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Growth and optical properties of RE doped bulk and fiber single crystals by Czochralski and micro pulling down methods

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Abstract

High quality oxide bulk and fiber crystals have been successfully grown by applying advanced single crystal growth methods. $REVO_4$ single crystals have been grown by a modified Czochralski method in which a high temperature gradient was maintained at the interface during growth. Nd:$GdVO_4$ single crystals showed superior lasing properties than those of Nd:YVO_4 and Nd:YAG single crystals in slope efficiency, threshold pump power and output power. Birefringence of $REVO_4$ were more than 0.22. High concentration Nd^{3+} ions doped $NaRE(WO_4)_2$ (RE=Y, Gd) single crystal fibers were grown. Stimulated Raman scattering spectra of undoped NGW fiber was measured, and the Raman shift was observed to be larger than that of KGW. Nd^{3+} doped fibers showed superior optical properties such as high doping level and large stimulated Raman scattering shift for efficient multicolor laser. Crack-free and homogeneous $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$ fiber crystals were grown with various pulling down rates. The crystals showed an excellent second harmonic generation properties.

Keywords: $REVO_4$; $NaRE(WO_4)_2$; $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$; Modified Czochralski method; Micro pulling down method

1. Introduction

It is well known that the development of oxide optoelectronic materials started with $LiNbO_3$ (LN) single crystal growth using the Czochralski (CZ) method by Ballman in 1965 [1]. Subsequently, many investigations for optoelectronic applications have been carried out by numerous research groups [2–4]. Only a few crystals such as LN, $LiTaO_3$ and Nd:$Y_3Al_5O_{12}$ (YAG) have been successfully used. Recently, the development of new crystals has again become a focus of considerable interest because of the progress of optoelectronics. However, high quality alternative crystals have not yet been produced by conventional growth techniques due to problems inherent to the materials themselves such as composition inhomogeneity and incongruency.

In order to solve these problems, we had developed a micro pulling down (μ-PD) method [5]. The characteristics of this method are described as follows, (i) crystals of device size without degradation in quality or cracks can be grown. The dislocation density is nearly zero. (ii) melt convection is suppressed by the use of a narrow-distance nozzle by the capillary effect. This method allows the growth of the crystals which melt incongruently because the effective segregation coefficients are close to unity. Moreover, (iii) it is easy to control the crystal shape. For example, LN single crystal have been grown by CZ method, but, it is not so easy to grow the high optical grade crystal. On the contrary, we had successfully grown higher quality LN micro single crystals with independent of melt composition, using μ-PD method [6].

In this paper, we have described the investigations focusing on the development of new optoelectronic and photonic materials. As promising laser and nonlinear optical crystals, $REVO_4$ (RE=Y, Nd, Eu, Dy, Gd, Er, Yb, Lu) bulk single crystals, $NaRE(WO_4)_2$ (RE=Y, Gd) and $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$ (KLN) fiber single crystals have been grown by CZ or μ-PD methods. Their optical properties have also been characterized.

2. Experimental

2.1. Bulk crystal growth

Wide application of $REVO_4$ crystals is limited by the growth difficulties preventing fabrications of large and high quality crystals. This phenomenon may arise from the

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opacity of the crystals during growth, which leads to poor radiative thermal conductivity [7]. This reason makes it very difficult to control the crystal diameter during growth and causes high tendency of spiral growth. We have found stable crystal growth conditions and grown large diameter crystals of YVO_4 by modified CZ method. The work coil position during growth process was continuously changed in order to maintain its relative position to the surface of the melt in the crucible. More details of this method are described elsewhere [8,9]. Here, Nd^{3+}, Yb^{3+}, Tm^{3+} doped $GdVO_4$ and $REVO_4$ (RE=Y, Nd, Eu, Dy, Gd, Er, Yb, Lu) single crystals were grown by a modified CZ method using RF power supply of 60 kW.

Lattice parameters, absorption and fluorescence spectra, lasing properties and refractive indices of grown crystals were measured. The concentrations of doping ions from the top to the tail part of the grown crystal boules were also studied by X-ray fluorescence analysis.

