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Single crystal fibre growth of magnetoplumbite family of materials and their properties

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Abstract

Single-crystal fibres of magnetoplumbite structure with compositions $MgLaAl_{11}O_{19}$ (MLA) and $MgNdGaAl_{10}O_{19}$ (MNGA) were studied in this work. Since the melting temperatures of MLA and MNGA are high, the laser heated pedestal growth (LHPG) technique was chosen to grow the crystal fibres as it is a powerful method for rapid growth of refractory oxides and does not need to use any crucibles. The crystal growth behaviors were investigated. The as grown crystal fibres were analyzed by X-ray powder diffraction to determine the crystallographic structures and lattice parameters. The X-ray Laue back reflection pattern was presented. Dielectric properties and thermal properties of the materials were examined in terms of their potential applications as substrates of epitaxial growth of high T_c superconducting thin films for microwave devices.

Keywords: B. Fibres; C. Dielectric properties; E. Substrates; Laser heated pedestal growth

1. Introduction

As a mini-variant of the Czochralski growth method, the laser heated pedestal growth (LHPG) technique has been widely used for single-crystal fibres growth. Since the pulling rate of LHPG is approximately 60 times greater than the conventional Czochralski technique [1] and the time of change from growing one kind of material to another is as short as only 30 min, LHPG is considered as a convenient and fast approach for not only producing materials in the form of single-crystal fibres but, more importantly, as a powerful method for rapid property characterizations of materials as well as for searching new materials of advanced applications. Advantages of LHPG are apparent. The method does not require a crucible or any furnace component; this enables the growth of refractory materials with high melting temperatures, where limitations of the crucible materials are otherwise a major consideration. In addition, the feature of container-free eliminates any sources of contaminations that the melt may pick up by dissolving the crucible material as in a normal crystal growth furnace, which allows obtaining single crystals with high purity. By utilizing the LHPG technique, crystal fibres can be grown both congruently and incongruently, and the compositions of the crystal can be controlled by controlling the compositions of the starting materials. The LHPG method is also a low-cost technique. The molten zone from which crystal fibres are pulled is typically small; the cost of the chemicals for starting materials is therefore relatively low. Plus benefiting from the advantage of crucible-free, where crucibles made of expensive metals, such as platinum, are needed by most traditional crystal growth methods, the LHPG is favored by materials research society for studies of novel materials [2–4].

In this work, compounds of magnetoplumbite structure with compositions $MgLaAl_{11}O_{19}$ (MLA) and $MgNdGaAl_{10}O_{19}$ (MNGA) have been grown by LHPG method. Properties of these materials were then studied to explore them as potential substrates for high-quality epitaxial growth of high T_c superconducting YBCO thin films for microwave applications. Property examinations were based on two viewpoints. First, lattice match analysis between YBCO and the substrates, as well as match of thermal expansion between YBCO and the substrates. Second, the dielectric properties of the substrate itself. The requirements on the dielectric properties (dielectric constant and loss tangent) of substrate materials depend on the

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end use. For instance, an UHF circuit working in low GHz frequency range favors a dielectric constant of 20–25, as a low dielectric constant is not desired because the package volume will be increased. However, for the applications as interconnect substrates in a high speed system, a low dielectric constant is expected to increase the propagation speed of electro-magnetic wave. As for the dielectric loss, since the conducting loss of the superconductor is dramatically decreased, the role of the dielectric loss of a substrate becomes critically important. Very low dielectric loss is therefore demanded [5].

2. Experimental

Water cooled, 55 W tunable flowing CO_2 gas laser (Apollo model 570, USA) was used as the heat source in our LHPG station. The laser power is tunable between 3.5 W and 45 W. The system also includes an optical layout and a stainless steel growth chamber. The optical layout is well designed to direct the CO_2 laser beam into the growth chamber with minimum deformation and controlled position. The translations of the pulling and feeding shafts are controlled by a high precision five-phase micro-stepper motor, producing a single step increment of 25 μm. The molten zone temperature during a stable growth was monitored and measured using an optical pyrometer. The pyrometer employs the principle of blackbody radiation, with a resolution of linear dimension of 0.1 mm. Detailed information of the apparatus was depicted elsewhere [6,7].

