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Analysis of Thermal Shock during Rapid Crystal Extraction from Melts

A time-dependent stress field in LiNbO_3 and SrLaAlO_4 single crystals immediately after their extraction from melts has been found analytically. Numerical calculations show that during rapid extraction from melts the crystals are subjected to thermal shock which can be high enough to produce considerable dislocation density if there exists a plasticity zone or to induce cracks. During LiNbO_3 crystal growth by the Czochralski method in a low temperature gradient high thermal stresses occur near the interface at the center and at the crystal periphery. After rapid extraction from the melt the thermal shock results in an increase in thermal stress over an order of magnitude. This can lead to the generation of high dislocation density at the bottom part of LiNbO_3 crystal causing residual stress distribution after its cooling to room temperature. Times for the relaxation of stresses caused by the thermal shock are about 30 minutes and 30 seconds for 55 mm diameter LiNbO_3 crystal and for 20 mm diameter SrLaAlO_4 crystal, respectively. The magnitude and relaxation time of the stress caused by the thermal shock depend mainly on the crystal diameter, its thermal conductivity and the axial temperature gradient in the growth system. From analytical investigations a suitable method of crystal extraction from the melt may be obtained.

Keywords: thermal shock; thermal stress; Czochralski growth; LiNbO_3 ; SrLaAlO_4

1. Introduction

Crystal growth by the Czochralski technique has to be accomplished by crystal separation from a melt. In some cases, especially for small crystal diameter or for convex crystal–melt interface, crystal is separated by rapid extraction. During the extraction process crystal always undergoes a thermal shock, which depends on operating parameters and thermophysical properties of the grown crystal.

A large thermal stress caused by the thermal shock can produce cracks or dislocations in the bottom part of the crystal if it has a plasticity zone. Mostly, oxide crystals cannot be deformed plastically (BRICE 1977) and excessive thermal shock results in cracking. However, some of them, like LiNbO_3 (VERE), have very narrow plasticity zone just below the melting point and dislocations can be produced in crystals near the interface if thermal stress exceeds some critical value.

VERE and PARK et al. have examined mechanical twinning and cracking in LiNbO_3 crystals. BRICE has presented simple theoretical model of maximum thermal strain induced in oxide crystals. Similar considerations, supported by experimental results, have been reported by GALAZKA. It has been demonstrated that cracking of LiNbO_3 crystals depends strongly on axial temperature gradient in the vicinity of the crystal–melt interface and it is caused by non-linearity of radial temperature profile in the crystals. MIYAZAKI et al. (1996,

1997 b) have studied theoretically the thermal stress distribution during Czochralski growth of LiNbO_3 and Gd_2SiO_5 crystals, respectively. To calculate thermal and von Mises stress fields the authors used stress-strain relations, the given temperature distribution and the shape of the interface. According to their results stress field strongly depends on the temperature distribution in the crystal, the shape of interface and the crystal orientation. It was found that high von Mises stress occurs at the centre and near the periphery of the crystal. The stress can reach a large value, which can produce dislocations or cracks in the crystal. Recently, MIYAZAKI et al. (1997 a) studied thermal shock cracking of LiNbO_3 single crystals. They heated LiNbO_3 specimen to about 470 K in a bath of oil, and induced thermal shock by plunging room temperature oil onto the oil bath. They observed that failure initiates from LiNbO_3 specimen sidewall, and most of the crack planes coincide with the $\{01\bar{1}2\}$ cleavage planes. The authors also found that the probability of thermal shock cracking is very small if the normal stress on the $\{01\bar{1}2\}$ cleavage planes is lower than 10 MPa.

Most of the previous investigations of stress fields considered stress distribution during crystal growth. However, analysis of thermal stress during crystal extraction from the melt has been not studied so far. Taking into account thermophysical properties of oxide crystals (for instance, low thermal conductivity) it can be deduced that their extraction from the melt should cause a large thermal shock.

In this paper evaluation of thermal stress in LiNbO_3 and SrLaAlO_4 crystals immediately after their extraction from melts, in comparison with stress distribution just before extraction, is presented. Some preliminary results of such a modeling have recently been presented elsewhere (BAJOR, GALAZKA). It should be noted that, due to the assumptions used for an idealized case (neglecting anisotropy of crystals, planar interface), the present investigation should be treated as semi-qualitative.