2.2. Fiber crystal growth

Undoped and Nd^{3+} doped $NaRE(WO_4)_2$ (RE=Y, Gd) and KLN fiber crystals were grown by using a μ-PD technique. A Pt crucible was directly heated resistively in air. The raw materials were melted in the Pt crucible and allowed to pass through the micro nozzle. The single crystal was formed by attaching the seed crystal to the tip of the micro nozzle and was slowly pulled downward with a constant velocity. Crystal diameter was maintained constant by controlling the temperature of the main and after heaters during growth process. Starting compositions of $K_3Li_{2-x}Nb_{5+x}O_{15+2x}$ were used with $-0.3<x<0.3$. $NaRE(WO_4)_2$ crystals were grown from the melts of stoichiometric composition.

Evaluation of their optical properties was investigated. Moreover, the blue second harmonic generation (SHG) of KLN fiber crystal [10] and stimulated Raman scattering of undoped $NaRE(WO_4)_2$ fibers were measured [11].

3. Results and discussion

3.1. $REVO_4$ single crystals

Fig. 1 show typical grown (a) YVO_4 and (b) Tm: $GdVO_4$ single crystals. All crystals showed step faceting on the side of the crystals. The facets were parallel to (100) showing four-fold axis (001) symmetry. This is a common phenomena observed in $REVO_4$ crystals and one of the most difficult problems to solve. Keeping the steep temperature gradient, this intense faceting could be controlled, and stable crystal growth conditions could be realized. According to X-ray powder diffraction analysis, all grown crystals had a single phase zircon structure. All of the diffraction peaks were identified as those of $REVO_4$ crystals and no peaks of second phase were found. The crystal size, lattice constants and color of grown $REVO_4$ were shown in Table 1.

The values of effective distribution coefficient (k_{eff}) were calculated from Eq. (1) [12]:

$$C_s/C_0 = k_{eff}(1-g)^{k_{eff}-1}, \quad (1)$$

where C_0 and C_s represent the doped ions concentration in the starting melts and in the crystal at the solidification fraction (g) respectively. By taking logarithm, Eq. (1), the values of k_{eff} for doped ions were determined. The k_{eff} values of Nd^{3+}, Yb^{3+} and Tm^{3+} ions were 0.20, 0.66 and 0.74, respectively.

The absorption coefficient of Nd: $GdVO_4$ (Nd: 1%) was estimated to be 59.3 cm^{-1}. This is twice greater than that of Nd: YVO_4 (Nd: 1%), and approximately the same as that of Nd: YVO_4 (Nd: 3%). The input–output cw lasing characteristics of Nd: $GdVO_4$ were compared with those of Nd: YVO_4. It should be noted that threshold pump power and slope efficiency of Nd: $GdVO_4$ were found to be one-third and 1.4 times greater than those of Nd: YVO_4, respectively. So, Nd: $GdVO_4$ is a promising new material for single mode micro-chip laser and intracavity SHG

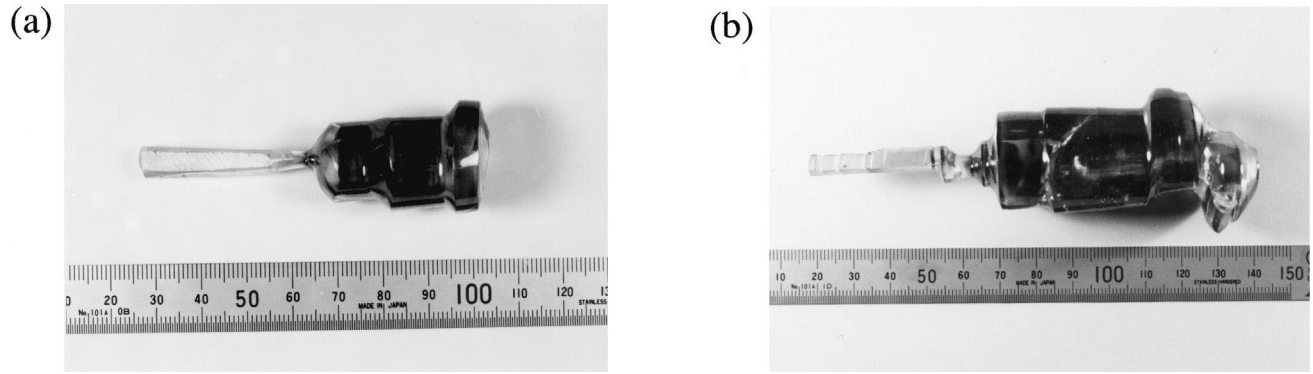

Fig. 1. As-grown $REVO_4$ single crystals grown along the c-axis; (a) YVO_4 and (b) Tm: $GdVO_4$.

