystallization

TABLE II Activation energy for crystal growth, E, obtained from the modified Ozawa-type plot and the activation energy for viscous flow, E_η, in the temperature region where exothermic peaks are found

Volume fraction	$(m/n)E$ (kcal mol^{-1})	E (kcal mol^{-1})	E_η (kcal mol^{-1})
Quenched glass		$(m/n = \frac{3}{4})$	
0.3	53	71	69
0.7	52	69	(580–630° C)
peak temperature	53	71	
Reheated glass		$(m/n = 1)$	
0.3	80	80	76(540–590° C)
0.7	78	78	
peak temperature	78	78	

mechanism changes with the sample size as reported previously [13, 25] and with the thermal history as is found in the present study, and, therefore, the apparent activation energies obtained from the so-called Kissinger plots of Ozawa plots do not agree in different cases.

Recently, some authors [3–10] developed a convenient method for obtaining the activation energy for crystallization, starting from the Johnson–Mehl–Avrami equation which was derived for isothermal crystallization. Although their methods seem to give reasonable activation energies in some cases, they must be restricted to the case of $m/n = 1$.

The Equation 11 in the present study was derived for non-isothermal conditions and a more exact approximation was made by using the Doyle's p-function. It was found that, in order to obtain the activation energy for crystal growth, the crystallization mechanism and especially the ratio of m/n should be known, and in this respect, the modified Ozawa-type plot was very useful and convenient.

6. Summary

The equation correlating the thermal analysis curve with heating rate and the activation energy for crystal growth was derived more precisely than previously. The validity of this equation was tested by applying it to the crystallization of $Li_2O \cdot 2SiO_2$ glass. The crystallization mechanism should be known in order to obtain a meaningful activation energy and it is very useful and convenient to use the modified Ozawa-type plot.

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References

1. H. E. KISSINGER, *Anal. Chem.* **29** (1957) 1702.
2. T. OZAWA, *J. Thermal Anal.* **2** (1970) 301.
3. J. COLMENERO and J. M. BARANDIARÁN, *J. Non-Cryst. Solids* **30** (1979) 263.
4. J. COLMENERO and J. ILARRAZ, *Thermochim. Acta* **35** (1980) 381.
5. A. MARROTA, A. BURI, F. BRANDA and S. SAIELLO, "Advances in Ceramics, Vol. 4, Nucleation and Crystallization in Glasses", edited by J. H. Simmons, D. R. Uhlmann and G. H. Beall (The American Ceramic Society, Coulombus, 1982) pp. 146–152.
6. A. MARROTA, S. SAIELLO, F. BRANDA and A. BURI, *J. Mater. Sci.* **17** (1982) 105.
7. A. LUCCI, L. BATTEZZATI, C. ANTONIONE and G. RIONTINO, *J. Non-Cryst. Solids* **44** (1981) 287.
8. D. W. HENDERSON, *ibid.* **30** (1979) 301.
9. E. M. MARSEGLIA, *ibid.* **41** (1980) 31.
10. K. HARNISCH and R. LANZENBERGER, *ibid.* **53** (1982) 235.
11. M. E. FINE, "Introduction to Phase Transformation in Condensed System" (Macmillan, New York, 1964) Chap. 3.
12. K. MATUSITA and S. SAKKA, *Phys. Chem. Glasses* **20** (1979) 81.
13. *Idem, J. Non-Cryst. Solids* **38/39** (1980) 741.
14. *Idem, Bull. Inst. Chem. Res. Kyoto Univ.* **59** (1981) 159.
15. D. TURNBULL and M. H. COHEN, "Modern Aspects of the Vitreous State", edited by J. D. Mackenzie (Butterworth, London, 1960) pp. 38–62.
16. K. MATUSITA and M. TASHIRO, *Phys. Chem. Glasses* **14** (1973) 77.
17. K. MATUSITA, T. MAKI and M. TASHIRO, *ibid.* **15** (1974) 106.
18. C. D. DOYLE, *J. Appl. Polym. Sci.* **5** (1961) 285.
19. *Idem, ibid.* **6** (1962) 639.
20. K. MATUSITA and M. TASHIRO, *J. Non-Cryst. Solids* **11** (1973) 471.
21. E. G. ROWLANDS and P. F. JAMES, *Phys. Chem. Glasses* **20** (1979) 1 & 9.
22. K. MATUSITA and M. TASHIRO, *Yogyo-Kyokai-Shi* **81** (1973) 500.
23. N. K. CHAKRABORTY, S. K. DAS, S. K. NIYOGI and R. L. THAKUR, Proceed. Xth ICG, No. 14 (The Ceramic Society of Japan, Tokyo, 1974) pp. 75–82.
24. J. GÖTZ, *Phys. Chem. Glasses* **18** (1977) 32.
25. A. MARROTA, A. BURI and F. BRANDA, *Thermochim. Acta* **40** (1980) 397.
26. S. RISBUD, *J. Amer. Ceram. Soc.* **56** (1973) 440.
27. K. MATSUURA and K. SUZUKI, *J. Mater. Sci.* **14** (1979) 395.
28. D. D. THORNBURG and R. I. JOHNSON, *J. Non-Cryst. Solids* **17** (1975) 2.
29. A. H. ABOUELELA, M. K. ELMOUSLY and K. S. ABDU, *J. Mater. Sci.* **15** (1980) 871.
30. J. A. LEAKE and A. L. GREER, *J. Non-Cryst. Solids* **38/39** (1980) 735.
31. C. ANTONIONE, L. BATTEZZATI, A. LUCCI, G. RIONTINO and G. VENTURELLO, *Scripta Metall* **12** (1978) 1011.
32. A. INOUE, Y. TAKAHASHI, C. SURYANARAYANA, T. MASUMOTO, *J. Mater. Sci.* **17** (1982) 3253.
33. Z. ALTOUNIAN, T. GUO-HUA and J. O. STROM-OLSEN, *J. Appl. Phys.* **53** (1982) 4755.

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