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Simultaneous growth of high quality $Ca_{1-x}Sr_xF_2$ boules by optimised Bridgman-Stockbarger apparatus. Reliability of light transmission measurement

J. T. Mouchovski[1]*, K. A. Temelkov[2], N. K. Vuchkov[2], N. V. Sabotinov[2]

[1] *Acad. Ivan Kostov Central Laboratory of Mineralogy and Crystallography,*
Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 107, 1113 Sofia, Bulgaria
[2] *Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences,*
72, Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

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Calcium-strontium fluoride boules with different Sr-content were grown simultaneously in crucible with axis-symmetrically disposed nests by utilizing an original Bridgman-Stockbarger (BS) apparatus. Implemented control upon the position of crystallization front (CF) within an unusually broad adiabatic furnace zone (AdZ) minimizes the radial heat exchange that ensures in practical planar CF-shape for proceeding a normal growth. The CF-positions are determined by empirical formulae taking into account various impacts altering the thermal field inside the load and are related to characteristic parameters, representing: 1) the mean value and 2) the alteration of absorption + light-scattering losses per unit of optical path of monochromatic beam transmitted through optical windows prepared from different sections of the boules. The irradiation is induced utilizing either CuBr vapour laser operating with wavelengths in ultraviolet (UV) or visible (Vis) regions as well as SrF_2 vapour laser operating in infrared (IR) region, or high sensitive spectrophotometer operating in UV–near IR. The use of vapour lasers allows the measurement of external transmittance (transmissivity) being carried out rapidly at wavelengths of practical interest under highly sensitive control upon the area and the position of the beam spot. The grown boules represent complete solid solutions of CaF_2 and SrF_2 with uniform compositions and negligible amounts of structural defects. Thus, they appear to be a high-grade optical material for manufacturing various elements with wide applicability in UV–IR optical systems.

Key words: optical mixed fluoride crystals, optimum growth control, structural imperfection, UV-lithography.

INTRODICTION

The increasing industrial demands for integrated circuits with increasing number of components and increasing integral density in layouts cause a rapid development of semiconductor fabrication technology in direction of improving the efficiency of optical reduction system as key section in the exposure device for any micro-lithographic apparatus. Since the demand for an ever-decreasing minimum size is very high, it becomes increasingly important to enlarge the resolution of micro-lithographic techniques. This can be accomplished by shortening the light-wavelength used in fabrication procedure but retaining at the same time significantly high light-transmittance. An optical material, whose transmissivity is high enough to satisfy the demands of 193- and even of 157-micro-lithography, is calcium fluoride. However, this single fluoride crystal reveals a relatively high degree of intrinsic (spatial-dispersion-induced) birefringence, which is dependent strongly on the direction of light propagation [1]. For this reason the transmissivity and refraction in CaF_2 elements vary unevenly across a beam incident. The final impact is blurring and/or reduction of image sharpness as well as loss of the light through the optical reduction system.

A generally used approach for eliminating the birefringence effect in any optical system appears to be a relevant combination of catadioptric design to crystal orientations and clocking strategies [2]. Another approach consists in nulling out the birefringence effect at a given wavelength in each optical element by combining CaF_2 with some other crystal materials (SrF_2 and BaF_2) having birefringence values that are opposite to those of CaF_2 [3]. Since the cubic fluorite symmetry of CaF_2, BaF_2, and SrF_2 is preserved when they form solid solutions, the optical properties of $Ca_{1-x}Sr_xF_2$, $Ca_{1-x}Ba_xF_2$, and $Ca_{1-x-y}Ba_xSr_yF_2$ mixed crystals are supposed to be intermediate between those of end members, CaF_2 and SrF_2, as the variations can be thought to be linearly dependent on composition. The techniques for growing mixed fluoride compounds vary from Bridgman-Stockbarger (BS) method [4] or its modifications [5], gradient freeze technique (GFT) [6] to the newly developed single crystal technology (SCT) [7].

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* To whom all correspondence should be sent:
E-mail: jmouhovski@abv.bg

The external transmittance determining the absorption and light-scattering losses, refractive losses, structural homogeneity, and overall residual stress-induced plus spatial-induced birefringence appear to be key parameters for efficient control of crystal quality so that they have to be correctly determined and interpreted. The absorption + light scattering losses turn out to be especially convenient for linking crystal quality to growth conditions and this manner to provide growth optimum with planar or slightly convex CF-shape for single boules [8] as well as for group of boules with different composition [9].

