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特约专栏

Review of the Research on the Nonlinear Optical Crystal：LiB₃O₅

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Abstract：The development of research on the borate nonlinear optical (NLO) crystal，LiB_3O_5(LBO)，is reviewed. We first summarize the background and present status of borate NLO crystals. The main considerations are focused on the discussion of the typical borate NLO crystal LBO，from the discovery of LBO as an NLO material to crystal growth and its applications. Finally，we introduce recent research on this crystal in our group and give the outlook for study of LBO in near future.

Key words：lithium triborate(LiB_3O_5, LBO)；crystal growth；nonlinear optical materials

非线性光学晶体 LiB_3O_5 研究进展

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摘 要：综述了硼酸盐非线性光学晶体 LiB_3O_5(LBO)的研究进展。首先介绍了硼酸盐非线性光学晶体的背景及现状，重点介绍了硼酸盐非线性光学晶体的典型代表——LBO 晶体的相关研究内容。然后从 LBO 晶体作为非线性光学晶体材料的发现到晶体生长和它在全固态激光中的应用等方面进行了讨论。最后，介绍了研究组过去几年中在 LBO 晶体研究方面取得的成果并展望了 LBO 晶体研究的未来发展方向。

关键词：三硼酸锂(LiB_3O_5, LBO)；晶体生长；非线性光学材料

1　Introduction

In 1961，immediately after the creation of the first laser[1]，the second harmonic generation (SHG) was observed for the first time as a ruby laser beam passed through a quartz crystal[2]. Since then，intensive research has been carried out in the field of nonlinear optical (NLO) crystals，as they can expand the range of laser wavelengths. At present，NLO crystals are widely used，for example，in laser display，laser medicine，optical communication，and in the expanding field of integrated optics.

For NLO applications，a good NLO crystal needs to have the following properties like[3]：① a relatively large NLO coefficient，② a moderate birefringence，③ a wide transparency，④ high laser-induced damage threshold，⑤ small walk-off effect，⑥ large angular，spectra and temperature bandwidths，⑦ good chemical stability and mechanical properties.

In the two decades after the discovery of SHG phenomena in quartz crystal，many NLO crystals were discovered. The typical crystals were $LiNbO_3$(LN)[4]，$KTiOPO_4$(KTP)[5] and KH_2PO_4 (KDP)[6]，which are still widely used nowadays. However，the former two crystals can not be used in the ultraviolet (UV) range，while the latter one has a small NLO coefficient[7].

Significant progress has been achieved in the area of UV NLO crystals with the advent of the borate crystal β-BaB_2O_4 (BBO) about 27 years ago[8]. BBO crystal has very good NLO properties，such as large NLO coefficient，short UV cut-off edge，moderate birefringence，high laser-induced damage threshold，but it exhibits disadvantages with large walk-off angle and small angular bandwidth[7]. To overcome these disadvantages，another borate crystal LiB_3O_5 (LBO) was discovered[9]. Since then，a lot of NLO borate crystals have been discovered and great progress has been made. The reason why NLO borate crystals have received so much attention lies in good properties of NLO borate crystals as follows[10]. Firstly，because of various boron-oxygen groups，there are a large number and many kinds of NLO borate crystals. Secondly，as the electronegativity of B atom and that of O atom differs sharply，NLO borate crystals usually have high transparency in the visible and UV region. In addition，NLO borate crystals possess high laser-induced damage threshold in general. Thus NLO borate crystals are superior in the generation of the visible and UV lasers to other commonly used NLO crystals such as LN，KTP or KDP.

In this review，the development of NLO borate crystals will be summarized in brief and then we will focus on the LBO crystal. The discovery and crystal growth of the LBO crystal will be reviewed. Then，we will report the recent development of this

crystal achieved by our group and the new application of LBO crystal.

