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Effect of the growth pulling direction on 3D anisotropic stress during different stages of semitransparent Li_2MoO_4 growth

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The three dimensional thermal stress field was calculated for different growth stages of Li_2MoO_4 (LMO) crystal growth in an inductively heated Czochralski furnace using the anisotropy and temperature-dependent mechanical properties. Four pulling directions were considered, including [100], [010], [001] and [110]. The elastic and thermal expansion matrices corresponding to a , b and [110] directions are computed by a tensor transformation method from the available experimental coefficients characterizing LMO crystal pulled along the c -direction. The crystal-melt interface convexity and the input heat power obtained numerically for the final growth stage meet the experimental values for absorption coefficient close to 0.2cm^{-1} . Compared to an assumed opaque case, von Mises stress increases strongly at the semitransparent LMO interface due to the internal radiative heat transfer inside the crystal which leads to a large convexity of the crystal-melt interface.

The thermal stresses for [100] and [010] pulling growth directions were the same since they present the same crystallographic axes and are larger than the c -pulling case, especially for the earlier stages where the increase rate is about 36%. Three and two-fold symmetries are shown for c and a (or b) pulling cases, respectively, in the distribution of von Mises stress at a cross section of LMO crystal. Thermal stresses along [110] direction were almost the same compared to [100] and [010] pulling axes with two-fold symmetries. The gas convection and temperature dependence of the mechanical properties have an important effect on the thermal stress values and distributions and have been taken into account in accurate computation of the stress field.

1 Introduction

Lithium molybdate single crystals of chemical composition Li_2MoO_4 (LMO), which belong to the trigonal system with space group $R\bar{3}^{1-7}$, are widely used in a variety of modern high-tech applications. Barinova et al.² first tested the applicability of this oxide crystal in fundamental physics as cryogenic scintillating bolometer for searches neutrinoless double beta decay (DBD). This material is used also in applied physics for the neutron flux detection through n captures by 6Li as well as in astroparticle physics and neutron spectroscopy³.

Velázquez et al.⁶ measured several physical properties as a function of temperature that is required for crystal growth simulation. These properties are used in the present work for computing temperature and velocity fields in the molten LMO and thermal stress

field in the crystal at different stages of the growth process.

The cracks occurring in LMO crystals can result from the internal thermal stress which is related to the thermal history of the growth process⁸. The advanced understanding of transport phenomena in the Cz growth furnace is then crucial for controlling heat and momentum transfer and reducing then the induced thermal stress.

Since LMO single crystals have anisotropic mechanical properties such as elastic constants and thermal expansion coefficients, the exact thermal stress computation has to be performed in three dimensions by taking into account this anisotropy.

Furthermore, for semitransparent crystals, such as LMO, internal radiation plays a key role in heat transfer and strongly affects crystal-melt interface convexity⁹⁻¹⁸. Therefore, temperature distribution inside the crystal is not uniform and, then, accurate computations of the stress inside the crystal requires to take into account the temperature dependence of anisotropic elasticity and thermal expansion tensors.

Only few works have been published on the 3D computation of thermal stress in crystals using the anisotropy and temperature-

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dependency of the mechanical properties, where internal radiation is incorporated. Miyazaki et al.^{19,20} were the first who carried out a three-dimensional analysis of thermal stress field in LN and LT crystals, of about one inch in diameter, by using the temperature distribution obtained by global simulation of heat transfer for opaque assumed crystals.

Taking into account the internal radiation, the anisotropy and the temperature dependence of both of elasticity and thermal expansion coefficients, the coauthors of this work computed the 3D thermal stress in semitransparent sapphire²¹ and langatate crystals^{22,23}. Zermout et al.²¹ compared numerically the isotropic and anisotropic analyses for a semitransparent sapphire crystal grown by Kyropoulos method. They have shown that von Mises stresses are smaller and non-axisymmetric in the anisotropy analysis, where the coefficients are functions of temperature, compared to the isotropic one. Lasloudji et al.²² computed the von Mises stress in LGT crystals using the anisotropy and temperature dependency of elasticity and thermal expansion tensors. They have shown that the addition of an afterheater attached to the crucible side wall reduces strongly the thermal stress. The crystal quality is then improved which was confirmed by experiment.

