Single Crystals for Functional Devices

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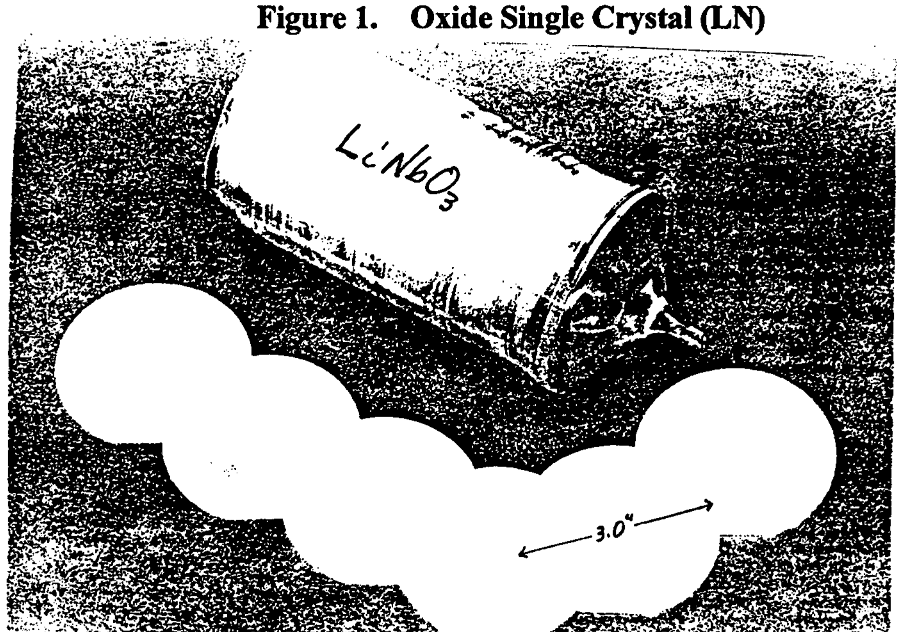
Introduction

Crystal growing is no longer art, in fact is emerging science and technology as it continues to explores basic understanding of its growing mechanism and to develop techniques of growing new crystals. Unparalleled progress in the semiconductor technology where single crystals of silicon and III-V compounds are essential to the realization of new devices. Accordingly, the single crystal growing technology has impetuously been developed for the incentive applications of single crystals of both semiconducting and non-semiconducting (oxides) materials. In Figure 1, the evolution of single crystals is shown with respect its size: $LiNbO_3$ started from few mm to 76 mm dia.

Figure 1. Oxide Single Crystal (LN)



Device developers have extensively searched for materials, which have heretofore not been available in single crystals. Relentless effort in growing new/different crystals has greatly helped in producing for special device applications. In particular, ever since Laser has become practically available as light source for optical transmission (telecommunication), demand for optical devices have been continuously realized. For example, semiconducting single crystals has become readily available in a large quantity with various sizes up 200mm dia.while non-semiconducting (oxides) crystals (LiNbO3, LiTaO3) are gradually produced. Both types of single crystals grown by CZ technique have been extensively used in sophisticated devices.

Some of the oxide crystals are listed in below:

Table 1. Oxide Single Crystals (Bulk)

Crystal	Functionals
BO, LBO, KTP	Nonlinear Optical Crystals
BBO, KDP, $LiNbO_3$	Electro-Optic Crystals
YVO_4, α -BBO	Birefringent Crystals
TeO_2, $PbMoO_4$	Acousto-Optic Crystals
$BaTiO_3$, Fe:$LiNbO_3$	Photorefractive Crystals
Cr:YAG	Passive Q-switch Crystals
Nd:YVO_4, Nd:YAG, Cr:YAG	Laser Crystals

These bulk crystals are also commercially available for the devices in various shapes with sizes.

