Synthesis, Characterization and Applications of Shaped Single Crystals

© *William M. Yen*

Department of Physics and Astronomy University of Georgia Athens,
GA 30602, USA

In this paper we will review techniques for the growth of single crystal mostly of insulating material which are shaped in the growth process. In particular, we will focus on the growth of single crystal fibers of optically activated materials; the emphasis will be placed on the so-called Laser Heated Pedestal Growth (LHPG) method of pulling crystalline fibers. LHPG offers a number of logistical advantages which can be exploited as a tool for materials research. Progress in the synthesis of materials using LHPG is described, as are spectroscopic techniques which are employed in characterizing the optical and physical properties of the crystal fibers obtained through this method.

There has been interest on crystalline materials prepared in fiber form for a sustained period of time; this is partially because single crystal fibers occurring naturally in the form of whiskers often possess near ideal physical properties in crystallinity and in tensile strength. Earlier work addressed itself mostly to metallic materials, for example, in 1922 von Gompers [1] was successful in pulling single crystal metallic filaments directly from the melt. Later, in the 1950's, much of the work centered on the magnetic and mechanical properties of metallic whiskers [2]; however the size and composition of these could not be controlled accurately.

One method which allows the growth of crystalline fibers is the so-called Stepanov method in which the melts are drawn through shapers and crystallization is made to occur after passage through a die [3]. Another method that enabled us to grow single crystal fibers of the desired length and diameter, in the proper crystallographic orientation and of proper composition and doping is the Laser Heated Pedestal Growth (LHPG) method of fiber synthesis [4].

LHPG and the related float zone growth technique are micro-variants of the Czochralski growth method; the feed stoch used is generally in the shape of a rod and the melt is in the form of a self supporting bubble at the tip of the rod. A number of heating sources have been used to produce the melt; the most common method by far has been laser heating with focused single or multiple beams. A seed is dipped into the melt and is wetted by in; as the seed is pulled out, surface tension of the molten materials forms a pedestal around the seed, hence the name of pedestal growth. The melt is kept in place solely by surface tension, hence, this fiber growth method does not require crucibles and eliminates one source of sample contamination. This type of container-less growth also permits the synthesis of materials with extremely high melting points. The laser heated version of pedestal growth (LHPG) is illustrated in Fig. 1 [5].

In a typical LHPG fiber pulling system, a stabilized CO_2 cw laser typically with an output of between 15–75 W is used as a heating source. The usual focusing and turning optics for the beam are shown in Fig. 2 along with the pulling and feeding mechanisms. The fiber pulling assembly may be enclosed in a vacuum-tight chamber allowing growth in controlled atmospheres [6].

The source rods are cut out of polycrystalline ceramics produced by mixing host and activator materials, sintering and hot pressing the mixture into flat disks. Crystalline chips and fibers can be used as source materials as well. The source rods we have employed at the University of Georgia are typically $1 \times 1 \times 12\,mm^3$ and our fiber diameters are in the 0.15 mm to 1.0 mm range; pulling speeds are typically 0.1–2.5 mm/min.

1. Advantages of the LHPG Method of Fiber Growth

Several advantages of LHPG have become apparent, not only in the growth of fibers for applications but, more importantly, as a general way to explore material synthesis and the properties of crystal growth. Other practical advantages of the LHPG method have also become apparent, as follows.

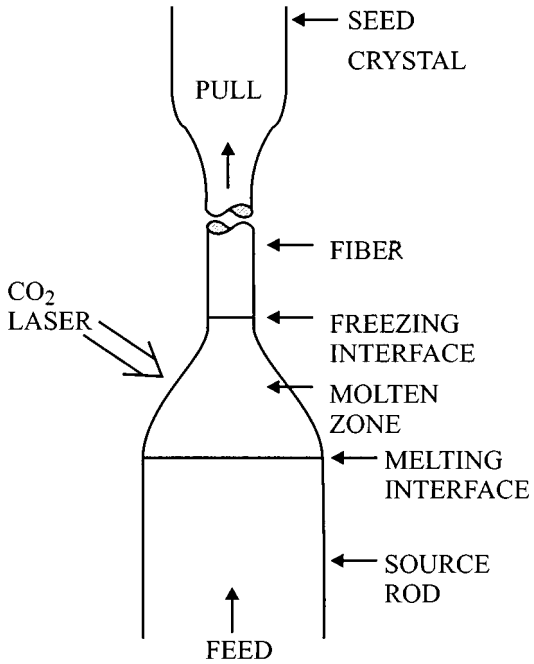

Figure 1. Schematic representation of the LHPG method for fiber growth showing the various regions involved in the growth.

