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Optical crystals survived in information technology systems

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Different optical crystals are reviewed from the viewpoint of their optical properties, among which typical crystals survived in the recent information technology (IT) systems. Most of revived or survived crystals are somehow traditional ones because of their established properties. Potential applications of oxide crystals into shorter wavelengths are focused as additional ripple effects of the impetuous deployment of the IT.

Some recent activities on developing new crystals are described briefly; $GdVO_4$ with a large walk-off angle as a birefringent crystal, Y_2O_3 as a new laser host, periodically poled ferroelectric $LiNbO_3$ and $LiTaO_3$ crystals as effective devices of frequency conversion, and traditional sapphire as a potential substrate of GaN-LEDs.

Keyword: oxides, optical crystal, birefringence, magnetooptic, electrooptic, solid-state laser, optical nonlinear, periodically poled crystals, optical fibre communication/information systems.

1. Introduction

The unprecedented growth of the optical information technology (IT), including Internet and digital data transmissions through optical fibres, has evolved wide uses of optical single crystals. Actually, the enormous progresses of the IT have owed to many oxide crystals. For example, high performance devices include optical modulators made of electrooptic crystals in transmission, optical interleavers made of birefringent crystals in recent wavelength division multiplexes (WDM), and optical isolators/circulators composed of birefringent and magnetooptic crystals in optical fibre amplifier components. The optical isolator composed of magnetooptic and birefringent crystals is indispensable for stabilizing the transmission systems, and Er-doped fibre amplifier (EDFA) strictly requires optical isolators. Some oxide crystals having excellent properties established in the past three decades are revived and/or survived, for example magnetooptic $Y_3Fe_5O_{12}$, rutile TiO_2 and ferroelectric/electrooptic $LiNbO_3$, although they are traditional ones.

Additional ripple effects of the impetuous deployment of the IT are on the development of new type crystals. Beside 1.3 and 1.55 µm wavelength bands of the optical fibre communication system, optical devices generating shorter wavelengths are in progresses, coupled with advanced LD-pumped solid-state lasers of traditional host crystals as well. Potential crystals for this purpose are periodically poled ferroelectric crystals and newly developed borates which enable us to manipulate higher-order frequency conversions efficiently. On the other hand, recently advanced GaN-based LEDs/LDs require huge amounts of substrate crystals for heteroepitaxy. Although new substrate crystals are reported elsewhere, traditional sapphire Al_2O_3 crystal has revived.

This paper will glance at optical crystals developed so far according to characteristic functions and focus on a new turn of optical crystals linked with far-reaching ITs. It will be extracted that most of optical crystals revived/survived today are traditional ones.

2. Retrospect of oxide crystals

Figure 1 shows retrospective R&D streams of oxide crystals, categorized by optical functions and/or properties, including prospective targets to be expected [1]. The streams are mainly divided roughly into two: active and passive crystals. Here, "active" is generally defined to be optically functional, which means that the propagation of the input light wave can be modulated when external signals, such as electric, magnetic, light and/or stresses, are applied to the media. On the other hand, "passive" means optically non-functional, that is, the propagation of the input light wave is changed by optical properties proper to the media, such as a birefringence.

As is shown in Fig. 1, so many crystals have been developed and investigated in the past three decades. A representative property of passive oxide crystals is a natural birefringence, while well-known characteristics of active crystals are of magnetic and dielectric. The recently deployed IT has opened the wide use of only well-established materials. As for birefringent crystals, a well-known crystal TiO_2 (rutile) and a laser host crystal YVO_4 have revived, because the optical fibre communication system uses inevi-