Furthermore, the pulling direction of the crystal has a great influence on the thermal stress and therefore on the quality of the crystal^{19,20,23,24}. Miyazaki et al.^{19,20} computed the thermal stresses for a tetragonal and trigonal lattices along a , b and c pulling directions of the growth. They have found that a and b -directions provide the same maximum thermal stresses, but along c -direction, the stresses are lower compared to a and b . The same results were found for Langatate crystals with a trigonal lattice²³.

Miyazaki et al.²⁴ computed the dislocation density during different growth stages along c , 110 -directions and for isotropic case. They have shown that dislocation density increases with length and that the higher value is found for the isotropic case.

In this work, a three-dimensional analysis of thermal stress inside LMO crystal grown by Czochralski technique is developed for different stages of the process using finite element method. The anisotropy and temperature dependence of elastic and thermal expansion coefficients are taken into account, and four pulling growth directions are considered and compared. A more special attention will be given to the last stage of the process which will be first validated with respect to experimentally available data and will be compared to the opaque assumed case. Temperature is computed in the whole furnace by taking into account all heat transfer modes, i.e., inductive heating in the turn coil, conduction and convection in the melt and the growth atmosphere, thermocapillary convection at the free surface of the melt, conduction and internal radiation in the crystal, conduction in opaque materials and radiative heat exchange between exposed surfaces. The external surface of the crystal is drawn similar to the real shape of the grown crystal and a deformed mesh method is used to compute the crystal-melt interface shape for the different stages.

2 Experimental setup

The Czochralski (Cz) crystal growth furnace used to grow Li_2MoO_4 single crystal is shown in figure 1a. It consists mainly of insulation zirconia material, a platinum crucible of 61mm in

diameter, 58mm in height and 2mm in thickness. Five turns of R-F coil surround the crucible; its center is located 8mm above the center of crucible side wall. An azimuthal current with 29.5KHz passes through the coil and, due to the important electrical conductivity of the metal crucible, a power is generated by Joule effect and insures melting of the raw material. The chamber of the furnace is filled with air atmosphere.

Fig. 1 A 3D schematic diagram of inductively heated (Cz) furnace (a). A [110]-oriented Li_2MoO_4 crystal (b). The real interface is about 15.5mm. The tip (2.5mm) is broken at the end of the growth.

The raw materials 5N5MoO_3 and $5\text{NLi}_2\text{CO}_3$ powders are used to prepare the initial charge. The stoichiometric mixture of Li_2CO_3 and MoO_3 was thermally treated in air in successive stages at 673K then 873K with intermediate grinding. Small crystal rotation rate (5 rpm) was applied to minimize the convection intensity in the melt. The average mass uptake and the pulling rates were about 3.5g/h and 0.6mm/h. At the end of the growth process, the cooling rate was 3.7°C/h, the remaining molten LMO charge is 28mm in height and the [110]-oriented Li_2MoO_4 grown crystal shown in figure 1b is obtained. The tip of this ingot (about 2.5mm) is broken after the growth.

The trigonal LMO unit cell with cell parameters $a = b = 14.34$ Å, $c = 9.593$ Å and $\alpha = \beta = 90^\circ$, $\Gamma = 120^\circ$, and the three

Fig. 2 Unit cell of trigonal lattice along c -axis (a). Crystallographic axes, from left: c -pulling axis; a -pulling axis; b - pulling axis (b).

principal crystallographic axes are presented in figure 2.

Table 1 Thermophysical properties of Lithium molybdate Li_2MoO_4

Description	Material	Value
Density ρ_i ($Kg.m^{-3}$)	$Li_2MoO_4(s)$	2940
	$Li_2MoO_4(l)$	2900
Thermal conductivity k_i ($W.m^{-1}.K^{-1}$)	$Li_2MoO_4(s)$	1.1
	$Li_2MoO_4(l)$	1.1
Specific heat C_{pi} ($J.Kg^{-1}.K^{-1}$)	$Li_2MoO_4(s)$	1085
	$Li_2MoO_4(l)$	1239
Heat of fusion ΔH ($W.m^{-1}.K^{-1}$)	$Li_2MoO_4(l)$	285.7
Melting point T_m (K)	$Li_2MoO_4(s)$	975
Thermal expansion coefficient β_l (K^{-1})	$Li_2MoO_4(l)$	-0.00014
Surface tension σ_l ($J.m^{-2}$)	$Li_2MoO_4(l)$	0.3325
		-0.00012828.T
Dynamic viscosity μ_l ($Kg.m^{-1}.s^{-1}$)	$Li_2MoO_4(l)$	0.008
Absorption coefficient κ_s (m^{-1})	$Li_2MoO_4(s)$	[5–20]
Refractive index n_s	$Li_2MoO_4(s)$	1.7
Prandtl number $\mu_l C_{pl} / k_l$	$Li_2MoO_4(l)$	9