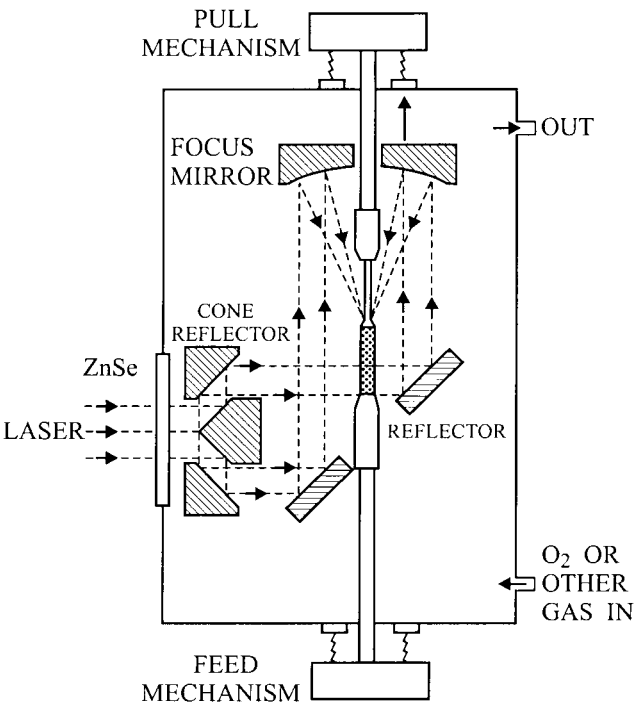

Figure 2. Cross sectional view of the LHPG growth chamber showing details of the reflixicon and optical focusing system.

a) The LHPG relies on surface tension to maintain the integrity of the melt and hence it is a method of growth which does not require crucibles; nor does the enclosure containing the fiber growth region possesses walls heated to high temperatures as is the case in crystal growth furnaces. Both crucible and furnace surfaces are generally understood to be the primary sources of unintentional contamination in normal crystal growth, hence, it follows that the absence of these surfaces allows the growth of very pure crystal materials. The impurity levels found in LHPG fibers are solely determined by the purity of the starting materials of the source rods.

b) The source rod length as well as the melt volume in LHPG are typically small, of the order of 10 mm and 1 mm^3, respectively. The cost of the chemical compounds required for the growth of single cristal fibers is, as a consequence, relatively small. Because of this, it is possible to grow fiber crystals of materials which would be prohibitively expensive to grow by traditional methods, specially on a basis [7]. Further, it is also generally accepted that thermal gradients within the melt container are responsible for introducing stresses and other defects in bulk crystals, because of this LHPG pulled fibers can be made practically stress free. The small volume of the growth area also facilitates the introduction of external perturbations during synthesis of the crystal. The application of an external field to the melt may influence the growing process by encouraging the inclusion of domains or the formation of other stoichiometric combinations [8].

c) One of the most attractive features of the LHPG methods is the rapidity with which fibers can be grown by this method. With our pulling speeds, a fiber sample of length of 1 or 2 cm, sufficient for spectroscopic characterization, can be grown and characterized in a relatively short time [7]. The information feed back made possible by this time scale allows for the rapid re-adjustment of stock compositions and growth conditions for optimized materials. It is this feature method that makes this method such a powerful tool in the synthesis and engineering of crystalline materials in general.

d) Finally, for those of us interested in the optical spectroscopic properties of activated materials, the fiber configuration is ideal experimentally for conducting absorption, emission and other ancillary dynamical and static optical measurements.

We have been able to pull a great variety of oxide and fluoride crystal fibers doped with rare earth and transition metal ion activators in a great range of concentrations; a list of the materials we have been able to grow is shown in table.

2. Characterization of LHPG Materials

Characterization of the fibers with regard to physical and mechanical properties can be done using the myriad of standard techniques such as *X*-ray diffractometry, crystal birefringence, microprobe analysis and optical microscopy [4].