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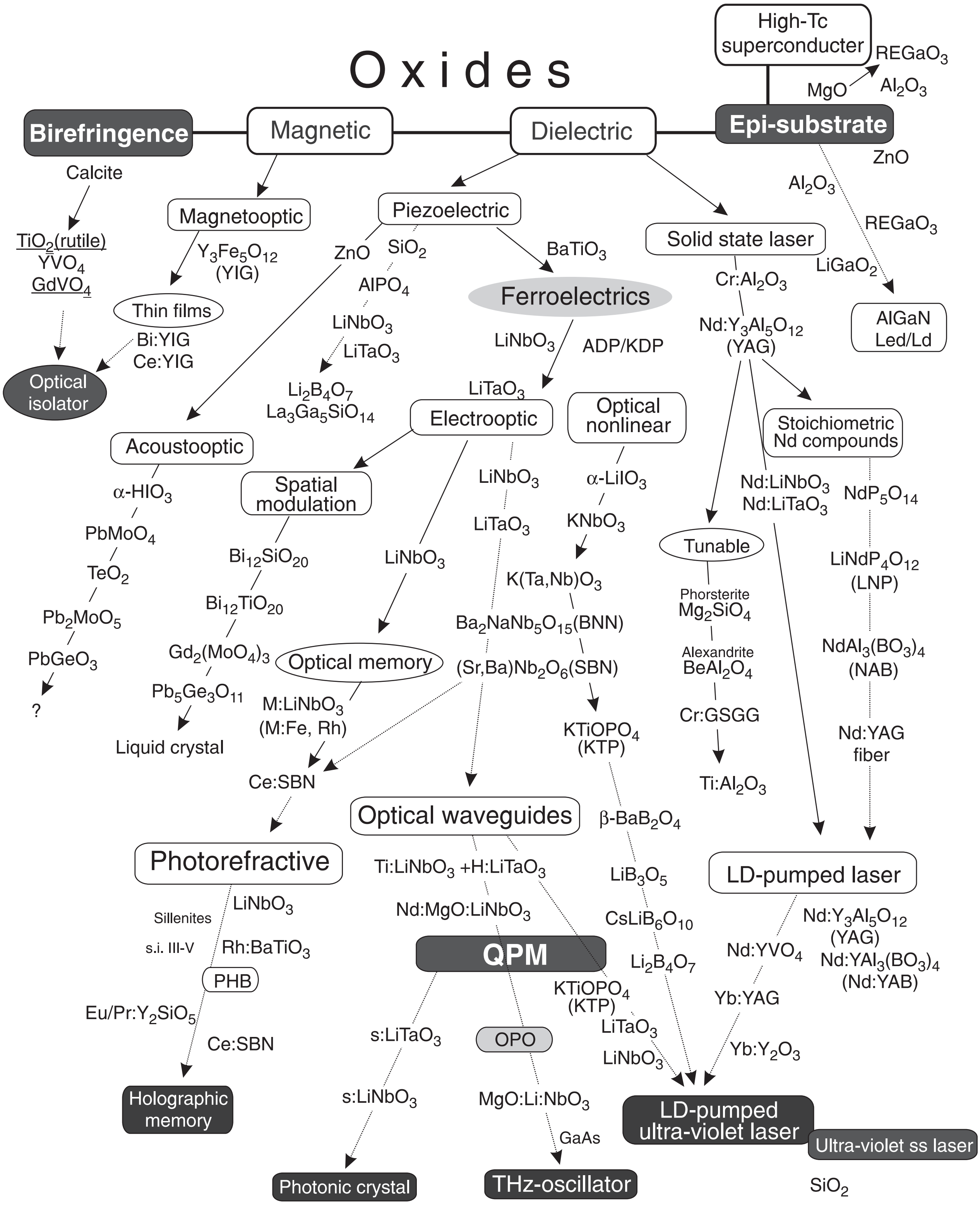

Fig. 1. Retrospect of R&D of passive and active optical crystals. The lowest terms are of expected devices.

tably the optical isolator composed of birefringent crystals for stabilizing laser operation. Another useful and practical application of passive crystals is substrate for thin-film epitaxy, on which high-Tc superconducting thin films and recently advanced GaN-related thin films are epitaxially grown. Various kinds of oxides have been developed for heteroepitaxial substrates, but only a few crystals have become of major interest lately. As a representative, Al_2O_3 is now in practice as substrates of both violet/blue GaN-based LEDs and LDs and High-Tc superconducting films for a microwave application. More suitable and cheaper substrate materials are still demanded.

As to active device crystals, a well-established magnetooptic crystal $Y_3Fe_5O_{12}$ (YIG) survived in the form of thick films doped with Bi^{3+} and/or Ce^{4+} that increases the Faraday rotation power. Now in the present optical fibre communication systems, Bi:YIG thin film is actually adopted to make the optical isolator with birefringent crystals. In respect to dielectrics, ferroelectric $LiNbO_3$ and $LiTaO_3$ single crystals have notably been investigated in the past three decades. As a result, $LiTaO_3$ achieved stardom in surface acoustic wave (SAW) devices indispensable for mobile/handy telephones, and early developed langasite $La_3Ga_5SiO_{14}$ [2] is still under investigations.