Table 1
Crystal data of $REVO_4$ single crystals grown by modified Cz method

Crystal	Size (dia.×length, mm)	Color	Lattice parameter (Å)	
			a	*c*
YVO_4	18×38	Brownish yellow	7.116 (1)	6.286 (2)
$NdVO_4$	18×100	Purple	7.328 (1)	6.435 (1)
$EuVO_4$	18×70	Pale pink	7.229 (1)	6.366 (2)
$GdVO_4$	18×150	Pale yellow	7.213 (1)	6.348 (2)
$DyVO_4$	15×80	Yellow	7.154 (1)	6.313 (1)
$ErVO_4$	17×38	Pink	7.102 (1)	6.275 (1)
$YbVO_4$	18×22	Brownish yellow	7.043 (1)	6.242 (1)
$LuVO_4$	18×38	Pale yellow	7.026 (2)	6.234 (2)

laser. In addition, optical properties of Yb and Tm doped $GdVO_4$ crystals were also examined. Approximately, four times higher absorption coefficient (22 cm^{-1}) and similar fluorescence lifetime (1 ms) of Yb: $GdVO_4$ were observed when compared with those of Yb: YAG. A Tm atomic cross section (3.3×10^{-20} cm^2) and wide fluorescence bandwidth (100 nm) were obtained. The lifetime associated with the energy transition from $^3F_4$ to $^3H_6$ was estimated to be 930 μs. These results showed the superior features of Yb and Tm doped $GdVO_4$ single crystals as a high power and high efficiency LD pumped micro-chip laser in the 1 and 2 μm region.

The comparison between refractive indices for ordinary ray and birefringence of these crystals and other uniaxial crystals is given in Table 2. The grown crystals had a sufficiently large refractive index and birefringence in comparison with that of calcite ($CaCO_3$) type crystals. $REVO_4$ crystal is also one of the candidates which might substitute for calcite or rutile.

3.2. $NaRE(WO_4)_2$ (RE=Y, Gd) fiber crystals

$NaRE(WO_4)_2$ fiber single crystals were grown with various Nd^{3+} concentration (0, 1, 3, 6, 10, 20, 50 and 100 at.%). Fig. 2 show typical $NaGd(WO_4)_2$ (NGW) fibers

Table 2
Refractive index and birefringence of $REVO_4$ at 633 nm and other uniaxicial crystals

Crystal	Refractive index		Birefringence
	ordinary	extraordinary	
YVO_4	1.958	2.168	0.210
$GdVO_4$	2.008	2.244	0.236
$DyVO_4$	2.025	2.257	0.232
$ErVO_4$	2.027	2.254	0.227
$YbVO_4$	2.036	2.256	0.220
$LuVO_4$	2.031	2.249	0.218
TiO_2	2.616	2.903	0.287
$CaCO_3$	1.658	1.486	0.172
$MgCO_3$	1.700	1.509	0.191
SiO_2	1.544	1.553	0.009