The ceramic sources of $MgLaAl_{11}O_{19}$ and $MgNdGaAl_{10}O_{19}$ were served as both pulling and feeding rod in LHPG growth. The ceramic materials were synthesized using conventional mixed oxide solid state reactions. Mixtures of stoichiometric compositions of oxides were calcined several times in alumina crucibles at about 1400–1500 °C and then sintered at around 1610–1650 °C for 6 h. The sintered ceramic pellets were then cut into cylindrical rods using a high-precision diamond saw.

X-ray powder diffraction (General Electric XRD 236, USA, Cu K_α radiation, $\lambda = 1.54059$ Å) was intensively used in this study to characterize the crystallographic structures of the as-grown crystals, as well as to optimize calcining and sintering conditions of the ceramic source materials to obtain the desired pure phases. Crystal fibres were also examined by X-ray Laue back reflection pattern. Thermal expansion measurements were conducted by a self-designed push-rod dilatometer equipped with a high sensitivity linear variable differential transformer. Dielectric properties of crystal fibres were measured by a HP 4274A LCR meter (Hewlett-Packard, USA). The crystal fibres were carefully sliced and polished into disks approximately 1 mm thick for dielectric measurements. Gold was sputtered on both sides of the crystal disks as electrodes for dielectric measurements.

3. Results and discussion

Figs. 1 and 2 are pictures of MLA and MNGA single-crystal fibres. The as-grown crystal fibres of MLA (Fig. 1) were colorless and transparent, typically 20 mm long and 0.35 mm in diameter, while MNGA (Fig. 2) were in light bluish color and transparent as well with 20 mm length and 0.35 mm diameter. (For interpretation of the references to color in text, the reader is referred to the web version of this article.) The growth of MLA was accomplished by 9 mm/h pulling rate and 8 mm/h feeding rate. The pulling and feeding rate for growing MNGA were all 8 mm/h. A relatively long stable molten zone was usually observed in the growth of MLA and MNGA. The growth temperature of the molten zone is 1922 °C (MLA) and 1820 °C (MNGA), respectively. The zone with a meniscus angle larger than zero was the stable configuration for both MLA and MNGA growth. Table 1 lists the parameters obtained during the growth.

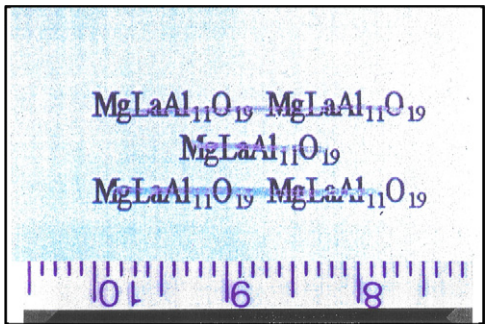

Fig. 1. Single-crystal fibres of $MgLaAl_{11}O_{19}$ grown by LHPG.

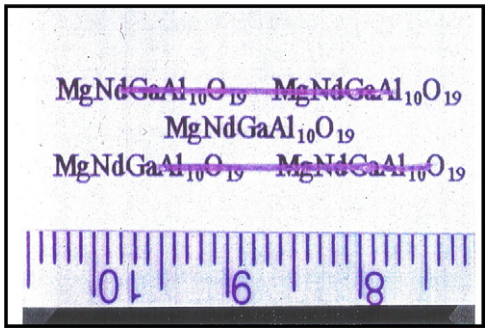

Fig. 2. Single-crystal fibres of $MgNdGaAl_{10}O_{19}$ grown by LHPG.

Ceramic and single crystal MLA and MNGA samples were analyzed by X-ray powder diffraction. The X-ray diffraction patterns of ceramic powder of MLA (Fig. 3a) and MNGA (Fig. 4a) present a pure single phase of magnetoplumbite structure, which could be confirmed by comparing with the theoretically calculated pattern of magnetoplumbite structure [8]. No apparent trace of second phase and unreacted starting materials were identified.

Figs. 3b and 4b are the X-ray diffraction patterns of crushed single crystal fibres of MLA and MNGA, respectively. Comparing the patterns of ceramics and those of crushed

Table 1
Growth parameters for MLA and MNGA.