Today, optical waveguides have become key devices and a strong contender in active optical components. Most of ferroelectric crystals have large electrooptic and optical nonlinear effects, and optical devices using the electrooptic effect have long been investigated and developed. However, only $LiNbO_3$ is now one potential high-speed electrooptic material, because of commercial availability of large single crystals with excellent quality. External $LiNbO_3$ optical modulators in the form of optical waveguide structure are actually used in long-haul optical fibre communication systems. On the other hand, $LiNbO_3$ lends its optical nonlinear properties to frequency conversion devices with a quasi-phase matching (QPM) structure [3] and also its photorefractive characteristics [4] to holographic memory applications in the near future.

The other practical applications of oxides are solid-state laser crystals. Solid-state lasers started from ruby ($Cr:Al_2O_3$), and today Nd:YAG ($Y_3Al_5O_{12}$) laser is widely used industrially. As a practical tunable laser, $Ti:Al_2O_3$ is commercialised, which is very attractive for a femto-sec laser source. Recent progresses of LDs pushed up the development of LD-pumped solid-state (LPSS) lasers that enables us to make more compact such solid state lasers. In a sense, LPSS lasers expelled miniature lasers made of Nd-stoichiometric laser crystals investigated earlier. A new laser host crystal involves self-doubling nonlinear crystals and a new active ion to be doped into the host crystal is Yb^{3+}.

Additional impetus of the IT has stimulated the development of frequency conversion devices using LPSS lasers, either from blue to ultraviolet regions or toward THz-wavelength. For ultraviolet emission, frequency conversion techniques are of interest and for use in applications such as laser drilling light sources and photolithography. New optical nonlinear crystals have been developed both theoretically [5] and experimentally, namely borate crystals such as β-BBO (BaB_2O_4), LBO (LiB_3O_5), and CLBO ($CsLiB_6O_{10}$) [6]. Additional deployment has come from quasi-phase matched (QPM) nonlinear optical media [3], namely periodically poled $LiNbO_3$ (PPLN), $LiTaO_3$ (PPLT) and $KTiOPO_4$ (KTP), which offer compact, efficient, low threshold alternatives to conventional birefringently phase-matched media. With notably easy progress using LN, these QPM media stimulated optical parametric oscillation (OPO) technology. The availability of QPM crystals and of efficient DPSS lasers has enabled the development of high-performance cw OPO devices as realistic sources of far-infrared THz-regions. $LiNbO_3$ is still of interest today and THz-waves have been observed successively with PPLN by means of OPO [7]. Traditional LN and LT are survived here.

3. Birefringent crystals

Because of the worldwide deployment of optical fibre communication systems, the optical isolator is indispensable so as to stabilise laser sources, especially in the recent WDM system. The optical isolator is generally composed of birefringent crystals and magnetooptic Bi^{3+}:YIG thin films. The natural calcite ($CaCO_3$) is famous as a crystal with a large birefringence, and the artificial growth of calcite was tried so far, but large sized single crystal with high optical quality was limited. Then, a traditional crystal rutile (TiO_2) has revived for manufacturing compact and practical isolators because of its large birefringence, and they are easily grown by Verneuil technique, typically 1.5" in diameter and 100 mm in length. Figure 2 shows typical as-grown and as-annealed rutile crystals by SHINKOSHA Co.

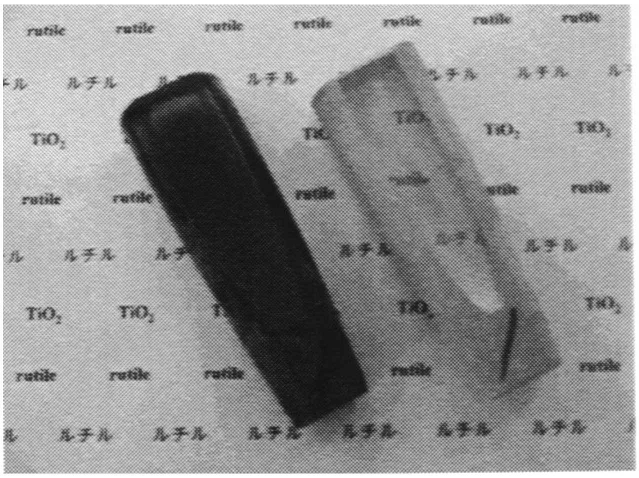

Fig. 2. As-grown (left) and annealed (right) rutile crystals.