The methodologies for measurement of birefringence and transmissivity in VUV region (below 193 nm) demand relatively sophisticated devices and apparatuses [10]. Thus, the VUV-external transmittance is being measured precisely using complicated and very expensive highly-sensitive spectrophotometers. At $\lambda \geq 193$ nm either highly sensitive UV-spectrophotometer is used or the method of laser irradiating the samples and measuring the beam attenuation is implemented. The vapour lasers irradiation (VLIr) technique has already been applied by us to measure the transmissivity, t, of optical windows, finished from different sections of calcium fluoride single boules [8] as well as of calcium-strontium fluoride boules with different Sr content, grown simultaneously in multicameral crucible with axis-symmetrical nests [9]. Our originally constructed vapour lasers are two types: 1) CuBr, operating in UV region at 248.6 nm and Vis region at 510.6 nm; 2) $SrBr_2$, operating in middle IR at 6.45 μm [11–13]. The total absorption + light-scattering losses, L_{abs+sc}, are distinguished from twice the reflectivity of the first face of used optical window, $2r$, calculated for operating wavelengths, where $t + L_{abs+sc} + 2r = 1$. We have traced a way for improvement of the control of growing conditions in order to produce boules with stable optical characteristics. The applied approach consists in derivation of empirical relationships between the CF-position inside the furnace unit and two structural parameters, the mean absorption + light-scattering losses per unit of opti-cal path, $L_{abs+sc/lwin}$, and the difference in $L_{abs+sc/lwin}$-values along the height of grown boules. Since the accurate determination of these parameters depends on the reliability of applied t-measurement technique we apprehend the necessity of comparative analysis between spectrophotometrical (SpPh) and VLIr techniques in order to assess their usefulness for specifying the needed empirical relationships. Thus, we hope to ensure much better growing control aimed at obtaining simultaneously several boules of calcium-strontium fluoride crystals with different ratio of alkali earth elements. Boules grown by such technique are unique for research purposes since the crystallization optimum may be reached, in practice, for each one of the boules, independently of alterations of solidus/liquidus temperatures.

The goals of the present study are: *first*, to analyse comparatively the data from t-measurements, carried out consecutively by VLIr and SpPh techniques, on optical windows of calcium-strontium fluoride crystals with different composition grown simultaneously by improved BS-technique; *second*, to obtain reliable empirical relationships between quality-determining parameters – absorption + light scattering losses per unit of optical path and its alteration along boule's height, and key growing parameter – the shift in CF-position within the furnace unit; *third*, using the obtained relationships to verify their potential for efficient control of the CF-optimum during simultaneous growth of calcium-strontium fluoride crystals with significant variation in composition.

EXPERIMENTAL

The crystal growth is accomplished in specially designed Bridgman-Stockbarger Growth System (BSGS) [14]. Its key specifications are: 1) the diaphragm, which separates the upper hot zone (Z1) from the lower cold zone (Z2) in the furnace unit, is constructed to be much thicker than usually, in this way differentiating a broad adiabatic zone (AdZ), where the radial temperature non-uniformity is marginal and the vertical temperature gradient remains constantly sufficiently steep; 2) an introduction of additional shielding system of molybdenum devices for control of the ratio of radial to axial thermal heat transfer through the moving load; 3) a precise control of residual atmosphere inside the furnace chamber by quadruple mass-spectrometer, when growing is carried out in vacuum; 4) a device for preliminary deep gas purification (< 1 vpm) when working in argon atmosphere.

The applied multichamber crucibles have central and peripheral sections (nests), the latter provided by 8 axis-symmetrical interior or by up to 9 fixed cylin-drical inserts, all sections being end-tipped conically at angle 90° [14]. Highly concentrated fluorspar (≥ 99.7 wt.%) and a Suprapur® quality of SrF_2 (Merck) are used as starting materials for premelting mixtures. The optical windows are finished to meet requirements: 3 arc minutes – for parallelism, 40–20 scratch-dig – for surface finishing of both surfaces, 1–2 waves at 632.8 nm for both surfaces – for surface figure, and 80% – for clear aperture. Two windows were prepared from each boule, the "lower" windows, adjacent to conical boules' section, are located at a mean distance of (2.18 ± 0.50) cm from the "upper" windows. The mean windows' thickness, l_{win}, varies within 0.59 and 0.67 cm interval, while the diameter takes values of (24.3 ± 0.1) mm, (29.1 ± 0.1) mm or (32.3 ± 0.1) mm according to crucible modification. Two series of windows were specified along the boules' height: Ser. 1 – for sequence of the "lower" windows and Ser. 2 – for sequence of the "upper" windows. The windows were used for measuring consecutively transmissivity, t, by VLIr and SpPh techniques. The spectroscopic technique is applied for obtaining the light transmission spectrum within the UV–near IR region (190–900 nm), that is the operating range for the used highly sensitive spectrophotometer, type Varian Cary 100. The t-values at 248.6 nm, 510.6 nm and 900 nm are taken for comparison with t-values measured at 248.6 nm, 510.6 nm, and 6450 nm by VLIr technique. The comparison in the IR region is correct since the optical transmittance is proved to alter insignificantly within this spectral region in case of pure CaF_2 crystals [5].