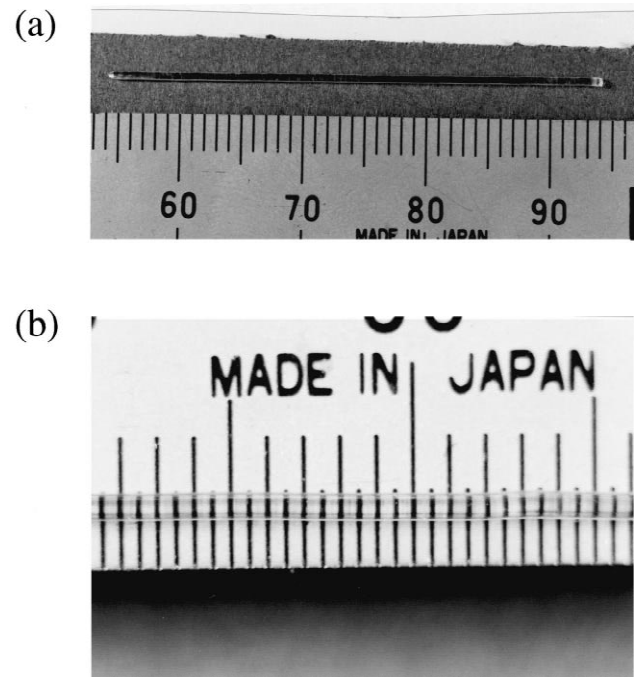

Fig. 2. Photographs of $NaGd(WO_4)_2$ fibers grown along the c-axis (a) and a-axis (b).

grown along the c-axis (a) and a-axis (b) with a diameter of 800 mm.

The fibers were transparent, from colorless to purple in color depending on the Nd^{3+} concentration. The Nd^{3+} distributed along the growth axis homogeneously. Since the highest Nd^{3+} doped fiber crystal had no crack, it is clear that NGW fiber crystals can be grown with high Nd^{3+} doping as compared to other oxide laser hosts such as YAG. The absorption spectra for Nd: NGW (Nd: 3 at.%) fiber crystals were measured by using π (E parallel to c) and σ (E perpendicular to c) polarized incident lights around 800 nm region. The maximum absorption coefficient for σ polarization was found to be 18.1 cm^{-1} at 804 nm with 10 nm bandwidth (Full Width at Half Maximum). The fluorescence peak as laser wavelength appeared at 1062 nm with 13.6 nm bandwidth at Nd=3 at.%. In accordance with ref. [13], the absorption coefficient and fluorescence bandwidth of Nd: NGW is larger than that of Nd:YAG (Nd: 1 at.%). The lifetime was shortened at higher Nd^{3+} concentrations. It is presumed that the laser efficiency at higher Nd^{3+} concentration has lowered, since the excited-state lifetime is a measurement of the energy storage capability of the laser host. The pump absorption increased linearly with Nd^{3+} concentration, whereas the radiative lifetime of the lasing transition decreases with the Nd^{3+} concentration in Nd: NGW. Based on the results presented here and in [14], it is thought that the Nd: NGW is more efficient than the Nd: $KGd(WO_4)_2$ (KGW) and may be a good choice for diode pumping at 808 nm so that

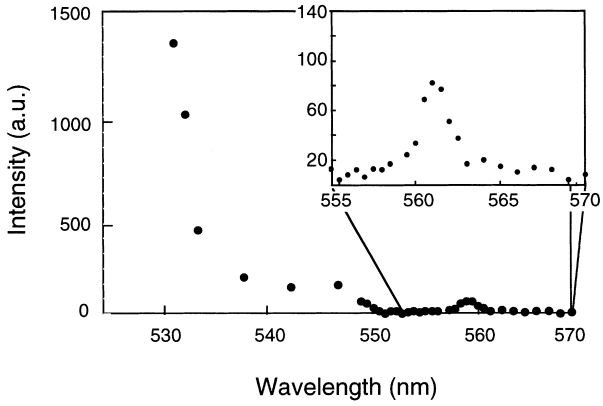

Fig. 3. Demonstrated solid-state stimulated Raman scattering with $NaGd(WO_4)_2$ fiber.