2. Temperature and stress fields

To find stress distribution, first temperature field in the crystal has to be found by solving time-dependent heat transport equation, provided that a radiative heat transport through the crystal can be neglected. To handle the mathematical problem, many simplifying assumptions have to be made. In the model considered here the crystal is cylindrical in shape with planar top end and flat interface. At the top on the lateral surfaces and on interface (after crystal extraction from the melt) heat is transferred by Newton's law of cooling. At the interface the temperature is equal to the melting point isotherm T_m . It is assumed that thermophysical properties of crystals do not depend on temperature and a quasi-steady state is achieved during crystal growth. After crystal extraction from the melt unsteady state is analyzed. Temperature distribution during the Czochralski crystal growth is governed by the conduction heat transport equation which can be expressed in cylindrical coordinates as follows:

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} = \frac{\rho c_p}{k} \left(\frac{\partial T}{\partial t} \right), \quad (1)$$

where ρ is the density of the solid state, c_p is the heat capacity and k is the thermal conductivity. The boundary conditions after a rapid extraction of crystal from the melt are the following:

$$T = T_m, \quad (z = 0, t = 0); \quad (2a)$$

$$k \frac{\partial T}{\partial r} + h(T - T_a) = 0, (r = a); \tag{2b}$$

$$k \frac{\partial T}{\partial z} + h(T - T_m) = 0, (z = l); \tag{2c}$$

$$k \frac{\partial T}{\partial z} - h(T - T_a) = 0, (z = 0, t > 0); \tag{2d}$$

where h is the heat transfer coefficient, l is the crystal length, a is the crystal radius, and T_a is the ambient temperature. The boundary conditions denote that the crystal is extracted from the melt in infinitely short time so that for $t = 0$ temperature is equal to the melting point T_m (2a) and immediately the bottom part of the crystal is quenched to the ambient temperature T_a (2d).

To calculate the stress field it is assumed that stress levels are dominated by radial temperature gradient within the crystal. This assumption is widely used for semiconductors (ZOU et al.), and is also fulfilled for oxides if the crystal length is greater than its diameter. Following above the assumption, the stress field is calculated by integration of thermal field within the cylindrical body:

$$\sigma_r = \frac{\beta E}{1-\nu} \left(\frac{1}{a^2} \int_0^a T(r, z, t) r dr - \frac{1}{r^2} \int_0^r T(r, z, t) r dr \right), \tag{3a}$$

$$\sigma_\theta = \frac{\beta E}{1-\nu} \left(\frac{1}{a^2} \int_0^a T(r, z, t) r dr + \frac{1}{r^2} \int_0^r T(r, z, t) r dr - T(r, z, t) \right), \tag{3b}$$

$$\sigma_z = \frac{\beta E}{1-\nu} \left(\frac{2}{a^2} \int_0^a T(r, z, t) r dr - T(r, z, t) \right), \tag{3c}$$

where σ_r , σ_z and σ_θ are the radial, axial and azimuthal stress components, E is the Young modulus, ν is the Poisson ratio and β is the thermal expansion coefficient. The stress field after rapid crystal extraction from the melt is the following:

$$\sigma_r = \frac{\beta E(T_m - T_a)}{1-\nu} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} A_{mn} \left[\frac{J_1(\gamma_m)}{\gamma_m} - \frac{J_1(\gamma_m r/a)}{\gamma_m r/a} \right] D_{mn}(z, t), \tag{4a}$$

$$\sigma_\theta = \frac{\beta E(T_m - T_a)}{1-\nu} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} A_{mn} \left[\frac{J_1(\gamma_m)}{\gamma_m} + \frac{J_1(\gamma_m r/a)}{\gamma_m r/a} - J_0(\gamma_m r/a) \right] D_{mn}(z, t), \tag{4b}$$

$$\sigma_z = \frac{\beta E(T_m - T_a)}{1-\nu} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} A_{mn} \left[\frac{2J_1(\gamma_m)}{\gamma_m} - J_0(\gamma_m r/a) \right] D_{mn}(z, t) \tag{4c}$$

where

$$A_{mn} = \frac{2lB^2}{a\mu_n(B^2 + \gamma_m^2)J_0(\gamma_m)}, \tag{5}$$

$$D_{mn}(z, t) = \left[\frac{a\mu_n}{lB} \cos\left(\frac{z}{l}\mu_n\right) + \sin\left(\frac{z}{l}\mu_n\right) \right] \exp\left[-\left(\gamma_m^2 + \frac{a^2\mu_n^2}{l^2} \right) \frac{t}{\tau} \right], \tag{6}$$