The structural parameters for the studied mixed fluorides crystals are estimated based on the equations:

$$L_{\text{abs+sc/lwin}} = [1-t-2(n_{mix}-1)^2/(n_{mix}+1)^2]/l_{\text{win}} \qquad (1)$$

$$L_{\text{abs+sc/h2–1}} = [1-t-2(n_{mix}-1)^2/(n_{mix}+1)^2]/\text{h}_{2-1} \qquad (2)$$

where the reflectivity, r_{mix}, is replaced by its functional expression of refractive index, n_{mix} [15], the dependence of which on the crystal composition is considered linear:

$$n_{\text{mix}} = (1-x)n_{\text{CaF2}} + xn_{\text{SrF2}} \qquad (3)$$

although a polynomial of second order may be a better expression, taking into account the difference between calcium and strontium ionic radii. Nevertheless, the linear approximation seems rather reasonable comparing the very close λ-dependence of the index of refraction for end-members: CaF_2 ($x = 0$) and SrF_2 ($x = 1$) [9]. The divergence from linearity should be so small that the relative errors upon estimating the quantity $2r_{\text{mix}}$ by applying the formulas for calculating errors of complex functions [16] are expected to be insignificant within investigated spectral range (Table 1).

The method of Quenched Interface (QI) determination in a fixed crucible [14] is applied to determine the position along the furnace unit of the CF shift in particular bowels according to the thermal conditions and mixtures' content. The derived formulas for CF-positions are:

$$x_{\text{CR}} = x_{\text{CF}}(x_1 = 0) - 0.36x_1(\text{z}) - [0.6T_1(x_1) + 0.18T_2(x_1)] + 0.0017[x_1(\text{z}) - 80][(T_1(x_1) - T_2(x_1)]$$

$$\text{for } 0 \le x_1(\text{z}) \le 110 \text{ mm} \qquad (4a)$$

$$x_{\text{CR}} = x_{\text{CF}}(x_1 = 110) + 0.23[x_1(\text{z}) - 110] - [0.6T_1(x_1) + 0.18T_2(x_1)] + 0.0017[x_1(\text{z}) - 110]\,[T_1(x_1) - T_2(x_1)]$$

$$\text{for } x_1(\text{z}) > 110 \text{ mm} \qquad (4b)$$

where $x_1(\text{z})$ is the distance of crucible movement in z-direction beginning from starting position fixed at 22 mm from the upper plane section of Z1, while $T_1(x_1)$ and $T_2(x_1)$ represent the set up rises of temperatures at given x_1-value for Z1 and Z2, respectively.

Table 1. Maximal theoretical relative errors for refractive index, n_{mix}, and twice reflectivity, $2r_{\text{mix}}$, of optical windows made of mixed fluoride crystals $Ca_{1-x}Sr_xF_2$.

Wavelength λ, nm	$(\Delta n_{\text{mix}}/n_{\text{mix}})_{\max}$	$[\Delta(2r_{\text{mix}})/2r_{\text{mix}}]_{\max}$
248.6	0.003602	0.0597
510.6	0.001485	0.0280
900	0.001411	0.0310
6450	0.002772	0.0644

Two growing experimental runs were carried out at different temperature regimes for both furnace zones, manifesting in different dwell levels and rises of T_1 (run 1) and T_2 (run 2). The speed of crucible withdrawal towards Z2 is maintained constant between 2 and 6 mm/h. The mutual configuration of the fixed and moving parts for additionally inserted molybdenum shielding system differs in the number of rings slipped on crucible tail. The mole part of strontium x in final $Ca_{1-x}Sr_xF_2$ crystals varies within 0.007–0.307 (9 boules for run 1) and 0.383–0.675 (8 boules for run 2). The coefficient of distribution for calcium/strontium in such crystallized solid solutions remains uniform within the experimental error along the boules' height [17]. The phase diagram of $Ca_{1-x}Sr_xF_2$ compounds is built on the basis of newly obtained data for liquid/solid phase temperature functionalities of calcium strontium solid solutions [18], corrected by estimated quantities based on assumption of linear lowering on calcium content ($1-x$) in both curves, starting at initial value of 43 K for $x = 0$.

RESULTS AND DISCUSSION

The x-dependence of $L_{\text{abs+sc/lwin}}$ shows a similar course within the studied UV–NIR range independently of the technique applied for t-measurement (Fig. 1a–c).

The minimum absorption + light-scattering losses per unit of window's thickness vary for x within 0.5 and 0.6 according to the operating wavelengths. At fixed composition (x = const) $L_{abs+sc/lwin}$ decreases rapidly when the wavelengths become longer as the difference diminishes for x within 0.5–0.6. This is a reflection of the peculiarities in growing conditions for the two runs. At wavelengths within UV and VIS the calculated $L_{abs+sc/lwin}$-values for Ser. 2-windows (Fig. 1a, b), based on t-data using VLIr technique, appear higher than the corresponding $L_{abs+sc/lwin}$-values, obtained by SpPh technique. The found differences diminish around function minima, where the growing conditions are supposed to be optimal to ensure a normal growth of boules with stable optical properties. Such result is grounded on the specificity of VLIr technique itself, where the relatively large size of the beam spot supposes a stronger effect of any structural defects as light-scattering centres. Nevertheless, the sizes of these centres are, evidently, too small to cause a noticeable internal light-scattering within the IR range, so that VLIr technique gives more reliable results especially in the middle IR region (Fig. 1c).