Table 2 Mechanical properties of Lithium molybdate Li_2MoO_4 ^{6,25}

Elasticity matrix elements	Thermal expansion coefficient elements
$C_{11} = -0.0024(T - 273.15) + 64.4$ (GPa)	$\alpha_{11} = 2.0810 \cdot 10^{-8}T + 4.4310 \cdot 10^{-6}$
$C_{12} = -0.016(T - 273.15) + 38.8$ (GPa)	$\alpha_{33} = 1.7910 \cdot 10^{-8}T + 1.0910 \cdot 10^{-5}$
$C_{13} = -0.007(T - 273.15) + 24.7$ (GPa)	
$C_{14} = 0.4$ (GPa)	
$C_{15} = -0.7$ (GPa)	
$C_{33} = -0.031(T - 273.15) + 87.5$ (GPa)	
$C_{44} = -0.004(T - 273.15) + 16.1$ (GPa)	

3 Results and Discussion

A global two dimensional axisymmetric model is developed to compute the temperature field in the whole furnace and the velocity in the melt and the growth atmosphere. As temperatures are high in the growth chamber, heat is transferred mainly by radiation between exposed surfaces of the furnace. Heat conduction is present in all elements, convection in the melt and gas and internal radiation in the crystal.

In the 3D study part, the temperature field obtained from the global analysis of heat transfer in the furnace is used to compute the thermal stress inside the crystal and seed for the three principal growth orientations, i.e., when the pulling axis is parallel to a -axis ([100]), b -axis ([010]), c -axis ([001]) and along the [110] growth direction.

The thermo-physical and mechanical properties of LMO crystal and melt used in the present work are listed in tables 1 and 2. Most of them are taken from the paper of M. Velázquez et al. ⁶. In the following, some numerical results are presented and discussed for the final growth stage corresponding to the crystal shape in figure (1b) and for four intermediate stages.

3.1 Validation of the numerical model

Our numerical model was validated with respect to available experimental data by comparing two values; c-m interface convexity and input power.

Fig. 3 Two interface deflections found numerically for $\kappa_s = 20m^{-1}$ (a) and for $\kappa_s = 5m^{-1}$ (b).

Since the absorption coefficient of LMO is not well known at high temperatures, it can vary from $5m^{-1}$ to $20m^{-1}$, these two limiting values, i.e, $\kappa_s = 5m^{-1}$ and $\kappa_s = 20m^{-1}$ are considered and the corresponding crystal-melt interface deflections are then given in figure 3. The deflection represents the axial distance of the interface at the centerline from the axial position of the melt/crystal/gas tri-junction ($r = r_s$).

The crystal in figure 1b shows that the experimental value of the interface convexity is about 13mm. However, as said above, the crystal tip is broken after the growth, then we should add 2.5mm, and, therefore, the real convexity of this LMO crystal is about 15.5mm

A good agreement is found for $\kappa_s = 20m^{-1}$ where the difference is about 7% from the real convexity for the same experimental parameters as in figure 1b. However, for $\kappa_s = 5m^{-1}$, the difference is 20% compared to the experimental value. This result suggests that the absorption coefficient of LMO crystal is closer to $\kappa_s = 20m^{-1}$ than to $\kappa_s = 5m^{-1}$.

The input power found numerically, corresponding to the inter-

section of fusion isotherm with the triple point, is about 790W, then a difference of about 2.5% from the experimental value (810W), was found.

3.2 Flow and temperature fields

In figure 4a, the flow patterns of melt and gas (left side) and temperature distributions (right side) in the melt, crystal and gas atmosphere are given for the validated case, i.e., for $\kappa_s = 20m^{-1}$. For the present growth condition, i.e., 5rpm crystal rotation rate, the melt flow is driven mainly by buoyancy and thermocapillary convections. As the melt density decreases with temperature, hot (light) fluid particles near the crucible side wall (the hotter part in the furnace) rise from the bottom to the free surface, and coldest (heavy) fluid particles near the interface go down. A clockwise vortex is then generated by buoyancy and occupies almost the whole melt volume.