Recent interest in birefringent crystals has captured $LiNbO_3$ and YVO_4. As it was discussed before, $LiNbO_3$ is well-known traditional material, and its optical quality and crystal size are well standardized commercially. More recently, YVO_4 crystal has gathered many attentions, competing with TiO_2, because it has a large walk-off angle comparable with that of $LiNbO_3$. The first application of YVO_4 was a host crystal of solid-state laser doped with Nd, and the laser has been commercialised. Concerned with YVO_4, we paid much attention to its isostructural $GdVO_4$ and grew large diameter single crystals. While most of YVO_4 crystals commercialised to date is of 30–50 mm in diameter, more than 70 mm in diameter $GdVO_4$ crystals were successfully grown. Figure 3 shows typical $GdVO_4$ single crystals grown by Cz-pulling [8].

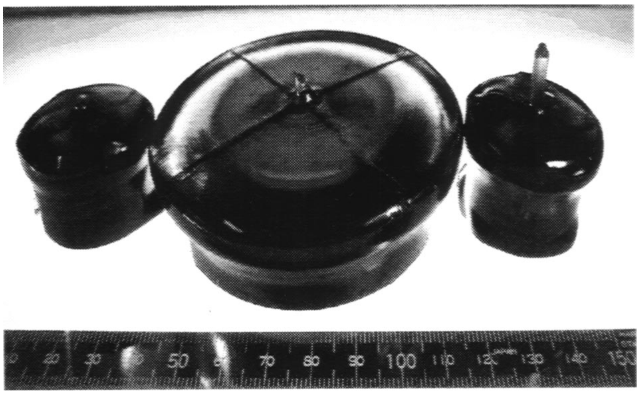

Fig. 3. Cz-grown $GdVO_4$ single crystals.

Table 1 compares typical properties of $GdVO_4$, YVO_4, and TiO_2. One can find that $GdVO_4$ has a thermal conductivity larger than that of YVO_4, and also its walk-off (beam splitting) angle is the largest [8]. In addition, since temperature dependence on refractive indices *dn*/*dT* of TiO_2 was negative, while that of $GdVO_4$ is positive, temperature-compensated optical components would be expected using $GdVO_4$ combined with TiO_2. This will permit us to miniaturize optical isolators to be risen to high power applications.

Table 1. Comparison of some properties of typical birefringent crystals.

	$GdVO_4$	YVO_4	TiO_2 (rutile)
Refractive index (n_o) (n_e)	1.957 2.169	1.9447 2.1486	2.4532 2.7094
Birefringence (Δn)	0.212	0.204	0.256
Max.walk-off angle (°)	5.90	5.70	5.68
Thermal conductivity (W/mK)	9–12	5–5.3	~12.5

4. LD-pumped solid-state lasers

Impetuous development of the IT gave us a spin-off of high power solid-state lasers pumped with LDs. Nd:YAG has widely used for laser marking, laser cutting and laser drilling for manufacturing microelectronics components derivative of the IT. High power solid state lasers will be demanded as a fundamental source for frequency conversion applications, namely sources of 266 nm and 193 nm wavelengths. As for a pumping source, high power AlGaAs-LDs are now commercialised, but Al-free devices will be required, because Al in devices would be oxidized during long operations, resulting in degradation of their output power and/or stability. Al-free, InGaAs-based high power LDs have already been developed for a pumping source of an Er-doped fibre amplifier (EDFA) in the present optical fibre communication system.

Therefore a stable and high power emission will become important and its stability is namely owed of thermal conductivity of the host crystal. From this point of view, Yb^{3+} will replace the usual active ion Nd^{3+}, because Yb^{3+} does not have any energy levels higher than the lasing upper state level. The doping amount of Yb^{3+} into the host crystal can be increased in order to absorb the pumping light efficiently, allowing the suppression of temperature increase, and to minimise the crystal size. Moreover, an emitting wavelength of InGaAs-based LD matches absorption band of Yb^{3+}-doped solid-state laser as a pumping source.

What kind of host crystals will be a candidate? A few discussions have been reported so far, where appatite-type crystals have been suggested [9], because of their splitting of the lower level larger than in other host crystals. As a candidate, Y_2O_3 has gathered much attention because of high thermal conductivity. The growth of Y_2O_3 single crystal with laser quality seems to be hard, because of its high melting, ~2440°C. SHINKOSHA Co. already succeeded in the growth of undoped and Nd-doped Y_2O_3 single crystals by own Verneuil technique [12]. Figure 4 shows examples of the crystals. Now, optical characteristics are under re-examinations. More recently, a transparent ceramic Yb:Y_2O_3 laser has been developed by Lu *et al.* [10]. Yb:Y_2O_3 laser will be realized in the near future.