The calculated data for $L_{abs+sc/lwin}$ were used for performing a correlation analysis (Table 2).

Comparing the data, obtained consecutively by the applied techniques, one can see very high R-values throughout the studied spectral range. R is highest (0.9825) in the UV region (248.6 nm) where the relationship becomes, practically, a functional one. With increasing the wavelength, R-values reduce to 0.7287 in NIR–MIR range that is clearly shown in Fig. 2. These results indicate: *first*, both techniques provide a reliable qualitative analysis for recording and explanation of any alterations in absorption and light-scattering losses per unit of optical path, when monochromatic light passes through the studied optical windows, depending on the wavelength, composition of grown boules, and growing conditions; *second*, there are some structurally inhomogeneous areas inside testified samples, revealing themselves upon rising up the scattering probability when λ becomes longer. On the other hand, the spectrophotometrical technique itself leads to R-values varying near to 1 (0.9375–0.9943) for the chosen values of λ within UV–NIR spectral range. Such strong correlations confirm the high reliability for SpPh-technique and the used spectrophotometer.

At the same time, the VLIr technique itself manifests significantly lower R-values in comparison with those obtained by SpPh, as R declines fast, decreasing λ towards IR region due to disordering of data points and increase in their SD. More likely, the reason for such behaviour lies in the relatively large spot of laser beam, different in size for the used vapour lasers, which should promote an increasing effect of any structural inhomogeneity on the total attenuation for passing beam.

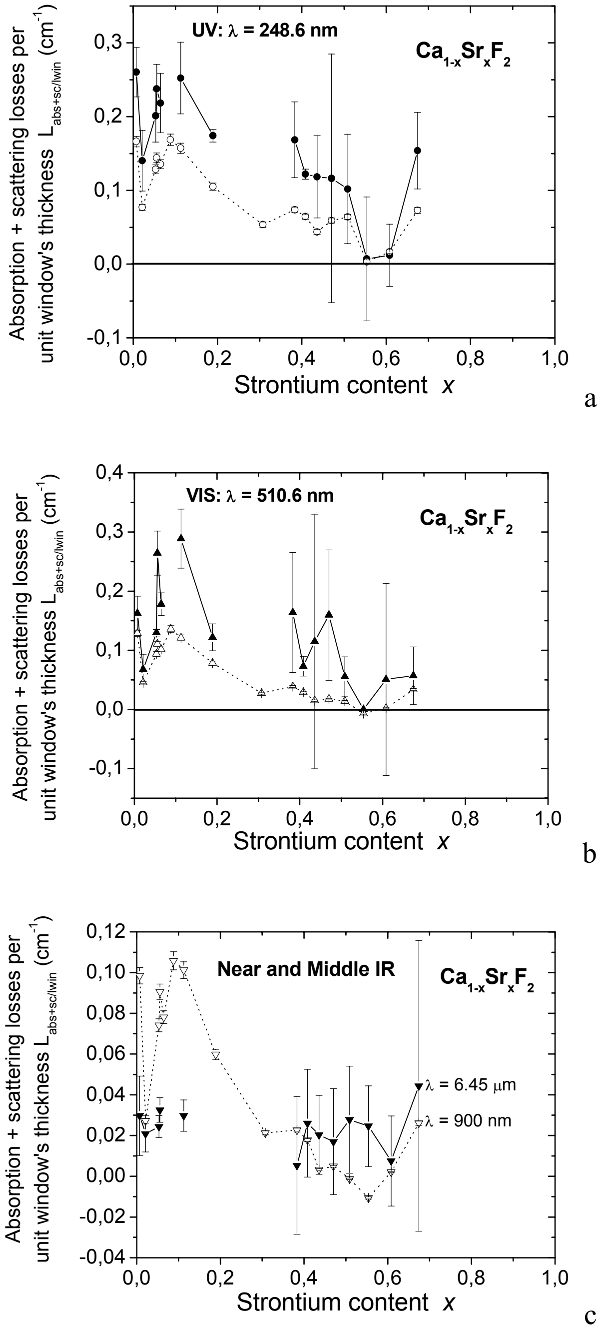


Fig. 1. Absorption plus internal light-scattering losses as part of the total losses for Ser. 2 $Ca_{1-x}Sr_xF_2$ optical windows with different strontium contents measured in UV–IR range by using of vapour laser irradiation and spectrophotometric techniques. a) 248.6 nm: (●) - VLIr, (o) - SpPh; b) 510.6 nm: (▲) - VLIr, (Δ) – SpPh; c) NIR (900 nm): (▼) - VLIr and MIR (6.45 μm), (▽) - SpPh.

Table 2. Correlational analysis of absorption plus internal light-scattering losses in $Ca_{1-x}Sr_xF_2$ optical windows obtained from VLIr and SpPh t-measurements.