Due to surface tension gradients at the melt free surface, the thermocapillary convection induces shear stress enhancing then mainly the flow in the upper part of the melt. This Marangoni convection acts in the same direction as buoyancy and pushes the vortex center upward, increasing then the flow strength near the free surface.

When the crystal rotates, forced convection acts radially in the opposite direction to the buoyant flow. It pushes then the fluid particles from the central axis under the interface to the free surface and the crucible wall. However, the forced convection for the actual Reynolds value ($Re_s = \frac{\rho_l \omega_{rot} r_s^2}{\mu_l}$) is weak ($Re_s = 54$), and, therefore it cannot generate a secondary vortex in the melt, but it increases the velocity in the zone under the interface, as shown in figure 4a.

Dimensionless intensities of buoyant and thermocapillary forces can be expressed through Grashof ($Gr = \frac{\rho_l g \beta_l \Delta T_l R_c^3}{\mu_l^2}$) and Marangoni ($Ma = \frac{\rho_l \frac{d\sigma}{dT} |\Delta T_l R_c|}{\mu_l^2}$) numbers. In our case, they are equal to 73400 and 2482, respectively, where R_c and ΔT_l are the crucible radius and the temperature difference across the melt given as $T_{max} - T_{min}$, respectively.

Due to the large value of Prandtl number ($Pr = \nu/\alpha$) characterizing LMO melt, which defines the ratio of momentum diffusivity ν to thermal diffusivity α , ($Pr = 9$), the temperature field is strongly influenced by melt flow convection and isotherms have then an “wave-like” structure at the crucible bottom.

In the gas atmosphere, isotherms have a “wave-like” structure due to convection transfer mode. One small and intense counterclockwise vortex is located directly above the free surface and two other weak vortices are in the upper part of the furnace.

On the other hand, heat is transferred by conduction and mainly by internal radiation in the semitransparent LMO crystal. By comparing the optically thinner case for $\kappa_s = 20m^{-1}$ (figure 4a) to the opaque assumed case for $\kappa_s = 10^4m^{-1}$ (figure 4b), the role of internal radiative heat transfer within the LMO crystal can

Fig. 4 Melt flow pattern (left parts) and temperature contours with isoline gap of 5K in crystal, 2K in the melt and 10K in the gas (right parts) for two absorption coefficient values of the crystal; $\kappa_s = 20m^{-1}$ (a) and $\kappa_s = 10^4m^{-1}$ (b). The interface deflection is indicated in each case to present the convexity values. The c-m interface convexity decreases of about 60% from optically thinner crystal to the optically thicker one

Fig. 5 c-m interface convexity (red line) and maximum von Mises stress at c-m interface region (blue line) for different absorption coefficient values. Thermal stresses are larger for semitransparent LMO crystal because of the big convexity. Both of the convexity and thermal stress decrease strongly in the optically thinner range (small values of κ_s) and become almost uniform for larger values of the absorption coefficient.

be clearly shown.

For the opaque-assumed crystal, $\kappa_s = 10^4 m^{-1}$, the isotherms are almost stratified due to conductive transfer mode and, when absorption coefficient decreases, the thermal conduction becomes weaker and isotherms in the crystal are pushed toward the upper part of the crystal and toward the crystal-melt interface. A thermal boundary layer is then formed close to the c-m interface in the LMO melt.

As heat flux is increased by internal radiation inside the crystal, the growth interface area has to be enlarged to compensate for the larger radiative heat loss. The variation of interface convexity with the absorption coefficient is plotted in figure 5 (red line). A strong decrease is found for the smaller absorption values and a slight decrease is found for larger values of the absorption coefficient for which the optical depth becomes very important. The decrease of interface convexity with the absorption coefficient (or the optical depth) is in a good agreement with the experimental work of Cockayne et al.²⁶ for YAG and sapphire crystals. Kobayashi et al.^{11,12} and Böttcher et al.¹⁸ have confirmed this result numerically for NbO_3 and $NdScO_3$ crystals, respectively.

Let us now discuss the earlier stages of this process. Figure 6 shows the temperature and velocity fields in the molten LMO for three earlier stages corresponding to the crystal sizes deduced from the real geometry of the LMO grown crystal. The last stage corresponds to the experimental photograph given in figure 1b and also to the computed fields in figure 4a. The crystal length for the five considered stages, measuring the axial distance from the triple point to seed-crystal interface, is equal to $L_1 = 16.63mm$, $L_2 = 20.79mm$, $L_3 = 28.9mm$, $L_4 = 50.77mm$ and the validated case.