Material	MLA	MNGA
Zone length	2 mm	1.5 mm
Meniscus angle	3°	10°
Zone temperature	1922 °C	1820 °C

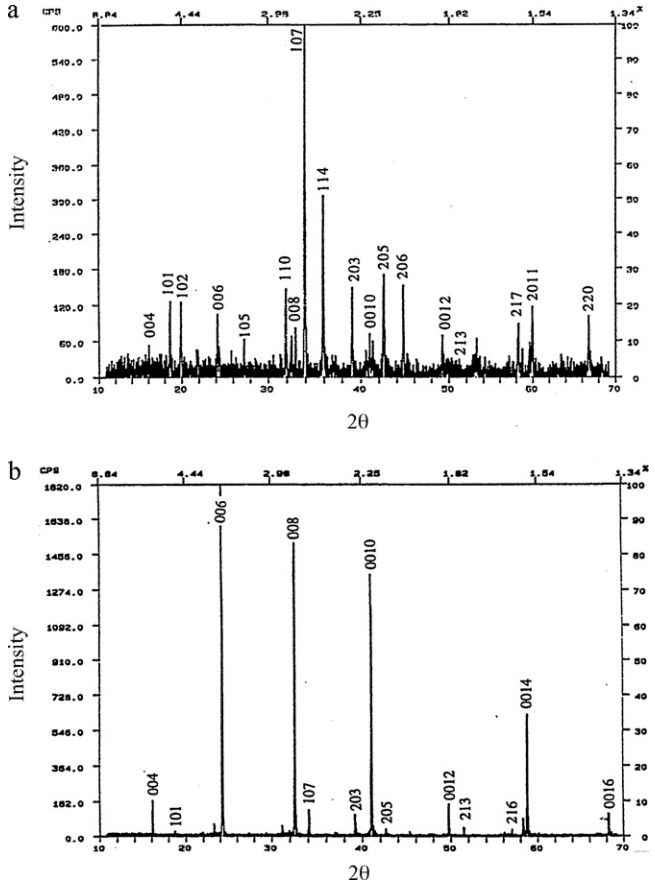

Fig. 3. Powder X-ray diffraction pattern of (a) MLA ceramic powder and (b) MLA crushed single crystal fibres.

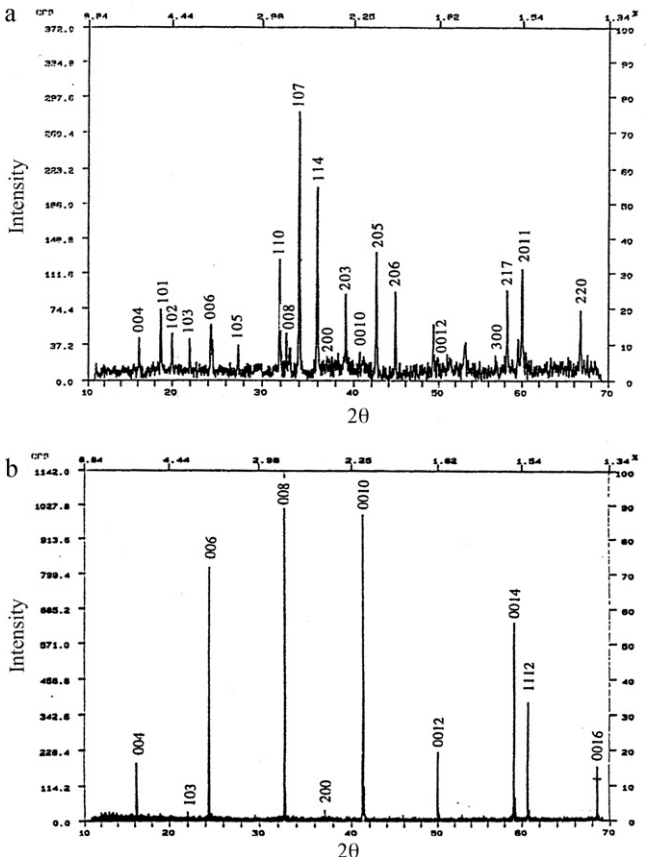

Fig. 4. Powder X-ray diffraction pattern of (a) MNGA ceramic powder and (b) MNGA crushed single crystal fibres.

single crystal fibres, it is noticed that diffraction peaks in crystal patterns are much less than the peaks in ceramic patterns and the peaks in crystal patterns coincide with the peaks in ceramic patterns, suggesting that the single crystal fibres keep the same magnetoplumbite structure of the ceramics. The reason of less diffraction peaks in crystal patterns is because orientation in ceramic powders is completely random and almost all the peaks would appear in the scanning range of 2θ. But for the crystals, the crushed fibre powders are highly oriented; hence some diffraction peaks that appear in the patterns of ceramic would not appear in the patterns of crushed single crystal fibres. The strong diffraction intensity of the high Miller indices suggests that the crystallinity of fibres is high.