Statistics		Coefficient of linear correlation R / (SD)					
$L_{ab+sp/lwin}$		Vapor Laser Irradiation			Spectrophotometer		
$L_{ab+sp/lwin}$	λ (nm)	248.6	510.6	6450	248.6	510.6	900
VLIrr	248.6	●	**0.8725**	**0.4359**	**0.9825**	**0.9537**	**0.9440**
			(1.1029)	(1.8789)	(0.4200)	(0.6794)	(0.7446)
	510.6	**0.8725**	●	**0.0932***	**0.7862***	**0.7766***	**0.7783***
		(1.1029)		(0.0885)	(0.0514)	(0.0524)	(0.0522)
	6450	**0.4359**	**0.0932***	●	**0.7159**	**0.7246**	**0.7287**
		(1.8789)	(0.0885)		(0.3758)	(0.3709)	(0.3685)
SpPh	248.6	**0.9825**	**0.7862***	**0.7159**	●	**0.9680**	**0.9375**
		(0.4200)	(0.0514)	(0.3758)		(2.8450)	(3.9446)
	510.6	**0.9537**	**0.7766***	**0.7246**	**0.9680**	●	**0.9943**
		(0.6794)	(0.0524)	(0.3709)	(2.8450)		(0.0053)
	900	**0.9440**	**0.7783***	**0.7287**	**0.9375**	**0.9943**	●
		(0.7446)	(0.0522)	(0.3685)	(3.9446)	(0.0053)	

* The standard deviation (SD) of the particular point is not taken into consideration.

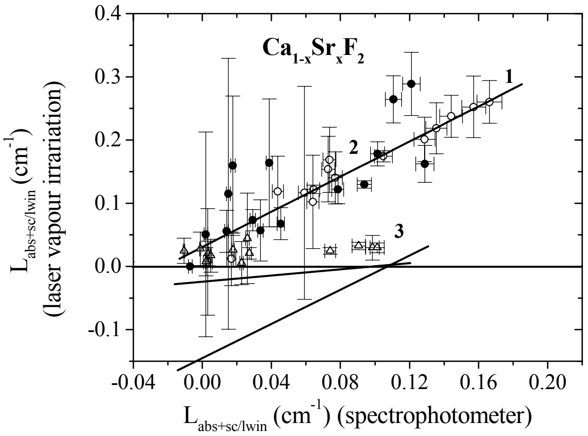


Fig. 2. Linear fit regression for two series of data for absorption + internal light-scattering losses in $Ca_{1-x}Sr_xF_2$ optical windows obtained consecutively by vapour laser irradiation and spectrophotometric techniques at wavelengths within UV–IR range: 1) 248.6 nm (R = 0.9825, SD = 0.42); 2) 510.6 nm (R = 0.7766, SD = 0.0524); 3) 900 nm/6.45 μm (R = 0.7287, SD = 0.3685).

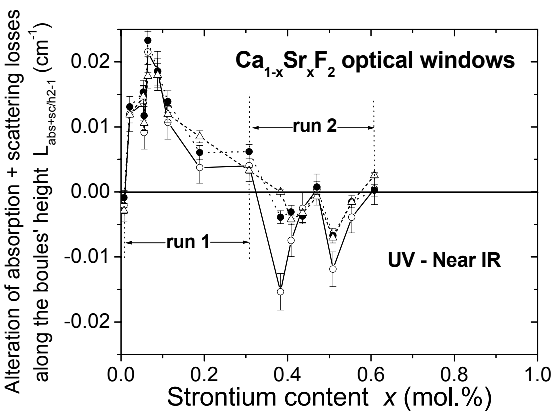


Fig. 3. Difference in absorption plus light-scattering losses, determined at particular wavelength within UV–NIR range, between pairs of optical windows prepared from non-adjacent parallel sections of $Ca_{1-x}Sr_xF_2$ boules as a function of the strontium content x at λ 248.6 nm (o); 510.6 nm (●) and 900 nm/6.45 μm (Δ).

Longitudinal inhomogeneity of the grown boules is assessed following the variations of $L_{abs+sc/h2-1}$ on strontium content x and λ within UV–MIR (Fig. 3). Since the shift of CF also depends on x [9], in this way we found out indirect relationship between structural and growing parameters. A larger absolute divergence from zero is seen for run 1-boules compared to run 2-boules. The differences for run 1 are positive with the exception of the boule with the lowest x (0.0073), whereas they appear negative or near to zero for run 2-boules.

Most of the studied run 1-boules show higher divergences in the Vis region compared to UV and IR regions that is just the opposite of run 2-boules, the $L_{abs+sc/h2-1}$-values of which approach zero in the Vis region. The established trend for increase in the parameter $L_{abs+sc/h2-1}$ towards the top section of run 1-boules testifies the changing towards worse growing conditions during crystallization. At the same time, the growing conditions during crystallization of run 2-boules turn out either constant (for three of the boules) or change to better (for the remaining five ones) that corresponds to the observed variations of $L_{abs+sc/h2-1}$-values near to or noticeably below zero. For two boules (with $x \approx 0.38$ and $x \approx 0.5$) the divergences appear insignificant and close to zero, which reveals high structural homogeneity along boules' height, and suggests reaching the optimum set of growing conditions. The opposite trend for $L_{\mathrm{abs+sc/h2-1}}$-alteration in the Vis region emphasizes again the importance of growing conditions for ensuring a normal growth with minimum structural defects acting in this case as internal scattering sites rather than colour (absorption) centres for Vis-light.