2　Borate NLO crystals

Although the second harmonic generation of the borate crystal, $YAl_3(BO_3)_4$, was reported in 1974[11], the first NLO borate described was $KB_5O_8 \cdot 4H_2O$ (KB5) in 1975[12]. However, intense research on borate crystals was not initiated until the discovery of BBO and LBO. In 1993, a theoretical model, the so-called 'anionic group theory', was introduced by Chen[10], which promoted the development of NLO borate crystals. Since then, many NLO borate crystals have been discovered, and the development of NLO borate crystals entered a golden age. For example, CsB_3O_5 (CBO) and $CsLiB_6O_{10}$ (CLBO), with the same $(B_3O_7)^{5-}$ group as LBO, were discovered in 1993 and in 1995, respectively[13-14]. The KBBF and SBBO family, such as $KBe_2BO_3F_2$ (KBBF)[15], $RbBe_2BO_3F_2$ (RBBF)[16], $Sr_2Be_2B_2O_7$(SBBO)[17], $Ba_2Be_2B_2O_7$ (TBO)[18], $BaAl_2B_2O_7$ (BABO)[19] were discovered in succession by Chen's group. Meanwhile, several other group also discovered other borate crystals, typical representatives being $K_2Al_2B_2O_7$ (KABO)[20], $YCa_4O(BO_3)_3$ (YCOB)[21], $GdCa_4O(BO_3)_3$ (GdCOB)[22], $BaAlBO_3F_2$ (BABF)[23], $BaCaBO_3F$ (BCBF)[24], $Li_2B_4O_7$ (LB4)[25] and BiB_3O_6(BIBO)[26].

For application of NLO borate crystals, the main limiting factors vary in different crystals. In general, one of the main limiting factors in most NLO borate crystals is crystal growth. NLO borate crystals are grown from high temperature melts or solutions, with the exception of KB5, which is grown from aqueous solution. Crystal growth from high temperature melts is a very efficient and suitable method to obtain large single crystals with congruent melting point using the Czochralski and Kyropoulos techniques[27-28]. For example, CBO and CLBO crystals can be grown by the Kyropoulos technique, and the YCOB, GdCOB and LB4 can be grown by the Czochralski technique. However, the crystal growth becomes difficult, if the melts are of high viscosity, as is mostly the case for borate melts. For crystals that do not melt congruently or suffer a phase transition below the melting point, they can often be grown from high temperature solutions by the flux method[27-28], such as the top-seeding solution growth (TSSG) technique. BBO, LBO, BABF and KBBF are such examples. Flux can also be used to lower the viscosity of the high temperature solution. However, the biggest problem for this method is to find a suitable solvent. Besides, this method reduces the utilizable amount of raw materials, prolongs the growth period, and flux-grown crystals usually tend to incorporate micro-inclusions of the flux.

In all NLO borate crystals, LBO crystal is the most widely used and is in maximum demand due to its good properties, such as high laser-induced damage threshold, large NLO coefficient, good chemical stability, and good mechanical properties. Researches on the crystal growth and application of LBO have been going on for decades, since the NLO properties of LBO were reported[9].

3　Discovery of LBO crystal

LiB_3O_5, initially reported in 1926, was wrongly attributed to a congruent compound by Mazzetti et al., who gave a crude phase diagram of $Li_2O-B_2O_3$. In 1955, Rottet et al. made significant changes in the previous phase diagram, and indicated that $Li_2O \cdot 3B_2O_3$ was an incongruent compound. In 1958, a precise phase diagram of $Li_2O-B_2O_3$ was reported by Sastry et al., and $Li_2O \cdot 3B_2O_3$ was reported to be melt incongruently at

834 ± 4 ℃ (Fig. 1)[29]. In 1961, Bouaziz et al. described the phase diagram of $Li_2O-B_2O_3$, and showed that there was a high temperature phase $Li_2O \cdot 4B_2O_3$, which was not found in the phase diagram given by Sastry et al.. Since then, the research on LiB_3O_5 stagnated for about 20 years, until König and Hoppe obtained small $Li_2O \cdot 3B_2O_3$ crystals with solid-state reaction and determined the crystal structure in 1978[30]. The space group of $Li_2O \cdot 3B_2O_3$ crystal was determined to be Pna2₁, and the unit cell dimensions were $a = (8.4473 \pm 0.0007) \times 10^{-1}$ nm, $b = (7.3788 \pm 0.0006) \times 10^{-1}$ nm, $c = (5.1395 \pm 0.0005) \times 10^{-1}$ nm, and $z = 2$[30]. The structure of LBO crystal was showed in Fig. 2. Furthermore, in 1980, a 1 mm × 1 mm × 4 mm LiB_3O_5 single crystal with the same structure as that grown by König was grown by Ihara and Yuge with the vapor deposition method. Furthermore, the high temperature phase $Li_2O \cdot 4B_2O_3$ reported by Bouaziz was determined to be actually the mixture of $Li_2O \cdot 3B_2O_3$ and B_2O_3 by Wu et al. in 1990[31].