Melt flow presented in Figure 6a (left parts in a, b, c and d) shows that only one clockwise vortex, induced mainly by buoyancy and thermocapillary forces, occupies all the melt volume for the three earlier stages, as found for the last stage presented in figure 4a and discussed above.

For the first stage corresponding to $L_1 = 16.63mm$, (Figure 6a), the volume of the melt is big and then the Grashof number calculated based on the melt height ($Gr_h = \frac{\rho_l^2 g \beta_l \Delta T_l h_l^3}{\mu_l^2}$) is larger 1.0810^5 . As a result, the flow of the fluid particles inside the melt is more intense, especially under the interface and close to the symmetry axis. The maximum melt velocity increases by 32%.

Furthermore, as the outer crystal surface becomes larger for the advanced stages of the growth, the external radiation (surface to surface) heat transfer from the crystal periphery surface to the adjacent surfaces of the furnace becomes stronger. As a result, a larger heat flux is generated in the crystal which has to be compensated by larger heat flux in the melt at the growth interface. A bigger interface area is then required to balance this heat loss when the crystal grows up. The increase of the interface convexity from the first to the last stage is clearly shown by the red curve in figure 7.

Fig. 6 Melt and gas flow patterns (left sides) and temperature contours with isoline gap of 5K in the crystal, 2K in the melt and 10K in the gas (right sides) for different crystal lengths $L_1(a)$, $L_2(b)$, and $L_3(c)$. C-m interface convexity is added in each case, it increases when crystal length increases.

Fig. 7 C-m interface convexity evolution during the growth (red triangles) and maximum von Mises stresses. Dashed curves corresponds to the results with constant elasticity coefficients and solid lines to temperature-dependent coefficients for c-pulling direction (blue) and the other directions (green). All values of thermal stress are overestimated when the elasticity tensor is constant. Thermal stresses are small for c-pulling case especially at the earlier growth stages where the growth direction has a significant effect.

3.3 Thermal stress field

In this subsection, thermal stresses for four pulling orientations will be presented and discussed. A special attention will be given to the stage which was validated with respect to experiment. Although the value of thermal stress at a point in the crystal provides incomplete information about the propagation of a crack in a given orientation, they can qualitatively inform us about the crystal cracking and quality.

As said above, the anisotropy of elastic constants and thermal expansion coefficients, as well as their temperature dependence, are mandatory for the exact computations of thermal stress, even for the axisymmetric shape of the crystal, since both of the anisotropy and temperature dependence affect considerably the distribution and intensity of thermal stress, as demonstrated by Miyazaki^{19,20}, S. Zermout et al.²¹ and I.Lasloudji et al.²².

The computation of thermal stress provides three components of the stress ($\sigma_1, \sigma_2, \sigma_3$), which can be used to determine the von Mises equivalent stresses $\sqrt{3J'_2}$, where J'_2 is the second invariant stress given by $J'_2 = \frac{1}{6}((\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2)$.

Let us first discuss the thermal stress obtained for the crystal at the last stage grown in the c-pulling direction.

Thermal stress field is thoroughly related to temperature distribution, as expressed in equation (27), and it is then strongly related to heat transfer modes inside the crystal, especially, to internal radiation.

Figure 8 shows the von Mises equivalent stress distributions in the whole crystal estimated with the second invariant of the deviatoric stresses for two values of absorption coefficient $\kappa_s = 20m^{-1}$ (8a) and $\kappa_s = 10^4m^{-1}$ (8b).

Fig. 8 Von Mises stress distribution for semitransparent $\kappa_s = 20m^{-1}$ (a) and opaque $\kappa_s = 10^4m^{-1}$ (b) cases and in the case where the gas convection is not considered (c). A quarter part of the crystal is removed to show the internal part of the crystal. Isostresses are so drawn as to divide the difference between the maximums and the minimum values into twenty equal portions.

Fig. 9 Von Mises thermal stresses (dotted lines) and temperatures (solid lines) at the crystal periphery with (red) and without gas convection (blue).