Optical properties and crystallization front position

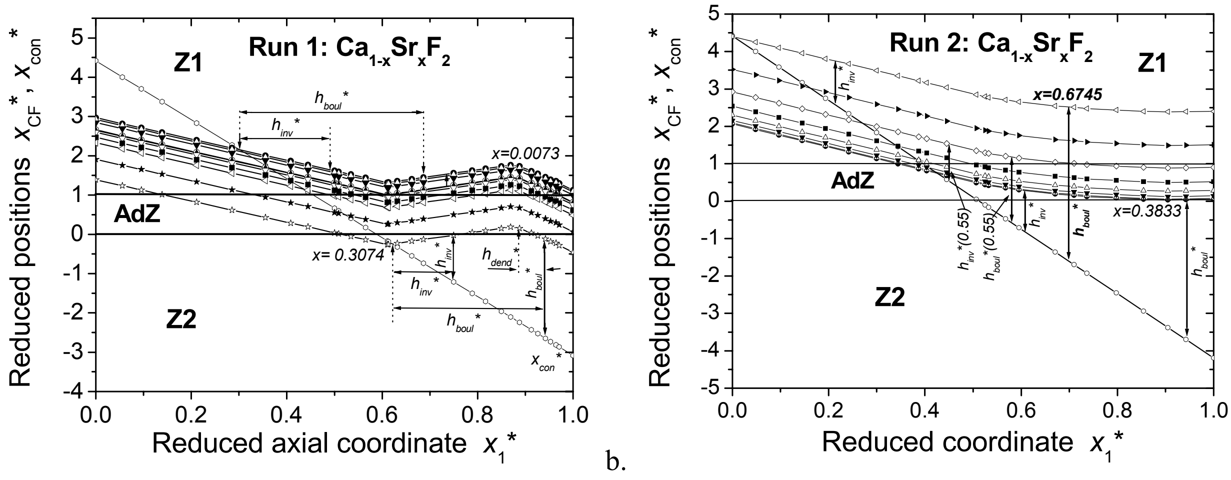
The optical quality of grown boules, assessed by involved semi-empirical parameters, is related to growing conditions *via* the shift of CF-positions, x_{CF}, according to formulas (4). The distance from conical tip of crucible's interior (where nucleation starts) to lower plane section of AdZ ($z = 0$) is marked by $x_{\mathrm{con}}(z)$. Then the height of crystallized volume is determined by the difference ($x_{\mathrm{CF}} - x_{\mathrm{con}}$), where for simplicity of analysis the quantities are reduced by division to 24 mm (AdZ thickness) and marked by asterisk. The variable x_1* represents the distance of crucible withdrawal towards Z2 as a part of total crucible movement during the run. The cross points of $x_{\mathrm{CF}}*(x_1*)$ curves with straight line $x_{\mathrm{con}}*(x_1*)$ specify a nucleation curve $x_{\mathrm{nucl}}*(x_1*)$ that manifests the crystallization start in particular nests.

Several peculiarities may be discussed following the dependences in this study (Fig. 4a, b):

1) The CF-positions shift equidistantly at constant slope towards Z2 during approximately 50% of total crucible movement, remaining within Z1 or AdZ. This determines planar or convex shape for CF that is favourable for normal growth with minimal built in structural defects.

2) The second half of the boules are crystallized under entirely different thermal conditions expressed in gradual decrease of the negative slope of x_{CF}*-curves (run 1) or in twice changed sign of the curves' slope (run 2), being implemented into AdZ or the adjacent lower section of Z1. This is due to redistribution of thermal exchange between the load and its surroundings causing significant radial heat losses [9]. Under such thermal conditions the CF-shape is expected to vary slightly around planarity, being closer to convex if CF-position turns out to be above the middle cross section of AdZ, which ensures an optimum for growing boules with perfect optical quality. This is a result of the effective removal of plenty of micro-defects (impurities, parasitic nuclei, and others) aside from the thin layer in front of the CF.

3). The starting point for $x_{\mathrm{nucl}}*(x_1*)$-curves varies widely between –0.27 (run 1, $x = 0.307$) and +4.41 (run 2, $x = 0.675$) that shows great differences in the initial nucleation conditions at the tip of particular nests for further propagation of normal growth. This way, two of run 1-boules, with the highest x (0.189 and 0.307), turn out under worst conditions in regards to the initial shape of the just nucleated CF, which remains firmly concave within the entire conical section, thus initiating dendroidal crystallization (Fig. 5).



a. b.