An interesting and practical application using DPSS lasers is a self-frequency doubling/tripling optical device. For this purpose, an early-developed stoichiometric Nd-compound $NdAl_3(BO_3)_4$ has revived in the form of Nd:$YAl_3(BO_3)_4$ (Nd:YAB). On the other hand, a ferroelectric/electrooptic crystal $LiTaO_3$ (LT) doped with Nd was investigated so far [11], and a cw-operation without any optical damage at room temperature was observed. Peri-

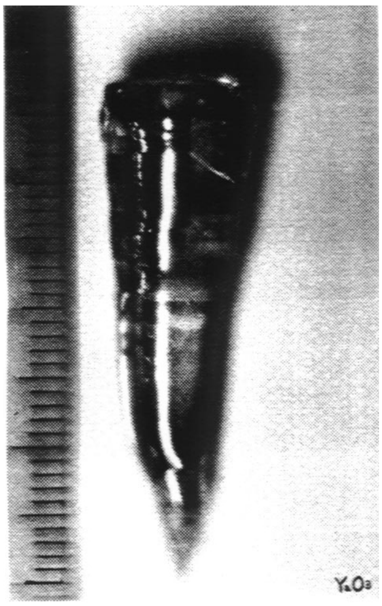

Fig. 4. Verneuil-grown undoped Y_2O_3 single crystal. A few cracks were observed.

odically poled ferroelectric domain structures of rare-earth doped crystals will enable us to realize LD-pumped self-doubling/tripling one-chip laser emitting 0.53 µm and 0.35 µm (see Section 6).

5. Crystals for frequency conversion

Additional impetus of the IT has stimulated the development of frequency conversion devices using LPSS lasers, either from blue to ultraviolet regions or toward THz-wavelength. Figure 5 demonstrates how to realize ultraviolet-green and near- and far-infrared wavelength regions from 1 µm LPSS lasers.

Nowadays, LEDs and LDs emitting from violet-blue to near-infrared wavelength regions were realized using compound semiconductor III–V materials. Especially, GaN-based ultraviolet-blue LEDs have been commercialised now. The state-of-the-art investigation on InN single-crystalline films has announced that the optical band-gap of InN lies around 0.7–0.8 eV [13], instead of ~2.0 eV appeared in the literature. This striking result gives us a hopeful possibility that III-nitrides will cover optical devices made of traditional III–V compounds GaAs/InP. Then, we have to develop optical crystals and devices that function at wavelengths shorter than those from III–V materials.

For ultraviolet emission, optical frequency conversion media are worth noting. They involve frequency doubling/tripling through optical nonlinear effects; SHG (second harmonic generation), SFG (sum-frequency generation) and DFG (differential frequency generation). New optical nonlinear borate crystals such as CLBO ($CsLiB_6O_{10}$) have been developed both theoretically and experimentally so far. Most of new borate crystals have been grown by TSSG (top-seeded solution growth), but CLBO was grown

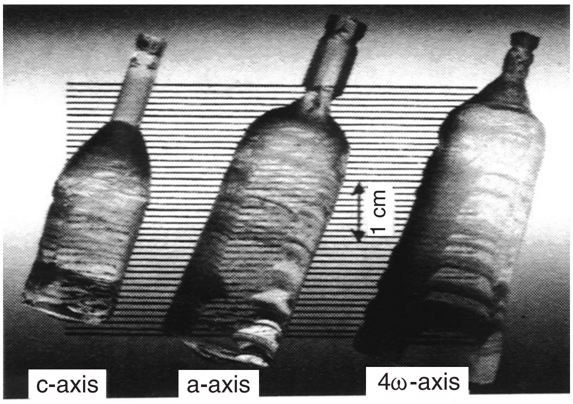

Fig. 6. CLBO single crystals grown by Cz along different axes.

successfully by Cz (Czochralski) pulling. Figure 6 shows typical CLBO single crystals grown by Cz-pulling from the stoichiometric melt [14]. Recent progresses in new crystals with large nonlinear coefficients and shorter optical absorption edge result in finding $KBe_2BO_3F_2$ (KBBF) and $Sr_2Be_2BO_7$ (SBBO), which enable us to generate wavelengths shorter than 200 nm. However, they include toxic Be ions and their crystal growth is difficult.