We have been able to derive many characteristic of our fiber samples by investigating the static and dynamic optical properties of the fiber [9]. Static measurements obtained under steady state conditions can be used to determine the dopant concentrations, whether the concentration is uniform along the length of the fiber and whether other species or active defect centers exist in the fiber. Dynamic measurements entail the determination of radiative and non-radiative lifetimes and can yield information on the microscopic interactions between the active ions and their surroundings. Other optical determinations such as fluorescence lifetime measurements can be used to provide a quick measure of the extent of self quenching or cross relaxation present and again allows for quick adjustments of the doping levels for optimized performance. Quite generally, the macroscopic optical properties and other physical properties of materials grown in fiber form through the LHPG method have been found to be identical to those in bulk materials [9–11].

As an example of the type of measurements which can be conducted in the fiber configuration we mention tensile stress studies. Many piezo-spectroscopic studies have been conducted in optically active insulating materials; in fact, both hydrostatic and uniaxial compressive stress studies of the behavior of the well known *R* lines of ruby have established the shift of the *R*-lines as a function of applied stress as a secondary pressure standard. Complementary studies in which tensile or decompressive stresses are applied have not been carried out because of experimental difficulties encountered in stretching a bulk crystal; the fiber geometry is in fact ideal for tensile stress studies [12]. Tensile

Material Grown with the UGA LHPG System

Material	Dopant	Material	Dopant	Material	Dopant
Al_2O_3	Pure	$LiGa_5O_8$	Co^{2+}		Pr^{3+}
	Cr^{3+}		Ni^{2+}		Tb^{3+}
	Mg^{2+}		Co^{2+} and Mg^{2+}		Ti^{3+}
	Si^{4+}	$LiNbO_3$	Pure		Tm^{3+}
	Ti^{4+}		Er^{3+}		V^{3+}
	Fe^{2+} and Cr^{4+}		Er^{3+} and Al^{3+}		Ca^{2+} and Mn^{4+}
	Co^{2+} and Si^{4+}		Er^{3+} and Cr^{3+}		Co^{2+} and Si^{4+}
	Cr^{3+} and Ti^{3+}	$LiYF_4$	Er^{3+}		Fe^{2+} and Cr^{4+}
	Cr^{4+} and Si^{4+}	Lu_2O_2	Pure		Fe^{3+} and Nd^{3+}
	Mg^{2+} and Cr^{4+}		Ce^{3+}		Mg^{2+} and Mn^{4+}
	Mg^{2+} and Mn^{4+}	Lu_2SiO_5	Ce^{3+}		Mo^{4+} and Ca^{2+}
	Ti^{2+} and Si^{4+}	$MgAl_2O_4$	Cr^{3+}		Ti^{3+} and Nd^{3+}
	Mo^{3+}		Ti^{3+}		Ti^{2} and Si^{4+}
$BaTiO_3$	Eu^{3+}	$MgCaSiO_4$	Cr^{4+}		Tm^{3+} and Ce^{3+}
$BaYF_8$	Er^{3+}	$Mg_{1.5}Mn_{0.5}SiO_4$	Cr^{3+}		W^{4+} and Ca^{2+}
	Nd^{3+}	Mg_2SiO_0	Cr^{3+} and Cr^{4+}	$YAlO_3$	Er^{3+}
CaF_2	Pb^{2+}	Mn_2SiO_4	Pure		Er^{3+} and Eu^{3+}
	Tb^{3+}	$NaLa(WO_4)_2$	Er^{3+}	YGAG	Ca^{2+} and Cr^{4+}
$CaWO_4$	Er^{3+}		Eu^{3+}	YGG	Mg^{2+} and Cr^{4+}
	Ti^{2+}		Nd^{3+}	YIG	Pure
CsB_3O_5	Pr^{3+}		Er^{3+} and Yb^{3+}	Y_2O_3	Ce^{3+}
DyF_3	Pure	$NaY(WO_4)_2$	Eu^{3+}		Dy^{3+}
$GdEuO_3$	Nd^{3+}	NdF_3	Pure		Er^{3+}
GGG	Cr^{3+}	$PbMoO_4$	Pure		Eu^{3+}
Gd_2O_3	Pure	$RbMnF_3$	Pure		Ho^{3+}
	Eu^{3+}	Sc_2O_3	Er^{3+}		Nd^{3+}
	Nd^{3+}		Nd^{3+}		Pr^{3+}
$GdScO_3$	Nd^{3+}		Ti^{3+}		Tb^{3+}
Gd_2SiO_3	Ce^{3+}	$SrAl_2O_4$	Cr^{4+}		Tm^{3+}
$LaAlO_3$	Cr^{3+} and Eu^{3+}	$SrTiO_3$	Cr^{3+}		Dy^{3+} and Tb^{3+}
$LaAl_{0.75}Ga_{0.25}O_3$	Tm^{3+}		Eu^{3+}		Pr^{3+} and Yb^{3+}
$LaAl_{0.5}Ga_{0.5}O_3$	Tm^{3+}		Nd^{3+}		Tm^{3+} and Yb^{3+}
LaF_3	Pure	YAG	Pure	$YScO_3$	Er^{3+}
$LaGaGeO_7$	Nd^{3+}		Ca^{2+}		Eu^{3+}
$La_3Ga_5SiO_{14}$	Pure		Ce^{3+}		Nd^{3+}
La_2O_3	Pure		Cr^{3+}	Y_2SiO_5	Eu^{3+}
	Ce^{3+}		Dy^{3+}	YSAG	Ca^{2+} and Cr^{4+}
$LiAl_5O_8$	Pure		Er^{3+}	YSGG	Mg^{2+} and Cr^{4+}
	Ni^{2+}		Eu^{3+}	YVO_4	Er^{3+}
	Co^{2+}		Fe^{2+}	$ZnGa_2O_4$	Mn^{2+}
$LiCaAlF_6$	Cr^{3+}		Mo^{4+}	$ZnSiO_4$	Cr^{4+}
LiF	Pure		Nd^{3+}		

