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STUDY OF THE CRYSTALLINE QUALITY OF CZOCHRALSKI GROWN BARIUM LITHIUM FLUORIDE SINGLE CRYSTALS

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ABSTRACT

The influence of crystallographic orientation and rotation rate on the crystalline quality of Czochralski grown $BaLiF_3$ crystals have been studied by neutron diffraction techniques. Analysis of the mosaicity of crystals showed that growth in the <111> direction with a flat interface resulted in crystals with good optical and crystalline quality. However, growth in the <100> direction with flat interface produced a low degree of optical quality but still with good crystallinity.

MATERIALS INDEX: perovskite, fluorides, barium, lithium.

Introduction

Recent investigations have shown that crystals with cubic perovskite-like structures are very interesting active media for laser applications. Examples of tunable lasers can be obtained with Cr^{3+} doped $KZnF_3$ and Pb^+ doped $KMgF_3$ crystals [1,2]. $BaLiF_3$ is an inverse perovskite and a potential laser crystal when doped with Pb^{2+}, Ni^{2+} and Co^{2+}. The optical properties of these crystals were investigated [3, 4] and their performance as laser media was shown to be dependent on their optical and crystalline quality, which are associated with the preparation conditions and growth process. Recently, Baldochi and Gesland [5] studied the conditions of synthesis and Czochralski growth of $BaLiF_3$ crystals that produce a good degree of optical quality. In this work we studied the influence of the growth process in the crystalline quality of the Czochralski grown $BaLiF_3$ single crystals.

During the growth of a single crystal, it is possible that more than one crystalline domain is formed. In general, the orientations of the domains are very close to one another. The crystalline quality of a crystal, regarding its macroscopic aspect, is dependent on how many domains are formed, the angular width of each one and the angular dispersion between them. These information are, in general, obtained by measuring rocking curves in the moving-crystal-stationary-detector procedure, i.e., the ω-scan in the normal-beam equatorial geometry [6] using x-rays or neutrons. A neutron beam has, in general, a large cross-sectional area and a sample can be completely immersed in the beam. The high penetration of neutrons in most materials makes it possible to observe all domains simultaneously. The same result is not possible to obtain with x-rays. Rocking curves measured with neutrons have been used classically to evaluate the quality of monochromators used in neutron diffractometers [7]. In this work, rocking curves were used to correlate crystalline quality of $BaLiF_3$ single crystals with uniformity, growth direction and rotation rate.

Experimental

The IPEN neutron diffractometer installed at the IEA-R1 reactor, was used to measure rocking curves of Czochralski grown $BaLiF_3$ single crystals. We used 8 samples with two different directions of growth, <111> and <100>. Their characteristics are given in Table I together with the reflections observed for each sample. Figure 1 is a representation of a crystal boule with the three considered regions: initial cone, main body and final cone (not used for the measurements). The average diameter of the main body of the samples ranged from 25 to 30 mm and their lengths from 20 to 30 mm. Samples of numbers #14C, #15C, #17C and #24I were obtained from experiments where the growth was interrupted by quickly raising the crystal from the melt in order to observe the interface shape. Samples #31 and #38 were obtained from boules after a complete growth procedure. Crystals #38 and #01 were cut as showed in Fig. 1. Other crystals were measured in their original shapes.

For each sample we measured at least one rocking curve corresponding to the growth direction. In some cases we measured four curves by rotating the sample around the growth direction in 90 degrees steps. This procedure allowed the observation of domains that could appear superposed in one of the curves. To observe the crystalline quality in directions other than the growth one, for samples #24I, #31 and #38 we measured reflections that are perpendicular to the growth direction. For these samples we also measured in the second growth direction considered in this study. For example, measured directions in sample #24I were: <100> (growth direction), <011>, <01$\bar{1}$>, <0$\bar{1}\bar{1}$>, <0$\bar{1}$1>, which are perpendicular to <100>, and <111> (second growth direction).