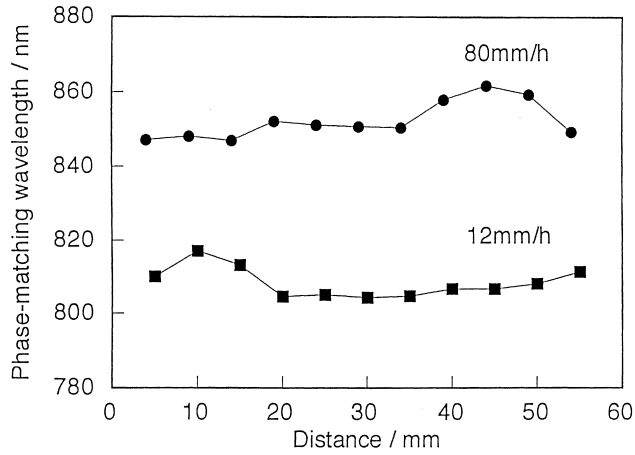

Fig. 4. Distribution of phase-matching wavelength for KLN fibers grown with the grow rates of 12 mm h^{-1} and 80 mm h^{-1}.

a highly efficient and compact laser system at 1.06 μm may be constructed. Fig. 3 shows the first Stokes line at 561 nm in the forward scattered radiation direction. It was attributed to internal symmetrical W–O oscillation within $(WO_4)^{2-}$ ion complexes. The Raman shift was evaluated to be 970 cm^{-1} from the difference energy between the Stokes line and the emission frequency of lasers. This value is larger than that of KGW (910 cm^{-1}) single crystals. These optical properties show that NGW fiber crystals have high performance as multicolor laser host. In addition, the NGW fiber crystals are one of the candidates as new self-doubling crystals which has large stimulated Raman scattering shift.

3.3. KLN fiber crystals

KLN crystals showed very uniform shapes and were free of cracks independent of the melt composition. Various pulling down rates were attempted and the highest rate for a crack-free single crystal was 120 mm/h. No fractures normal to the a- and c-axis as in Kyropoulos [15] and CZ [16] crystals have been observed. Also, the concentration in the solid was similar to that in the melt along the entire solidified fractions. The relatively low growth temperature of this material of about 1000°C combined with a tetragonal structure at room temperature make it particularly attractive for optical device applications.

KLN fibers showed blue SHG generation. In accordance with Ref. [10], SHG property of grown KLN fibers with pulling down rates of 12 mm/h and 80 mm/h were measured. The comparison of distribution of phase-matching wavelength along the growth axis is shown in Fig. 4. The deviation of phase-matching wavelength for both crystals are almost same, about 10 nm, which indicates that the smaller growth rate is not so effective to a compositional homogeneity along the axial direction. However, SHG conversion efficiencies of these crystals were quite different. The average conversion efficiencies of the crystal with pulling down rate of 12 mm h^{-1} was 0.03% W^{-1}, 15% of calculated value, while that of the crystal grown at pulling rate of 80 mm h^{-1} was 0.006% W^{-1}, about 3% of calculated value. This may be related to the crystallinity of the fiber or inhomogeneity in radial direction. We believe that further increase of the SHG efficiency will be obtained by optimizing growth conditions such as growth velocity, temperature gradient and meniscus shape.

4. Summary

We have successfully grown $REVO_4$ single crystals by using a modified Czochralski method. The LD pumped laser oscillations were demonstrated for Nd:$GdVO_4$ single crystal and it showed superior lasing properties than YVO_4 and YAG single crystals in slope efficiency, threshold pump power and output power. It is expected that they are an excellent synthetic substitute for calcite or rutile, and would provide crystal polarizers.

Crack-free high Nd^{3+} concentration doped $NaRE(WO_4)_2$ and KLN fiber crystals have been successfully grown by a micro pulling down method. In Nd: $NaGd(WO_4)_2$ fiber crystals, the absorption peak at 804 nm with 10 nm bandwidth and fluorescence peak at 1062 nm with 13.6 nm bandwidth were observed. Undoped NGW fiber crystal indicated Stokes line by induced Raman scattering in the forward scattered radiation direction, and the Raman shift was estimated to be 970 cm^{-1}. Nd^{3+} doped and undoped NGW crystal fibers are expected to be a promising new material for a high effective and more compact multicolor laser system.

High quality KLN fiber crystals were found to be suitable for blue second harmonic generation. The average SHG conversion efficiency of fibers grown with pulling down rates of 12 mm h^{-1} and 80 mm h^{-1} were 0.03% W^{-1} and 0.006% W^{-1}, respectively.

Thus, these crystals have received considerable attention for new generation of high speed, efficient, multi-func-

tional optoelectronic devices because of their extended interaction length and high optical intensity.

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