stress can readily be applied by simply attaching weight to the fiber; the behavior of the R line as a function of tensile stress is shown in Fig. 3. The shifts are to the blue rather than to the red as is observed with uniaxial compressive stress and are linear up to a tensile stress of 6 kbar, defining the yield point of the fiber. The tensile strength of the fiber was determined to be 7.7 kbar; the quality of the materials as measure by this parameter is comparable with those reported by LaBelle and Mlavsky [13]. Torsional stress can also be applied; the effects of torsional stress on the vibration Raman active modes of sapphire fiber have been reported [14].

3. Phonon Spectroscopy in Single Fiber Geometry

Cristalline fibers can be pulled so that their diameters are comparable to the mean free path, λ, of high frequency, non equilibrium (THz) phonons at low temperatures [15]. In other words, LHPG single crystal fiber can be mesoscopic with respect to the characteristic dimensions of elementary excitations of the solid. These excitations include magnons, phonons and plasmons in insulators and conduction electrons in the case of semiconductor fibers.

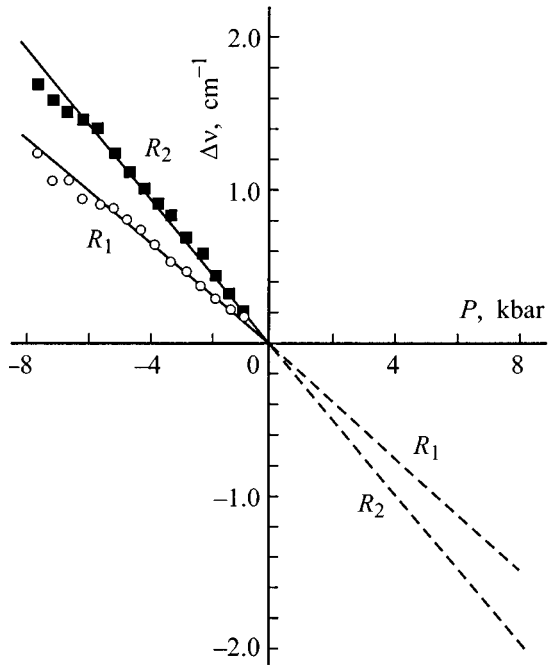

Figure 3. Tensile stress dependence of the blue shifts of the *R*-line in a ruby fiber. Shifts arising from uniaxial stress are to the red (dashed line). Tensile shifts are linear up to 6.0 kbar (yield point); the tensile strength of the fiber is 7.7 kbar.