γ_m and μ_n are the m -th and the n -th root of the equations $\gamma_m J_1(\gamma_m) = B J_0(\gamma_m)$ and $Tan(\mu_n) = 2a l B \mu_n / [(a \mu_n)^2 - (l B)^2]$, respectively, $B = ah/k$ is Biot the number, $\tau = \rho c_p a^2 / k$ is a time constant, and $J_0(\gamma_m)$ and $J_1(\gamma_m)$ are Bessel functions of the first kind of orders zero and one, respectively.

3. Numerical results and discussion

Although some properties of oxide crystals (elastic constants, thermal expansion coefficients) are anisotropic, the present analysis is axisymmetrical. For a cylindrical, axisymmetrical crystal the absolute maximum of the stress is located near the lateral surface of the crystal and is determined by radial, or tangential stress component. Therefore, to find the maximum of the thermal shock during rapid crystal extraction it is sufficient to analyze one of these components, for example, axial component.

For calculations, the thermophysical data and real operating parameters for LiNbO₃ and SrLaAlO₄ listed in Table 1 were used. Some of the thermophysical data of SrLaAlO₄ are somewhat arbitrary.

Description (unit)	Symbol	Value	
		LiNbO ₃	SrLaAlO ₄
Density (g cm ⁻³)	ρ	4.65	5.924
Heat capacity (J g ⁻¹ K ⁻¹)	c_p	0.6	0.104
Melting point (°C)	T_m	1253	1640
Thermal conductivity (W cm ⁻¹ K ⁻¹)	k	1.1*10 ⁻²	average 4.12*10 ⁻²
Crystal emissivity	ϵ	0.1	0.1
Thermal expansion coefficient (K ⁻¹)	α_c	2*10 ⁻⁶	1.71*10 ⁻⁵
	α_a	16*10 ⁻⁶	0.76*10 ⁻⁵
Young modulus (Pa)	E	2.32*10 ¹¹	2.64*10 ¹¹
Poisson ratio	ν	0.26	0.26
Convective heat transfer coefficient (W cm ⁻² K ⁻¹)	h_{con}	4.0*10 ⁻²	3.84*10 ⁻²
Radiative heat transfer coefficient (W cm ⁻² K ⁻¹)	h_{rad}	0.7*10 ⁻²	1.24*10 ⁻²
Total heat transfer coefficient (W cm ⁻² K ⁻¹)	h	4.7*10 ⁻²	5.08*10 ⁻²
Crystal length (cm)	l	8	5.5
Crystal radius (cm)	a	2.75	1
Growth rate (cm h ⁻¹)	f	0.36	0.1
Temperature above melt surface (°C)	T_o	1243	1630
Temperature at the cold end of the crystal (°C)	T_c	1220	1465
Biot number	$B = a h/k$	11.75	1.24
Peclet number	$P = a f \rho c_p / k$	0.046	0.0004

Tab.1: Thermophysical properties and operating parameters used for calculations.

In fig.1 axial stress component distribution just before LiNbO_3 crystal extraction from the melt is shown. In the central part of the crystal ($r = 0$) and near the interface ($z = 0$) the axial stress is negative, and on the periphery its positive value exceeds 20 MPa. The maximum value of the axial stress is not sufficient to generate cracks.

In fig.2 the time-dependent changes of the axial stress component in LiNbO_3 crystal on the periphery after its rapid extraction from the melt are presented. The figure shows that thermal shock results in an increase in the axial stress over an order of magnitude to the maximum value after about 1 min (t_{max}), and then decreases gradually to the same value as before extraction after about 15 min. The total time of relaxation of the stress caused by the thermal shock is about 30 minutes.

If the value of breaking strain is known, it is possible to find conditions for obtaining crack-free crystals. For LiNbO_3 crystals the maximum axial stress should not exceed a value of about 50 MPa. According to fig. 2 we can see that a rapid extraction of LiNbO_3 crystal from the melt could result in cracks on lateral surfaces. Therefore, 55 mm diameter LiNbO_3 crystal should be extracted over a period of at least 15 minutes.