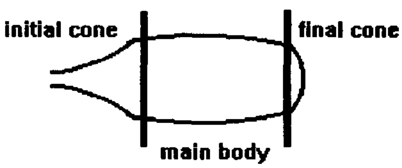

FIG. 1
A representation of a crystal boule with the three regions considered in the measurements.

TABLE I

Characteristics of the Samples and Measured Reflections

CRYSTAL	GROWTH DIRECTION	ROTATION RATE	INTERFACE SHAPE	SAMPLES	MEASURED REFLECTIONS
C#01/89	[100]	10	convex	#01 (main body)	100
I#14/89	[111]	20	semiflat	#14C (cone)	111
I#15/89	[111]	40	flat	#15C (cone)	111
I#17/89	[111]	60	concave	#17C (cone)	111
I#24/90	[100]	30	flat	#24I (boule)	100, 111, 011, $0\bar{1}\bar{1}$, $01\bar{1}$, $0\bar{1}1$
C#31/90	[111]	30	flat	#31 (boule)	111, 100, $0\bar{1}1$, $\bar{1}01$, $1\bar{1}0$, $\bar{1}10$
C#38/90	[111]	30	flat	#38C (cone) #38 (main body)	111 111, 100, $02\bar{2}$, $0\bar{2}2$, 202, $\bar{2}02$, $2\bar{2}0$, $\bar{2}20$

Results

a) *Uniformity*

Two different regions of the same crystal were initially compared: cone and main body. The former region is typically obtained in the growth of pulled crystals, where the initial seed is gradually increased up to a selected diameter. The latter one is a region where the diameter is kept constant. To study the uniformity, we used three samples: #38C, #38 and #31 from two crystals grown in similar conditions: <111> direction, 30 rpm and 1 mm/h pulling rate. Figures 2 and 3 show, respectively, the measured curves for the 111 reflection at $\phi = 0°$ and 90° and two reflections, $1\bar{1}0$ and $\bar{1}10$, which are perpendicular to the growth direction.

The cone region shows, in all measurements, more imperfections compared to the main body region. We observed from the rocking curves measured for samples #38C and #38 that the cone has two or more mosaic domains. Due to this fact, a cone cannot be classified as mosaic single crystal as well known by crystal growers. Cone formation is determined by changes in the growth rate and in the crystal diameter, and also by the thermal instability of the melt. High thermal instability will result in high concentration of distortions and defects in the crystalline structure. From the curves shown in the figure 3 we also note that there is a higher dispersion of mosaic domains for the reflections perpendicular to the growth direction, when compared to the dispersion in the growth direction itself. Moreover, when comparing these reflections with the same kind of reflections in the main body, the cone regions continue to present a wider dispersion of mosaic domains., It is noteworthy that for each reflection, although with greater angular dispersion, the results in the cone region agree with the results in the main body region.