The transport properties and the dynamics of narrow band, high frequency non–equilibrium phonons in crystalline fibers of ruby and of YAG : Pr^{3+} at low temperatures have been investigated recently [16], as have been the narrow band phonons 29 cm^{-1} phonons in a ruby fiber [17]. These experiments have allowed us to investigate phonon-interface interaction and the energy transport across boundaries as a function of the acoustic impedance encontered at the fiber boundaries.

These initial results simply illustrate that the availability of LHPG fibers can open up whole new areas to investigation simply by providing us with good materials configured in a useful geometry.

4. Technical Applications of LHPG Fibers

In addition to using the LHPG fibers to conduct spectroscopic studies of their properties and to synthesize and optimize the physical properties of crystalline materials, fibers grown with the proper care have been found to be defect free and of very high quality. It follows that these fibers can be employed whenever materials subjected to high tensile or torsional stresses are required simply because of their excellent physical characteristics.

Much of the impetus behind the development of crystalline fibers arose because of their potential to various optoelectronic applications. The interest in these applications is motivated, in turn, by the advent of fiber based systems which are impacting an ever increasing number of technologies. This interest is not likely to diminish in the future and we foresee additional applications of these fibers in a variety of technologies.

5. Conclusions

Though a variety of techniques are available for the growth of single crystal fibers, the LHPG method offers a number of advantages and is a cost efficient way for the synthesis of a large number of materials for fundamental material science studies and for a number of mechanical, electronic and optical applications.

References

[1] E. von Gomperz. Z. Phys. **8**, 184 (1922).
[2] C. Herring, J.K. Glat. Phys. Rev. **85**, 1060 (1952).
[3] A.V. Stepanov. Soviet Phys. — JETP **29**, 339 (1959).
[4] Robert S. Feigelson. "Growth of fiber crystals". In: Crystal Growth of Electronic Materials / Ed. by E. Kaldis. Elsevier Science Publishers, Amsterdam (1985). Chapter 11.
[5] For a comprehensive review of LHPG and its applications see: W.M. Yen. "Preparation of single crystal fibers". In: Insulating Materials for Optoelectronics: New Developments / Ed. by F. Agullo-Lopez. World Scientific, Singapore (1995). Ch. 2.
[6] M. Fejer, J. Nightingale, G. Magel, R.L. Byer. Rev. Sci. Inst. **55**, 1791 (1984).
[7] S.M. Jacobsen, B.M. Tissue, W.M. Yen. J. Phys. Chem. **96**, 1547 (1992).
[8] Kh.S. Bagdasarov. V.V. Ryabchenkov. Sol. Phys. Crystallogr. **33**, 394 (1988).
[9] W.M. Yen. Proc. SPIE **1033**, 183 (1988).
[10] W. Jia, H. Liu, K. Lim, W.M. Yen. J. Lumin. **43**, 323 (1989).
[11] W. Jia, L. Lu, B.M. Tissue, W.M. Yen. J. Cryst. Growth **109**, 329 (1991).
[12] H. Liu, K.-S. Lim, W. Jia, E. Strauss, W.M. Yen, A.M. Buoncristiani, C.E. Byvik. Opt. Lett. **13**, 931 (1988).
[13] H.E. LaBelle, Jr., A.L. Mlavsky. Nature **216**, 574 (1980).
[14] W. Jia, W.M. Yen. J. Raman Spectr. **20**, 785 (1989).
[15] A.A. Kaplyanskii, S.A. Basun. "Multiple resonant scattering of the 29 cm^{-1} phonons in optically excited ruby". In: Non–equilibrium Phonons in Nonmetallic Crystals / Ed. by W. Eisenmenger and A.A. Kaplyanskii. North Holland, Amsterdam (1986). Ch. 9.
[16] X. Wang, W.M. Dennis, W.M. Yen. J. Lumin. **53**, 44 (1992).
[17] S.A. Basun, S.P. Feofilov, A.A. Kaplyanskii, W.M. Yen. Phys. Rev. Lett. **67**, 3110 (1991).