Figure 7 shows the figure of merit d^2/n^3 (d is the nonlinear coefficient constant, n is the refractive index) of typical crystals as a function of optical absorption edge. Organic crystals and compound semiconductors have relatively large figure of merit, but their optical absorption edge lays around 400 nm. One can extrapolate that the shorter the absorption edge, the smaller the figure of merit. This would predict the limitation of materials for obtaining ultraviolet wavelengths efficiently by frequency conversions. Additional deployment has come from quasi-phase matching (QPM) optical nonlinear media [6], namely periodically

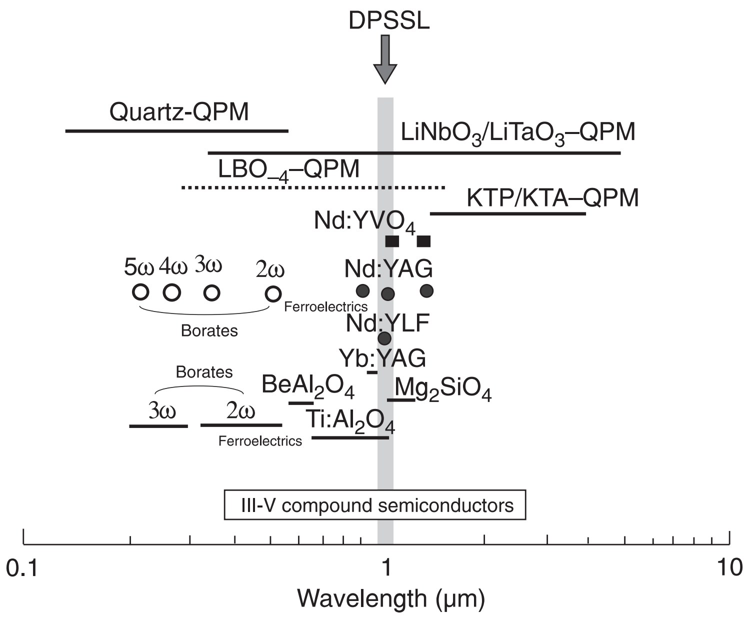

Fig. 5. Crystals for frequency conversion of fundamental DPSS lasers.

poled $LiNbO_3$(QPM), $LiTaO_3$ (QPM) and KTP(QPM). As is shown in Fig. 7, the figure of merit of PP-structured crystals (indicated by ■) increases by roughly one order. They would offer compact, efficient and low threshold devices alternatives to conventional birefringently phase-matched media. Here one can pay attention to QPM-SiO_2 (quartz), α-quartz has the shortest optical absorption edge, around 150 nm, among oxide crystals, high thermal conductivity and moderate optical nonlinear coefficient (0.3 pm/V at 1064 nm). Recent investigations on QPM of a-SiO_2 presented that a periodical inversion of domains was realised by applying thermal stress, of which domain wall is composed of Dauphine-twins [15].

With notably easy progress using LN, these QPM media stimulated optical parametric oscillation (OPO) technology. The availability of QPM crystals and of efficient DPSS lasers has enabled us the development of high-performance cw OPO devices as realistic sources of far-infrared THz-regions [7]. $LiNbO_3$ is also of interest today and THz-band waves have been observed successively with PPLN by means of OPO [16].

Since the first report on patterned domain-inversion in Ti-diffused $LiNbO_3$ appeared [17], periodically domain-inverted (poled) devices have been investigated so far, coupled with the theoretical concept [3]. After that, several techniques for patterned domain-inverted structure have been established, and periodically poled $LiNbO_3$ (PPLN) are now commercialised for a SHG device. This domain-inversion in ferroelectric crystals opened the door to use $LiTaO_3$ (LT), isostructural but optically positive, as an optical nonlinear medium, because PPLT makes good use of the largest electro-optic constant r_{33} and optical damage threshold is higher than $LiNbO_3$. More recently, a self-doubling/tripping device made of aperiodically poled Nd:$LiNbO_3$ has reported [18], where 3ω generated by differential frequency generation (DFG) of a fundamental and SHG-waves. Figure 8 illustrates this idealized device structure, where the outputs are expected to be direct-modulated

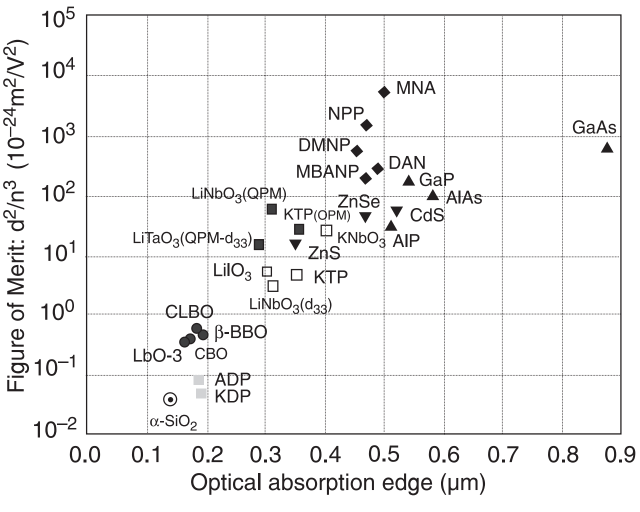

Fig. 7. Optical nonlinear figure of merit vs. optical absorption edge of different crystals.