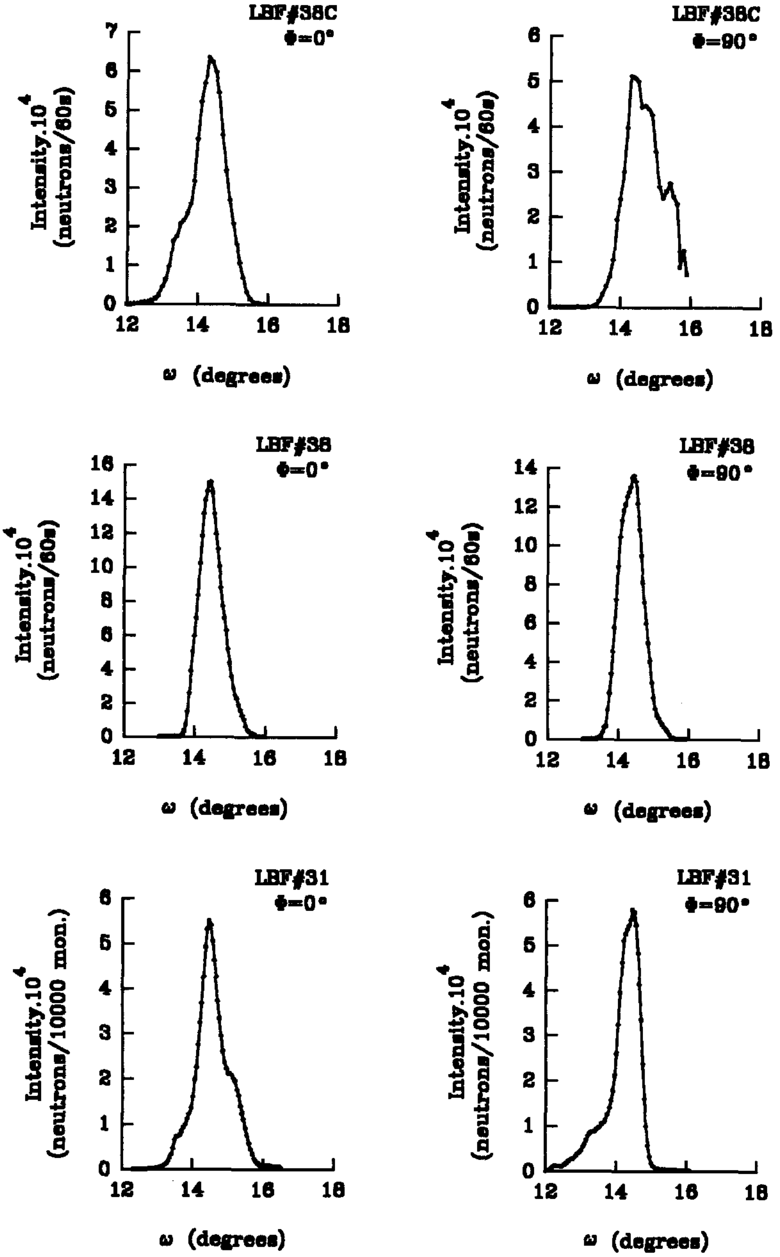

FIG. 2

Rocking curves of samples #38C, #38 and #31 for the growth direction.