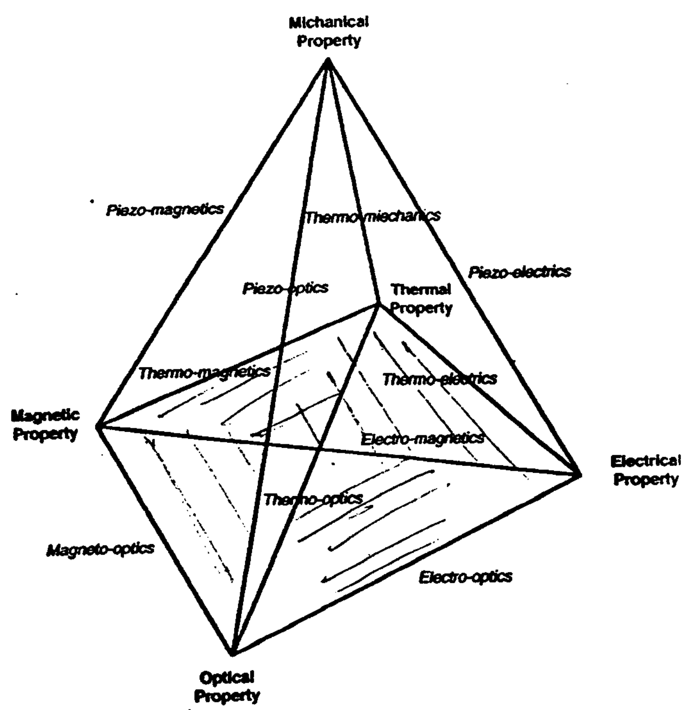
As evidenced in Table 1 the oxide single crystals are mostly for optical applications. Table II show a list of grown crystals by various techniques for small and large sizes. Recent trends in growing single crystals have shown that thin film form of single crystals be much attracted to new applications with its design capability for integrated optic devices. In view of current interest in bulk crystal devices, it is intended to review the extent of device applications where mostly single bulk oxide crystals in a various form are used.

Bulk Single Crystals

Single oxide crystals have recently more grown for optical device applications. Such crystals are known functional materials: Acoustic optics, Electro-optics, Magneto-optics and for non-optic applications, Piezoelectrics, Pyro-electrictics, Electro-magnetics. Since these single crystals are greatly increased in various applications, innovative techniques for growing new class of crystals are developed..

The relationships of the functional properties is illustrated in Figure 2A. It is called the functional property pyramid, showing binary functions as indicated in the foregoing. However, it is interesting to note that new type of single crystals, BGO gives a promise for multifunctional performance (Figure 2B).

Figure 2A. The Functional Property Pyramid



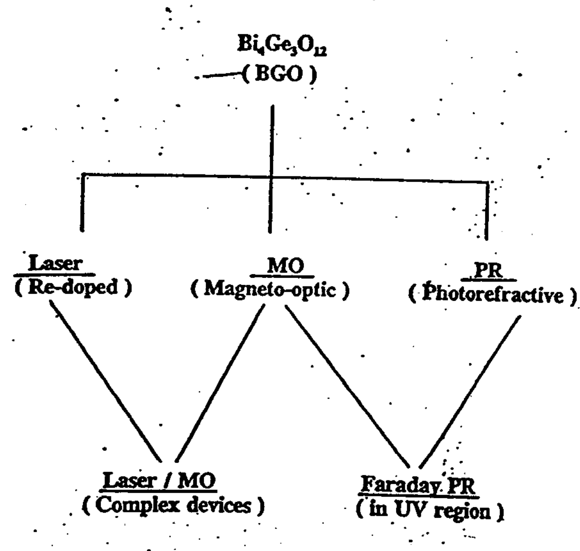


Figure 2B. Multifunction Performance

Table II shows some examples of single crystals grown by different techniques and some problems that are associated with the growing techniques.