A quarter part of the crystal is eliminated in these results to show the internal part of the crystal clearly. Iso stresses are so drawn as to divide the difference between the maximum and the minimum values into twenty equal portions.

For semitransparent case $\kappa_s = 20m^{-1}$, the larger von Mises stresses are found at the seed, neck and growth interface. The maximum value in this case is about $41MPa$. However, for the opaque assumed case, the shoulder and underneath region are more stressed and the maximum value in this case is about $13.8MPa$. The growth interface is less stressed because of its lower convexity. The strong relation between the interface convexity and the maximum stresses is well demonstrated by the curves in figure 5, which have almost the same variations when the absorption coefficient increases. In the internal part of the LMO crystal, the internal radiation increases strongly the thermal stress in the lower part of the crystal which is characterized by larger von Mises than the opaque case. We think that this is the reason why the tip of the crystal was broken after the growth (figure 1b). The axial thickness of this large stress region is almost the same as the broken part after the growth.

Let us now discuss the effect of gas convection. By comparing figures 8a and 8c, it can be clearly seen that the gas flow increases strongly the minimum value of the von Mises stress which characterizes mainly the shoulder part, the zone underneath and the internal crystal part. This value passes from $0.19MPa$ to $5.22MPa$. However, the stress at the growth interface decreases and becomes more uniform when gas convection is neglected. For more detailed analysis, temperature and von Mises stress are plotted at the crystal periphery in figure 9. The growth atmosphere convection acts to increase the temperature at the lower part of the crystal surface, where the small and intense counterclockwise vortex above the free surface transfers the heat from the crucible sidewall and free surface to the crystal periphery. Close to the shoulder region, the gas particles are almost at rest and, thus, the temperature values for the cases with and without convection are almost the same. However, the big gas vortex in the upper part of the furnace transfers the heat from the upper crystal surface to the seed and other furnace elements, and it acts then to cool the crystal surface near the seed. This can explain why the stresses are larger in this crystal surface part. Thus, we can conclude that gas convection has to be taken into account in such analysis as it affects not only the temperature and flow field in the gas and the melt, but also the thermal stress in the crystal.

When the crystal grows up, the temperature field changes inducing then important variations in the thermal stress field.

Figure 10 shows the von Mises stresses for the earlier stages of the growth, i.e., for L_1 , L_2 and L_3 . For the first growth stage (L_1), the stresses are stronger at the triple point and weaker at the bottom part due to the lower convexity compared to the last stage. As the crystal grows up, the temperature gradients increase, leading then to increased von Mises stress from a

maximum value of $22.76MPa$ for the first stage L_1 to $40.87MPa$ for the last stage.

It can be shown from figure 11 that both of von Mises stresses

Fig. 10 Von Mises thermal stress distributions for three earlier stages ($L_1(a)$, $L_2(b)$, $L_3(c)$) extracted from the last stage presented at figures (1b), (3a) and (3a). A quarter part of the crystal is removed to show the internal part of the crystal. Iso stresses are so drawn as to divide the difference between the maximum and the minimum values into twenty equal portions.

and temperature gradients are lower at the periphery of the crystal for the first stage compared to the last growth stage.

The strong relation between the maximum von Mises values and the interface convexity is clearly indicated by the plots in figure 7 given in red and solid green curves. Another stage has been added to these plots having a length of $10mm$ above the last stage of the experiment. For this additional stage, the remaining melt height is about $25.5mm$.

Both of the convexity and the maximum stresses increase during the growth. For the three earlier stages, the increase rate of the maximum stress is almost uniform and is more important than the last stages.

We have to mention here that these results have been found for the crystal shape in figure 1b and for the mechanical properties of LMO. However, for uniform crystal diameter and for crystals having different mechanical properties than LMO, the results can be different.

Let us now discuss the effect of the growth orientation on the thermal stress for the five considered stages. Figure 12 provides the results for the von Mises equivalent stress in 3D presentation for $[100]$, $[010]$ and $[110]$ growth directions at the last growth stage (L_4), which will be compared to the thermal stress for the

Fig. 11 Von Mises thermal stress (dotted curves) and temperature gradients at the crystal periphery (solid curves) for the first stage (L_1 , blue) and the last growth stage (L_4 , red). Green dashed line indicates the position of the triple point.

c -pulling case in figure 8a.

The computed thermal stresses are the same for a and b pulling axes. This is due to the fact that a -axis and b -axis are crystallographically equivalent.