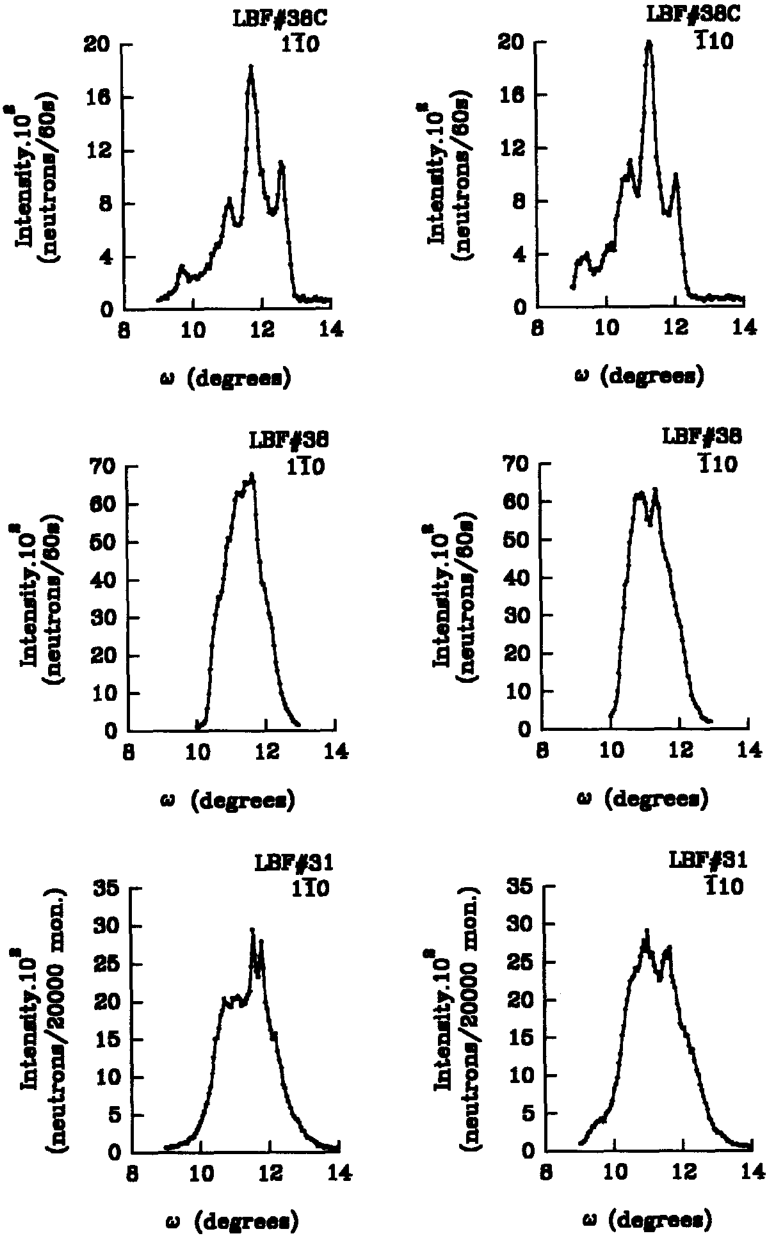

FIG. 3
Rocking curves of samples #38C, #38 and #31 for reflections that are perpendicular to the growth direction.

The measured curves in the growth direction of the sample #31 (boule) are similar to those obtained with sample #38 (only central region of the crystal). However, the measured curves for the reflections perpendicular to the growth direction show a lower dispersion for sample #38. This implies that sample #38 has a better crystalline quality than sample #31, although they were grown in the same conditions. One reason for this result could be the fact that, when measuring sample #31, both cone and central region contributed, simultaneously, to the measured intensity. Although the cone contribution is not large compared to the central region, since its volume is several times smaller than the volume of the central region, its presence can disturb the observed crystal quality. However, the difference observed between the two samples could be also due to intrinsic characteristics of the crystals. Crystals obtained in similar conditions will not necessarily have the same quality. To verify the influence of the cone in the crystalline quality of sample #31, we measured again this sample with the cone region covered by a cadmium foil. The observed curves showed no appreciable differences from the first ones. For this reason, we concluded that the differences were intrinsic to the crystals and not due to the presence of the cone.

We note from Figures 2 and 3 that the angular distance between two mosaic domains in the growth direction was approximately 0.4° and, in the perpendicular directions, 1.5°. So far it was possible, at least regarding growth direction, to consider the studied samples as single crystals. Figure 4a shows a tridimensional curve that permits a better visualization of the mosaicity of sample #38.