Fig. 4a, b. Reduced positions of the CF and of the conical crucible's tips along the furnace unit during two experimental runs carried out under different thermal conditions into a load, representing a multichamber graphite crucible charged with portions of pre-melted CaF_2-SrF_2 mixtures for growing of $Ca_{1-x}Sr_xF_2$ crystals.
a) run 1: (●) – 0.007, (△) – 0.021, (▼) – 0.054, (o) – 0.056, (▽) – 0.065, (■) – 0.088, (◁) – 0.113, (v) – 0.189, (✯) – 0.307, (▲) – Centre-0.213, (¤) – x_{con}*; b) run 2: (●) – 0.383, (△) – 0.408, (▼) – 0.436, (△) – 0.471, (■) – 0.509, (◇) – 0.554, (▶) – 0.608, (◁) – 0.675, (o) – x_{con}*.

4) The higher position of x_{nucl}* within Z1 suggests larger and more convex curvature of the CF favouring the efficiency of self-purifying mechanism. Here, it has to be taken into consideration that the magnitude of the vertical temperature gradient decreases upwards in the furnace unit approximately up to the middle cross section of Z1 that leads to increase in melt suppercooling within the thin layer in front of the CF, which, in turn, initiates deterioration in the normal growth with rapidly propagating dendroidal crystallization [20]. Besides, stronger radial inhomogeneities will arise into the load [21, 22] as far as CF shifts from AdZ, which would disrupt additionally the normal growth. As a whole, the growing conditions for run 2 seem to be much more favourable to ensure a normal growth at steeper vertical temperature gradient and gradually changing negligible shift for most CF within the AdZ that implies a perfect crystal quality.

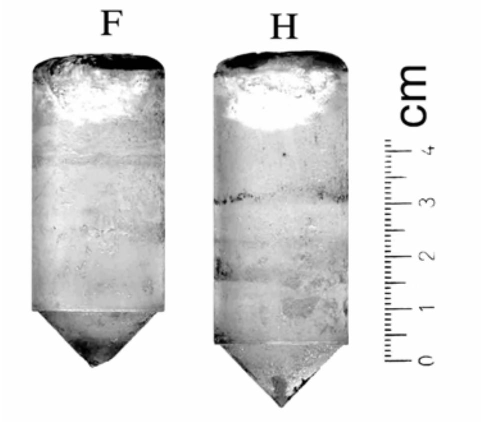


Fig. 5. Boules grown during run 1 with upper section of dendroidal crystallization: F – x = 0.307, H – x = 0.189.

CONCLUSIONS

Important relationships between structural, technological and characteristic parameters, controlling a simultaneous growth in multichamber crucible and originally modified furnace unit of BS apparatus of calcium–strontium fluoride boules of different composition, are firmly established. The growing conditions are set to be optimal *via* appropriate shift of the CF-position according to the composition of starting mixtures. The optimum is reached when the CF are positioned predominantly in an unusually broad adiabatic zone, while the real crystallization rate remains steady slightly over the set up crucible movement speed. A realistic assessment of the grown boules optical quality is being implemented by measuring the transmissivity t of optical windows, finished from different boules' sections, and separating the actual absorption from refractive losses. The t-measurements are performed by two different techniques using a highly intensive vapour lasers irradiation within DUV–NIR spectral range (VLIr) and a highly sensitive spectrophotometer (SpPh). The advantages of VLIr over SpPh technique lie in the higher efficiency of VLIr since it allows large statistics for a short time at particular wavelengths, high sensitivity and precise control of the area and position of the beam spot. The grown mixed fluoride crystals represent solid solutions with wide range of compositions and possess practically uniform distribution of Ca and Sr atoms inside the lattice and nearly perfect microstructure especially for boules with x between 0.5 and 0.6.

The applied original growing technique and reliable methods for assessing the key optical properties imply production of high-grade optical material with stable unique characteristics ranged from DUV to NIR. This material is favourable for UV-lithography optics being also suitable for optics of newly developed vapour lasers.

The successful reiteration of simultaneously grown calcium-strontium fluoride boules with widely altering composition has acquired also a definite scientific importance supplying the researchers with perfect material for new explorations in non-linear optics as appear to be cleaning of femto-second pulses and precise measurements of short high intensive laser pulses in UV.

REFERENCES

1. J. H. Burnet, Z. H. Levine, E. L. Shirley, *Phys. Rev. B: Condens. Matter. Mater. Phys.,* **64**, 241102-R (2002).
2. http://www.tf.unikiel.de/matwis/amat/elmat_en/kap_6/advanced/t6_6_1.html.
3. D. C. Allan, N. F. Borrelli, C. M. Smith, R. W. Sparrow, *U.S. Patent 6806039.*
4. D. C. Stockbarger, *J. Opt. Soc. Am*., **39**, 731 (1949).
5. J. T. Mouchovski, *Prog. Cryst. Growth Charact. Mater*., **53**, 79 (2007).
6. K. Hein, E. Buhrig, H. Gohler, *Cryst. Res. Technol*., **27**, 351 (2006).
7. K. A. Pandelisev, in: Plate Form Having Superior Properties. (Proc. 2nd Int. Symp. 157 Lithography, Dana Point, CA, USA, 2001).
8. J. T. Mouhovski, K. A. Temelkov, N. K. Vuchkov, N. V. Sabotinov, *J. Phys. D*: *Appl. Phys*., **40**, 7682 (2007)
9. J. T. Mouhovski, K. A. Temelkov, N. K. Vuchkov, N. V. Sabotinov, *Compt. Rend. Acad. Bulg. Sci.*, **62**, 687 (2009).
10. B. Wang, M. Ward, R. Rockwell, J. List, *Photonic Spectra*, 62 (2002).
11. N. K. Vuchkov, K. A. Temelkov, N. V. Sabotinov, *IEEE J. Quantum Electron.,* **37,** 1538 (2001).
12. N. K. Vuchkov, K. A. Temelkov, N. V. Sabotinov, *IEEE J. Quantum Electron.,* **41**, 62 (2005).