As for the c -axis case, crystal periphery is characterized by higher von Mises stresses than the internal part of the crystal for both of a and b cases. Loiacono et al.²⁷ have found the same result experimentally and related it to the subgrain density which is maximum at the outer surface of the bulk single crystal.

Moreover, when the pulling axis is parallel to a -axis (or b -axis), values of von Mises stress are larger than the c -pulling case and are not symmetric with respect to the symmetry axis. The unequal radial thermal expansion coefficient in the plane normal to the growth direction is the principal reason for the higher and non-uniform stresses in these two cases, as explained by Bonner and Zydzik²⁸.

In addition, isostresses at a cross section of the LMO crystal show a two-fold symmetry for a (or b) and $[110]$ direction pulling cases (figures 13a, 13b, 14a, 14b) and a three-fold symmetry for the c -pulling case (figure 13c and 14c) for both of the first and last stages.

The maximum von Mises stress evolution during the growth is plotted in figure 7 for the three growth orientations together with the variation of the c -m convexity from the first stage to the last one.

A big difference (36%) was found from the c -pulling case directions for the earlier stages and a small one (6%) for the last stage.

Therefore, the crystals growing along the c -axis can produce less cracked LMO crystals than those growing along a , b or $[110]$ pulling directions, which are easier to crack during the growth. This result is in a good agreement with the experimental work of Brandle²⁹ and numerical works of Miyazaki^{19,20}.

Besides, the effect of temperature dependence of elasticity

Fig. 12 Von Mises stress distribution in LMO crystal pulled along the a -axis (a), b -axis (b) and along 110 growth direction (c). A quarter part of the crystal is removed to show the internal part of the crystal. Isostresses are so drawn as to divide the difference between the maximum and the minimum values into twenty equal portions.

Fig. 13 Von Mises stress contours in a cross section at the shouldering region for the last stage in the cases, a -axis (a), 110-axis (b) and along c growth direction (c). For the b -pulling case the result is the same as in (a) because the axes a and b are crystallographically equivalent. Three-fold symmetry is found in the c -pulling case and two-fold symmetry is found in the other cases.

Fig. 14 Von Mises stress contours in a cross section at the shouldering region for an earlier stage L_1 in the cases, a -axis (a), 110-axis (b) and along c growth direction (c). For the b -pulling case the result is the same as in (a) because the axes a and b are crystallographically equivalent. Three-fold symmetry is found in the c -pulling case and two-fold symmetry is found in the other cases.

coefficients of LMO crystal is shown by comparing solid curves and dashed curves in figure 7, which refer to the maximum stress with constant coefficients and temperature-dependent coefficients for c -pulling direction (in blue) and other directions (in green).

From this comparison, we can conclude that all values of thermal stress are overestimated when the elasticity tensor is constant. The increase rate from the temperature-dependent case is about 32% for all growth stages when the pulling direction is parallel to the a , b or $[110]$ -direction and for the first stage of the c -pulling case.

This is due to the fact that the constant coefficients are larger than the temperature dependent ones. For example, the constant value of C_{33} coefficient taken from²⁵ is $C_{33} = 86.2$ GPa. When it is a function of temperature $C_{33} = -0.031(T(K) - 273.15) + 87.5$ (GPa), it is reduced to 65GPa at the melting temperature. Therefore, the increase rate of this coefficient (36%) is almost the same as the thermal stress overestimation given above.

4 Conclusion

In this work, a 3D numerical model was developed using finite element method for the thermal stress analysis inside LMO single crystal grown by Czochralski process. The validation with respect to experimental results was successfully shown. In addition to the qualitative observations concerning the convection cartwheels and post-growth fracture, a difference of about 0.7% and 2.5% from the real c-m convexity and the input power was found.

The temperature and velocity fields in the molten LMO, as well as 3D thermal stress taking into account the crystal anisotropy, were calculated for different stages corresponding to the real geometry of the grown LMO crystal.

The thermal stress is found to be strongly related to the internal radiation in the LMO semitransparent crystal and to the growth direction. The c -pulled LMO crystals can be less cracked than those pulled in other directions, especially in the earlier stages.

The comparison between different numerical results shown that accurate computation of the stress have to be performed using parameters closer to the experiment. The gas flow convection, anisotropy and temperature dependency of the mechanical properties were considered.

Conflicts of interest

There are no conflicts of interest to declare.

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