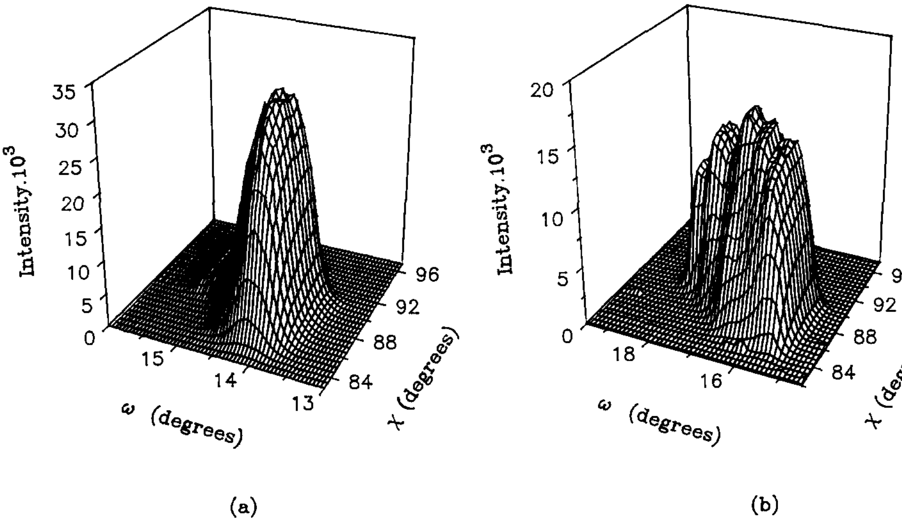

Fig. 4
Tridimensional rocking curves measured for the growth directions of: (a) sample #38, grown in the <111> direction with 30 rpm, and (b) sample #01, grown in the <100> direction with 10 rpm.

b) Growth direction

In general the orientation of growth affects the crystallographic perfection and the defect density in the final crystal. To study the influence of the growth direction we compared samples #24I and #31 that are crystals grown at, respectively, <100> and <111> directions both with a rotation rate of 30 rpm and a pulling rate of 1 mm/h. Figure 5 shows the measured curve for 100 reflection at ϕ = 0° and 90° and for two reflections, 011 and 01$\bar{1}$, with scattering vectors perpendicular to the growth direction. It is easy to note that sample #24I is a crystal with a better crystalline quality than sample #31. This is true not only because the rocking curves for the growth direction are very narrow but also because the same behavior is observed in the reflections perpendicular to the growth direction. This is not observed for samples #38 and #31 both from crystals grown in the <111> direction.

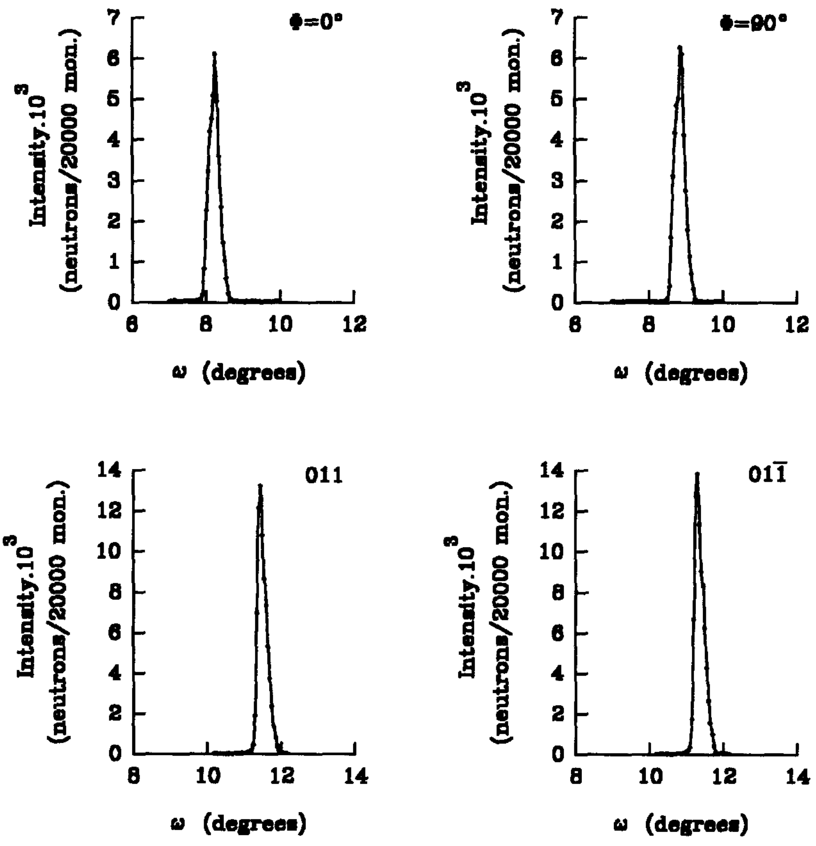

FIG. 5
Rocking curves of sample #24I for the growth direction and for directions perpendicular to the growth direction.