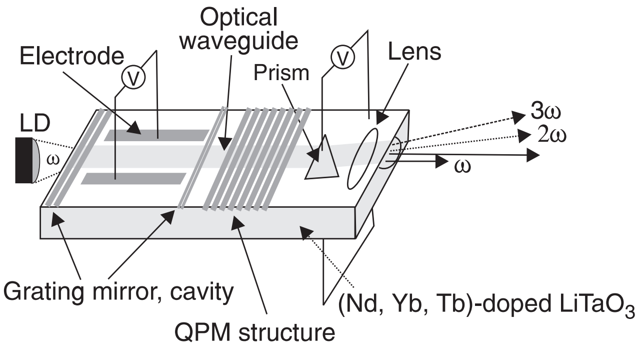

Fig. 8. An ideal structure of LD-pumped self-doubling/tripling laser chip using electrooptic rare-earth doped $LiTaO_3$.

through the electrooptic effect when the external signal is applied onto the lasing waveguide, where applying external electric signals can modulate the output, that is, a direct modulator of 2ω and 3ω wavelengths would be realized.

For domain-inversion of available congruent LN and LT, the external filed is on the order of kV/cm, which is due to a relatively large coercive field of materials. Therefore relatively thick device is hard to be fabricated, usually less than 0.5 mm in thickness. More recent investigations on the stoichiometry of both LN and LT, the crystals having its stoichiometric composition showed an excellent dielectric and optical properties, as compared with those of commercialised congruent crystals [19]. At present, while a reproducibility of optical quality on stoichiometric crystals has not well established, some interesting devices will be demonstrated in the near future. For example, ionic photonic crystals will be realized because of the easiness of the polarization inversion of micro-domains, on the order of sub-micron size in diameter. PP-stoichiometric LN and LT seem to be potential crystals for this purpose. Seeing stoichiometry of traditional crystals through new eyes would give rise to new crystals. For example, a study of $Bi_{12}TiO_{20}$ (BTO) showed that the existence of a solid solution range to some extend. Reproducibly grown crystals have used as an electrooptic prober detecting high-speed signals in ICs [20].

6. Oxide crystals for EPI-substrates

Oxide crystals are now expected as transparent substrates for epitaxial growth of III-nitride semiconductors and high-Tc superconductors. Coupled with global strategy for data storage for the near future IT systems, LDs emitting blue and violet wavelengths are in progress, and moreover solid state white light sources are stimulated by using ultraviolet LEDs. LEDs and LDs made of GaN-based semiconductors emitting around 380–450 nm involve the use of sapphire (Al_2O_3) substrates. Although another candidates such as $LiGaO_2$ [21], $NdGaO_3$, ZnO and SiC have been also developed extensively from the viewpoint of lattice matching to GaN, sapphire has become very common and practical, because large single crystals are available com-

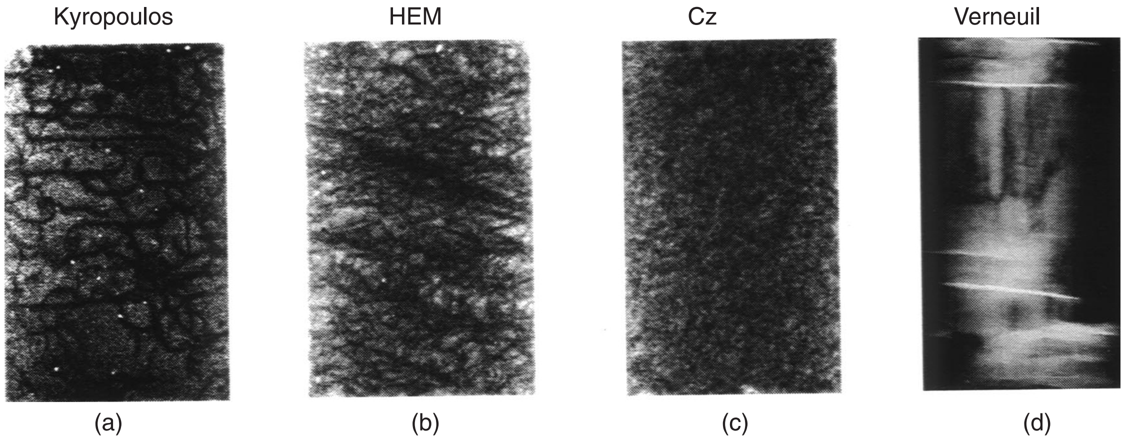

Fig. 9. X-ray transmission Laue topographs of sapphire wafers grown by different techniques.