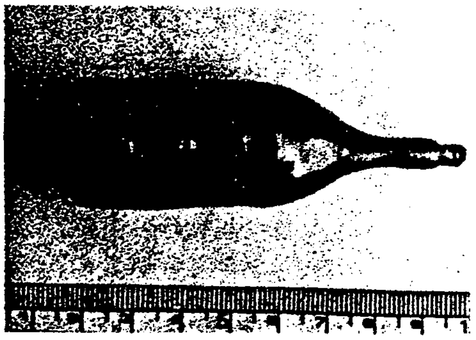
Table II. Crystals grown by Different Techniques

Crystals	Technique	Application	Remarks
$LiNbO_3$ (LN)	CZ	SHG (NLO)	Loss, n
LiO_3 (LI)	Hydro-Sol	SHG (NLO)	Solubility, Mach.
$SrBaNb_2O_5$ (SBN)	CZ	SHG (NLO)	Comp., Quality
$Ba_2NaNb_5O_{15}$ (BNN)	CZ	SHG (NLO)	Comp., Quality
β -BaB_2O_4 (BBO)	Flux,TSSG	SHG (NLO)	Impurity, Size
$KTiOPO_4$ (KTP)	Hydrothermo/Flux	SHG (NLO)	Impurity, Size
$Bi_{12}SiO_{20}$ (BSO)	CZ	PROM (EO)	Absorption, Stress
$PbMoO_4$ (PMO)	CZ	AO	Stiration, Color
$Y_3Fe_5O_{12}$(YIG)	FZ, Flux, LPE	MO (Friday Effect)	Absorp, Rep.
$MnZnFe_2O_4$ (Ferrite)	Bridgman	Recording	Reproducibility

It is evident that many single crystals can now be grown if there are needs for functional applications. However, as indicated in the remarks in the above Table there are different technical problems, thus for many cases, bulk single crystals are more interested in academic study than practical applications. Recently, many sophisticated devices show a strong trend of miniaturization for future integrated components. In fact, it has demonstrated that wafer form of single crystals has been extensively used in optical devices.

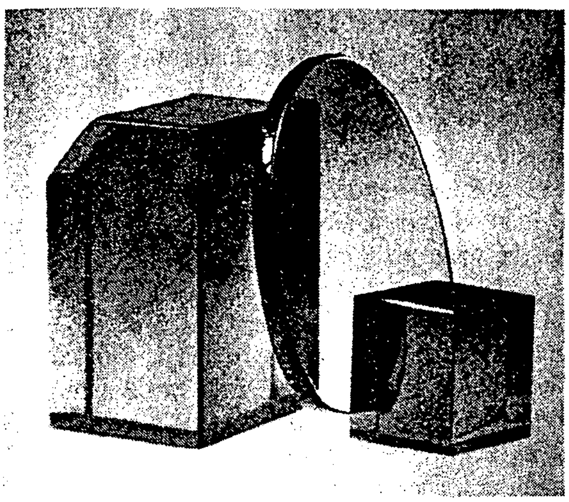
Figures 3 and 4 show some of single crystals grown by different techniques. It is interesting to note that most crystals have been successfully grown by CZ technique, which is extensively prevailing in the synthesis of new/old crystals. In addition, micro, needle, and fiber shape crystals have been successfully grown by micro-pulling-down techniques.

Figure 3. Single Crystal Grown by Different Techniques



Photograph of grown $Bi_{12}GeO_{20}$ crystal(0.3mol% Bi_2O_3 added; rotation rate: 18rpm; growth rate : 2mm/hr).

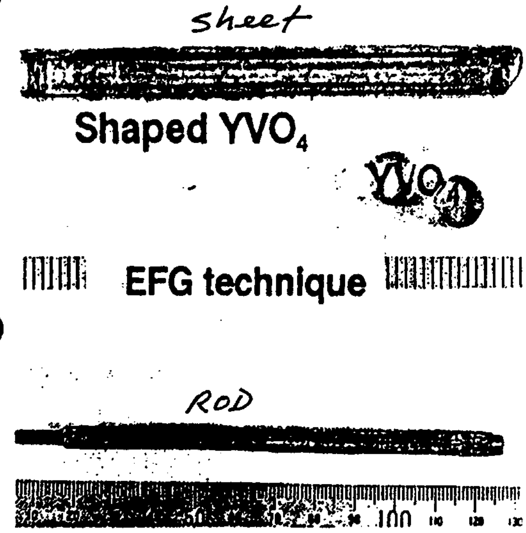
Figure 4. Single Crystal Grown by Different Techniques



SBN:60 single crystal grown by Czochralski technique.