Figure 6 shows the rocking curves for samples #24I and #31. A fitting done with gaussian curves is also shown in the figure. This fitting allows to determine number and characteristics of the mosaic domains in the crystal. Sample #24 has two mosaic blocks approximately 0.2° apart. One of the domains contributes very little when compared to the other whose height is approximately three times greater. The half width (β) and the mosaic width (η) of the domains are listed in Table II. Domains are numbered according the increasing values of their angular positions ω. It should be noted that the values for mosaic width in the table are affected by the experimental divergence. Sample #31 has three mosaic blocks with relative deviations between adjacent domains of approximately 0.5°. The greater domain in this sample has a mosaic width of 0.23° which corresponds to approximately twice the mosaic width of sample #24I.

TABLE II

Half and Mosaic Widths of the Domains in Samples #24I and #31

SAMPLE #24I			SAMPLE #31		
domain	β	η	domain	β	η
1	0.31	0.13	1	0.54	0.23
2	0.14	0.06	2	0.80	0.34
			3	0.84	0.36

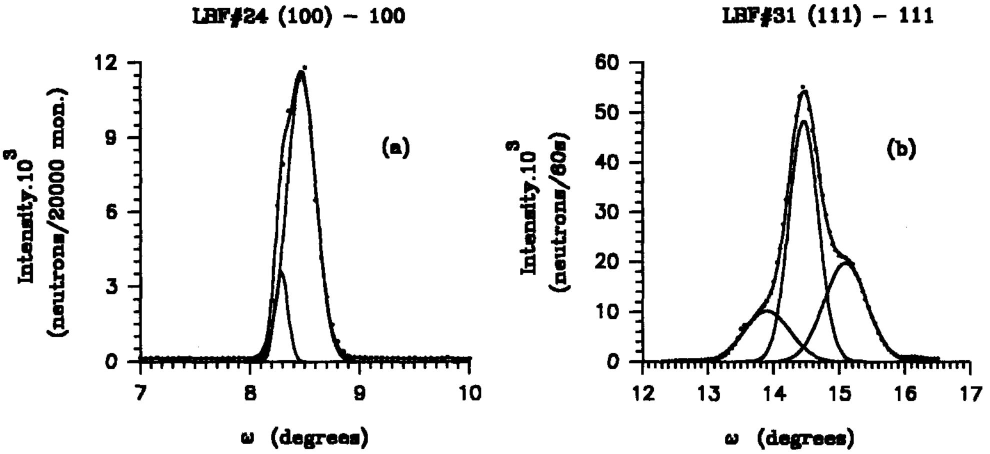

FIG. 6
Rocking curves of samples #24I and #31 for the growth direction. Continuous curves show the gaussian fitting to the experimental points.

c) Rotation rate

In the Czochralski geometry, crystal rotation causes a well defined heat flow in the melt that improves the thermal symmetry around the crystal axis. When impurities are added, rotation causes uniformity of their distribution across the interface. The flow of the liquid and the thermal geometry can affect significantly the shape and the quality of the resulting crystal. In melts of moderate thermal conductivity, like fluorides, heat transport is mainly done by convection. One well-known effect of convection on the growth of crystals is the change of the interface shape. This is due to isotherms which are flow determined. For the Czochralski $BaLiF_3$ single crystals used in this study, the solid-liquid interface became concave toward the melt above 50 rpm, flat or semiflat between 30-40 rpm and convex for low rotation rates such as 10 rpm [5].