mercially and wafer cost is cheaper, although the lattice-mismatching is as large as 13%. In retrospect, sapphire was only used as optical wave-plates, windows of vacuum-chambers, wrist-watches and so on, and only investigated to use as a substrate for Si-microelectronics devices, namely silicon-on-sapphire (SOS).

Single crystal growth of large sapphire is carried out by Cz, Kyropoulos, heat exchange method (HEM), edge-defined, film-fed growth (EFG), while the well-known Verneuil technique cannot produce high quality single crystals of more than 2" in diameter. However, crystalline quality of crystals grown by which techniques will meet the requirements for realizing high performance violet/blue LEDs and LDs has not been investigated so far. Then, crystalline quality of 2" -dia. sapphire wafers grown by various techniques was qualitatively revealed by X-ray transmission Laue topography.

Figure 9 shows typical X-ray topograph pictures of 2" -wafers prepared from boules grown by different techniques. The observed area was 5×8 mm^2 at the central part of wafers. We can easily verify the difference in crystallinity among them. A Verneuil-grown wafer contains many misoriented subgrains, while dislocations in a Cz-grown wafer has highly dense dislocations of which density was measured to be on the order of 10^4–10^5/cm^2, as shown in Fig. 9. A HEM-grown wafer has tangled but distinguishable dislocations of which density was (0.9–1.2)×10^3/cm^2. On the other hand, a Kyropoulos-grown wafer shows clearly low dislocation density on the order of 10–10^2/cm^2, as shown in Fig. 9(a). High dislocation density should lower the yield in wafer cutting, lapping and polishing processes. Therefore we have to pay attention for selecting wafers from crystal boules grown by which growth technique was used.

7. Conclusions

Typical oxide crystals developed in the past three decades were briefly reviewed at first from the viewpoint of crystal functionality, and optical crystals survived in the IT world were presented. The impetus of the IT has opened the door of developing new crystals, such as birefringent crystals, optical nonlinear crystals and quasi-phase matched crystals for frequency conversion devices, high efficient solid state laser materials doped with Yb^{3+}, and so on. In addition, "substrate" is one of functions of oxide crystals, indispensable for heteroepitaxial thin film devices. So, new substrate crystals are expected, especially for GaN-based optoelectronic/microelectronic devices.

As far as birefringent crystals, which are now indispensable for optical isolator/circulators combined with magnetooptic thin films, traditional rutile TiO_2 is still used, but traditional laser host crystal YVO_4 has been diverted to a purpose. As a new birefringent crystal, a large diameter $GdVO_4$ single crystal was grown successfully by Cz-technique, and it was found that $GdVO_4$ has some properties superior to YVO_4 and TiO_2.

Representative active optical crystals survived in recent widespread deployment of optical information technology (IT) are magnetooptic Bi^{3+}:$Y_3Fe_5O_{12}$ (YIG) and ferroelectric/electrooptic $LiNbO_3$ (LN). Bi:YIG is now used in the optical isolators/circulators, and $LiNbO_3$ optical waveguide is applied to high-bit rate optical modulators, both indispensable in the present optical fibre communication systems. Moreover, traditional $LiNbO_3$ and $LiTaO_3$ (LT) are survived for frequency conversion devices with a QPM structure, which enable us to use for generating ultraviolet-blue wavelengths by the well-known optical nonlinear effects. These QPM devices made of aperiodically poled structure would enable to realize a frequency tripling of the fundamental wavelength in one-chip and ionic photonic crystals similar to semiconductors.

One of potentials of optical oxide crystals includes substrates for heteroepitaxy of high-Tc superconducting and III-nitride thin films. It can be stressed that "substrate" is one of important functions of oxide crystals. Well-known sapphire Al_2O_3 of which single crystal growth techniques have been established is now in practice for epi-substrates of GaN-based violet/blue LEDs/LDs. By X-ray transmission Laue topography, the distribution of dislocations in wafers grown by different growth techniques were detected and it was noticed that the crystals grown by Kyropoulos and HEM techniques indicated to be excellent.

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