(a)

(b)



Wafer and Thin Film of Single Crystals

As mentioned in the foregoing, the wafers are sliced from the grown single crystals (boule) with retaining its crystal orientations. However, it is known that its fabrication of the wafers for given applications can be expensive. Majority of single crystal device applications is wafer form, on which passive and active devices are fabricated. For passive applications, it is interesting to find that a modified CZ (Stepanov technique) has allowed growing variable shape crystals (tube, rod, and

other shapes) in the near shape for the applications without further machining, however, not functional applications. It is also worth to mention that for a specific application like pivot and window for fancy crystal watch, sapphire crystals grown by CZ and EFG are extensively used.

It is knowledge that two types of thin films are fabricated: 1) polycrystalline/amorphous film and 2) epitaxial film (crystallographically oriented). It is usually followed by a secondary heat treatment for improving its quality.

Thin Films fabrication is a technology for thin film devices which is the most important process for the sophisticated devices in the 21st century.

The thin film deposition techniques are not here elaborated, but the applications of thin films for devices with emphasis of the optical fields.

In Figure 5, thin films of the functional materials are shown for various applications.

Figure 5. Applications of Thin Films

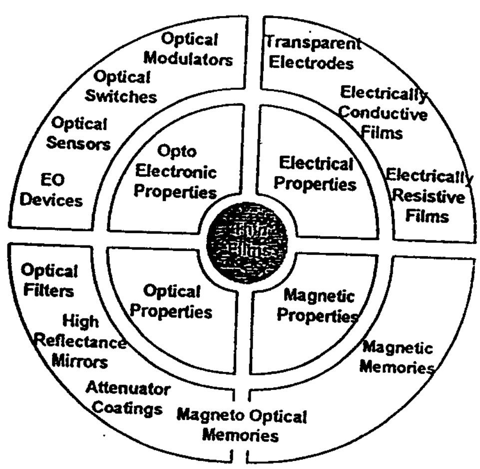


Figure 5. Applications of EMO thin films

Functional Application of Single Crystals

Historically, natural and man made quartz(man-made) crystals have been widely used as piezoelectric devices such as crystal filter, resonator, and

acoustic component. As the devices requirement increase with respect to its operating frequency, in 1980, at least in telecommunication, quartz crystal has become obsolete. In place of quartz, new crystals were synthesized to meet the requirements: $LiNbO_3$, $LiTaO_3$ and others for the applications.
With advent of Laser, which has intensively accelerated communication technology, strong demand for optical functional devices has been realized in both academic and technical fields. Especially, optoelectronic field has become important to telecommunication including fiber optic system. As listed in Tables I and II, it is evident that optical functional applications of single crystals are major and significant.
It is inevitable that future sophisticated devices are to be integrated. For instance, BGO crystal exhibits multi-function as many as 5. Obviously, it requires different crystals for multi-function applications for integration, namely , Laser, MO, PR, Laser/MO, and Faraday/PR.
Alternatively, an approach is to use thin film form of given functional materials as illustrated in Figure 5. A pie chart shows thin film applications to functional devices, and also it includes multilayer of thin films. For example, thin films of ferroelectric crystal are being intensively developed for FRAM (non-semiconductor memory). In fact, it has demonstrated that the EMO materials can be fabricated in thin films such as ferroelectric, ferro/ferri magnetic, superconductor, and optical materials. For obvious reason, thin films of the functional materials are of great demand in sophisticated device applications.

Summary

It is definite trend that the functional devices are to be integrated by miniaturizing of individual components. Bulk crystals turn into wafer form, while thin film of the functional materials is being fabricated for single and multi-layer devices. In addition, single crystals with multi-function performance would be desirable for further miniaturization. Crystal growers have the responsibility for synthesis single crystals work to meet ever increasing requirement of future devices.