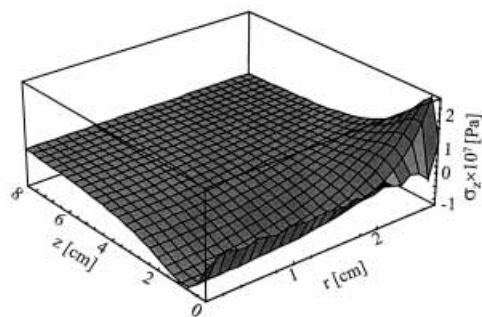


Fig. 1: Axial stress component distribution in an LiNbO_3 crystal just before its extraction from the melt (Z - axis: [0001]).

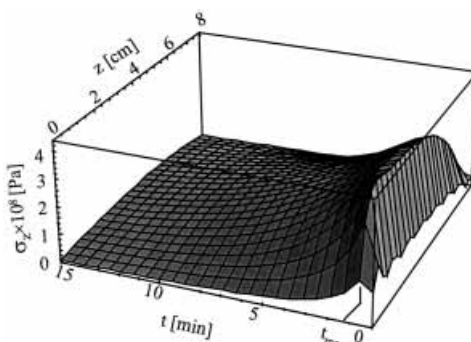


Fig. 2: Time-dependent changes of axial stress component in LiNbO_3 crystal on its periphery ($r = a$) after extraction from the melt (Z - axis: [0001]).

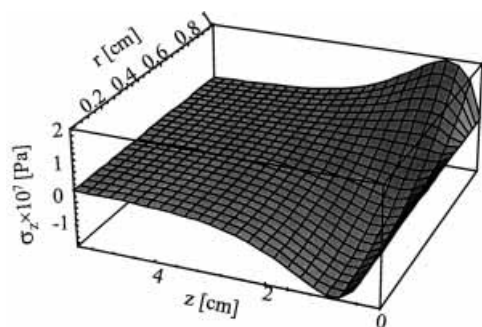


Fig. 3: Axial stress component distribution just before SrLaAlO_4 crystal extraction from the melt (c - axis: [001]).

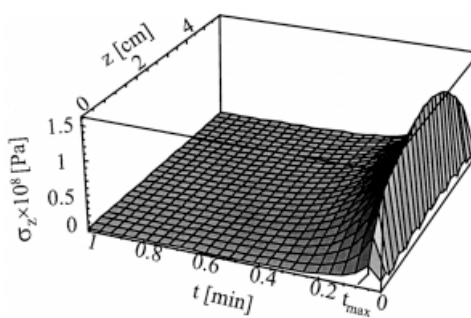


Fig. 4: Time-dependent changes of axial stress component on the periphery after SrLaAlO_4 crystal extraction from the melt (c - axis [001]).

In figs. 3 and 4 the distribution of axial stress component in SrLaAlO_4 crystal just before its extraction from the melt and time-dependent changes in axial stress component on the

periphery after its extraction from the melt are shown, respectively. The figures reveal that in the case of SrLaAlO₄ crystal, which is characterised by low Biot number and large temperature gradient, the axial stress component increases to the maximum value after about 6 seconds (t_{max}) and decreases to the same value as before extraction after about 15 seconds. Time relaxation of the stress caused by the thermal shock is less than 1 minute.

The model presented here of unsteady stress distribution in LiNbO₃ crystal after its long-time extraction from the melt is not directly valid for a crystal with convex interface. However, there are some oxide crystals like small and middle diameter garnets and perovskites, which are normally disconnected from the melt in a very short time of a few seconds. In these cases the model can be applied directly (after taking into account the shape of the interface) to calculate the maximum value of thermal stress or to estimate the maximum of the thermal gradient for a given diameter, or vice versa.

4. Conclusions

During rapid extraction of LiNbO₃ and SrLaAlO₄ crystals from melts they undergo high thermal shock which is sufficient to induce crack formation at the crystal periphery. The thermal shock results in an increase in the thermal stress over an order of magnitude. Times of relaxation of stress caused by the thermal shock is about 30 min. for 55 mm diameter LiNbO₃ crystal and less than 1 minute for 20 mm diameter SrLaAlO₄ crystal, respectively. The magnitude and time of relaxation of the stress caused by the thermal shock depend mainly on the crystal diameter, the axial temperature gradient and the Biot number. Using numerical calculations a suitable method of crystal extraction from the melt can be found.

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