13. K. A. Temelkov, N. K. Vuchkov, B. L. Pan, N. V. Sabotinov, B. Ivanov, L. Lyutov, *J. Phys. D: Appl. Phys.,* **39,** 3769 (2006).
14. J. T. Mouchovski, V. Tz. Penev, R. B. Kuneva, *Cryst. Res. Technol*., **31**, 727 (1996).
15. Optical Crystals by Optovac, Handbook 82, Optovac Inc., North Brookfield, Massachusetts, 5-3 (1982).
16. G. L. Squires, Practical Physics, McGraw-Hill, London, 1968, p. 246.
17. J. T. Mouchovski, *Bulg. Chem. Commun*. **39**, 3 (2007).
18. D. K. Kimm, M. Rabe, R. Bertram, R. Uecker, L. Parthier, *J. Cryst. Growth*, **310**, 152 (2008).
19. B. Kostova, J. Mouchovski, O. Petrov, L. Dimitrov, L. Konstantinov, *Mater. Chem. Phys*., **113**, 260 (2009).
20. V. A. Arhangelskaya, V. M. Reiterov, I. L. Smolyanskii, *Neorg. Mater*., **12**, 1560 (1976) (in Russian).
21. R. J. Naumann, *J. Cryst. Growth*, **58**, 554 (1982).
22. T. Jasinski, A. F. Witt, *J. Cryst. Growth,* **71**, 295 (1985).

ЕДНОВРЕМЕНЕН РАСТЕЖ НА КРИСТАЛНИ БУЛИ ОТ $Ca_{1-X}Sr_XF_2$ С РАЗЛИЧНО СЪДЪРЖАНИЕ НА Sr ЧРЕЗ ПОДОБРЕНА АПАРАТУРА НА БРИДМАН-СТОКБАРГЕР. НАДЕЖДНОСТ НА ТЕХНИКИТЕ ИЗПОЛЗВАНИ ЗА ИЗМЕРВАНЕ НА СВЕТОПРОПУСКЛИВОСТТА

Й. Т. Муховски[1]*, К. А. Темелков[2], Н. К. Вучков[2], Н. В. Съботинов[2]

[1] Централна лаборатория по минералогия и кристалография „Акад. Иван Костов“,
Българска академия на науките, ул. „Акад. Г. Бончев“, Блок. 107, 1113 София
[2] Институт по физика на твърдото тяло „Георги Наджаков“,
Българска академия на науките, бул. „Цариградско шосе“ № 72, 1784 София

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(Резюме)

Осъществено е едновременно израстване на кристални були от калциево-стронциев флуорид с различен количествен състав в симетрични спрямо аксиалната ос отделения на тигел като е използвана оригинална Бридман-Стокбаргер апаратура. Контрол върху положението на кристализационния фронт (КФ) в границите на необичайно широка адиабатна зона (АдЗ) на пещта, минимизира радиалния топлообмен, което осигурява практически равнинна форма на КФ за нормален растеж на отделните були. Положението на КФ е определено чрез емпирични формули, които отчитат различните фактори, влияещи върху термично поле в товара. Позицията на КФ е свързана с характеристични параметри, представляващи: 1) средната стойност и 2) изменението на сумата от абсорбционните загуби и тези от светоразсейване за единица оптичен път на монохроматичен светлинен лъч, пропускан през оптически прозорци, изготвени от различни сектори на булите. Излъчването е предизвикано или чрез използване на CuBr лазер с метални пари, работещ при дължина на вълната в ултравиолетовия (УВ) и видимия (Вид) диапазони, както и SrF_2 лазер с метални пари, работещ в инфрачервения (ИЧ) диапазон, или чрез високочувствителен спектрофотометър, работещ в УВ–близкия ИЧ диапазон. Използването на лазери с метални пари позволява измерването на външното светопропускане да бъде осъществено бързо за фиксирани дължини на вълната с интерес за практиката при високочувствителен контрол върху площта и положението на петното на лъча. Израслите були представляват еднородни твърди разтвори на CaF_2 и SrF_2 с незначително присъствие на структурни дефекти. Така получени, те са висококачествен оптически материал за изработване на разнообразни елементи с широка приложимост в УВ–ИЧ оптически системи.