Crystal structures and lattice parameters were also determined by least square analysis based on the X-ray powder diffraction patterns of crushed single crystal fibres. They are listed in Table 2. It is found that both MLA and MNGA belong to hexagonal symmetry with space group of $P6_3/mmc$. When the surface orientation of MLA and MNGA is $(1\ \bar{1}\ 0\ 0)$, they will yield a good lattice match with YBCO. In this orientation the lattice mismatch between the $(1\ \bar{1}\ 0\ 0)$ substrates and the (0 0 1) YBCO thin films is only about 2–3%.

Fig. 5 shows the typical X-ray Laue back reflection pattern of MNGA single-crystal fibres. The 6-fold symmetry can be seen suggesting that the preferred growth direction is perpendicular to the [0 0 1] direction.

Table 2
Crystallographic structures of the MLA and MNGA.

Material	Structure	Lattice constant		
		a (Å)	c (Å)	γ°
MLA	Hexagonal	5.5904	21.9690	120
MNGA	Hexagonal	5.5872	21.8707	120

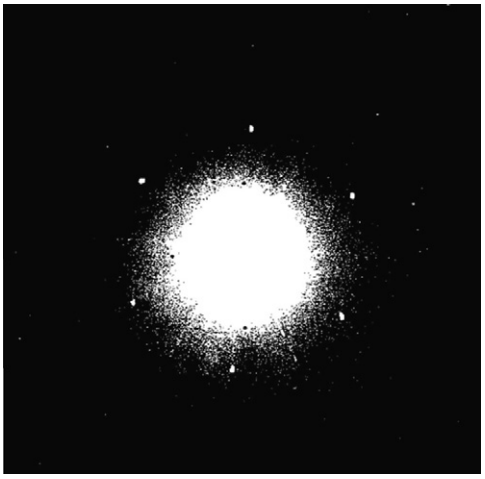

Fig. 5. X-ray Laue back reflection pattern of MNGA single-crystal fibres.

Table 3
Dielectric properties of single crystal fibres.

Materials	κ (@10 kHz, RT)	tan δ (@10 kHz, RT)
MLA	12.10	3.44×10^{-3}
MNGA	15.73	3.38×10^{-3}

Dielectric constants and losses of the single crystal fibres were measured. A special parallel plate holder was constructed for the purpose of high precision measurements. Table 3 lists the results. The results reveal that both MLA and MNGA have moderate dielectric constants and relatively low dielectric losses, which are suitable as substrates for high T_c superconducting thin film deposition.

Thermal expansion measurements were carried out using a lab designed vertical push-rod dilatometer equipped with a high sensitivity linear variable differential transformer (LVDT) [9]. Thermal expansion coefficient α_i is defined as $\alpha_i(T) = \delta(\Delta L(T))/(L_0 \Delta T)$, where L_0 is the dimension of the sample at ambient temperature, ΔL is the dimension of expansion. Thermal expansion coefficient of 9.7×10^{-6} for MLA and 7.2×10^{-6} for MNGA was attained. Matching of thermal expansion coefficients between the superconducting YBCO and the substrate materials is an important factor for obtaining high-quality epitaxial thin films. Good thermal expansion matching was found in both MLA and MNGA.

4. Conclusions

Magnetoplumbite aluminates $MgLaAl_{11}O_{19}$ (MLA) and $MgNdGaAl_{10}O_{19}$ (MNGA) have been successfully synthesized using conventional oxide mixing process at conditions of 1650 °C/6 h and 1610 °C/6 h respectively. Single crystal fibres of MLA and MNGA have been successfully grown by LHPG method. The growth temperatures are 1922 °C and 1820 °C for MLA and MNGA respectively and the typical growth rate used was about 8 mm/h. The element substitution in MNGA decreases the melting temperature and hence makes the crystal growth easier. Structure and property characterizations were studied for MLA and MNGA. The results show that they have moderate dielectric constants, low dielectric losses, good lattice and thermal expansion matching with YBCO and therefore identified as promising substrates for the epitaxy of YBCO thin films. Based on the tentative preliminary study of this investigation, future work could be done on the structure modification of magnetoplumbite family by further element substitutions and fine adjustment via nonstoichiometry and defect structure formation under the guidance of the principle of crystal chemistry to manipulate the property of the materials to meet the intricate requirements of substrates for high T_c superconducting thin films.

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