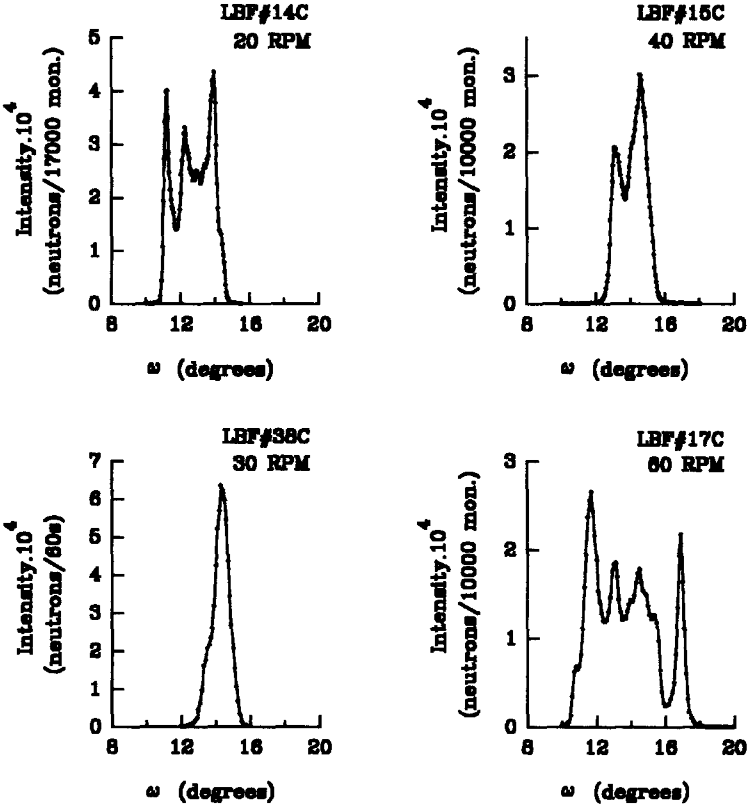

FIG. 7
Rocking curves of samples #14C, #15C, 17C and #38C for the growth direction with different rotation rates.

To determine the influence of the rotation rate and, consequently, the influence of the interface shape in the quality of the pulled crystals, we measured rocking curves for samples #14C, #15C, #17C and #38C. These crystals were grown in the <111> direction with the same pulling rate but with rotation rates of 20, 40, 60 and 30 rpm, respectively. These samples are cones where the growth was interrupted by quickly raising the crystal from the melt to preserve the interface shape, except #38C. As mentioned before, this sample was cut from a boule according to Fig. 1.

Concerning the rocking curves obtained with the samples mentioned above (Fig. 7), we noted that: both convex (#14C) and concave (#17C) interfaces led to the formation of several mosaic domains. The best crystalline quality is observed for crystals grown with flat (#38C) or semiflat (#15C) interfaces. Similar results are observed for the <100> direction. This means that crystalline quality decreases for crystals grown with convex and concave interfaces. Figure 4b shows a tridimensional rocking curve measured for sample #01, grown in the <100> direction with a low rotation rate (10 rpm). Differently from Fig. 4a, this curve shows several domains which is a characteristic of convex interfaces.

Conclusions

Rocking curves obtained with neutron diffraction showed to be a powerful tool to study the influence of the interface shape in the crystalline quality of Czochralski grown $BaLiF_3$ crystals. When a convex or a concave interface of growth is formed, a large number of mosaic domains appear with a large dispersion between them resulting into a crystal with poor crystalline quality. Crystals with improved crystalline quality were observed for flat and semiflat interfaces of growth with a decrease in the number and in the dispersion of the mosaic domains. Influence of the crystallographic orientation in the crystalline quality was also demonstrated by means of rocking curves. Considering crystals obtained with the same conditions, rocking curves for <111> oriented crystals showed mosaic widths two times greater than those of <100> oriented crystals. It is important to note that this result does not mean that <111> oriented crystals have a poor crystalline quality but only that they are not as good as the crystals grown in the <100> direction. In both types of crystals, the relative angular deviations between domains are very small. In conclusion, the utilization of neutron diffraction technique allowed to determine the best growth conditions for the obtention of crystals with good crystalline quality.

Acknowledgments

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