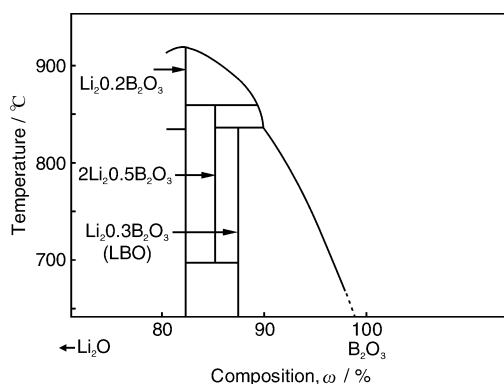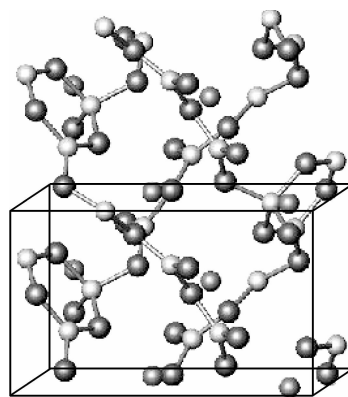Fig. 1　The partial phase diagram of $Li_2O-B_2O_3$ reported by Sastry et al.

Fig. 2　Scheme of LBO crystal structure

LiB_3O_5 (LBO) was first reported as a NLO material by Chen and Wu[32]. Later, the linear and nonlinear optical properties and the growth of LBO crystals were reported in detail by Chen and Wu et al. in 1989[9]. As a NLO material, the LBO crystal has several appealing properties, as shown in Table 1. For example, it has wide transparency in the range of 160 ~ 2 600 nm. The surface damage threshold of LBO was high as 25 GW/cm² (0.1 ns, 1 064 nm), which was the highest of all NLO borate crystals. LBO has a moderate effective NLO coefficient, about 3 times more than that of KDP. Moreover, several phase matching parameters of LBO are better than those of BBO, notably the acceptance angle and the walk-off angle. All these made LBO a novel and excellent NLO crystal. Since then, intensive research

on LBO crystal has been launched, both in the crystal growth and application.

Table 1　　Linear and nonlinear optical properties of LBO crystal

Space group	Transparency range /nm	Specific gravity /g·cm^{-3}	Mohs hardness	Linear thermal expansion coefficient, $\times 10^{-5}$/k			Linear absorption coefficient /pm·V^{-1}	NLO coefficient, d_{32}	Shortest SHG /nm	Birefringence, $\triangle n$	Walk-off angle /mrad		Laser-induced surface damage threshold /GW·cm^{-2}
				α_x	α_y	α_z					Type-I, xy	Type-II, yz	
Pna2$_1$	160 ~ 2 600	2.474	6	66.4	−52.8	27.3	0.000 35 (1 064 nm)	0.85	277	0.04 (1 064 nm)	18.3	9.30	25(0.1 ns, 1 064 nm)

4　LBO crystal growth

　　Because of its incongruent melting, large bulk single crystals of LBO have to be grown by flux methods. In the early, self-flux with excess B$_2$O$_3$ was mainly used and the TSSG technique was successfully applied. A great problem with the growth of LBO from self-fluxes is the rather high viscosity and the resulting difficulty of the mass transportation of the solution. To reduce melt viscosity, fluxes such as LiF and MoO$_3$ have also been applied. In this part, the growth of LBO with self-flux, MoO$_3$-based flux and other fluxes will be reviewed, respectively.

4.1　Crystal growth of LBO with self-flux

　　Growth of Large LBO crystal was first reported by Chen and Wu et al. in 1989[9]. They grew a 30 mm × 30 mm × 15 mm LBO crystal with a ϕ40 mm × 40 mm platinum crucible from a Li$_2$O-H$_3$BO$_3$ solution, but the composition of the solution was not shown. One year later, a LBO crystal with the size of 38 mm × 24 mm × 4 mm was obtained from a solution of 20% (amount of substance) Li$_2$O and 80% (amount of substance) B$_2$O$_3$[31] and a 35 mm × 30 mm × 15 mm LBO crystal grown from Li$_2$O-H$_3$BO$_3$ system with flux pulling method was reported in the same year[33]. In 1992, a 20 mm × 20 mm × 15 mm LBO crystal grown from a solution with 9% (mass fraction) Li$_2$O and 91% (mass fraction) B$_2$O$_3$ was reported by T Ukachi et al., and the suitable range of B$_2$O$_3$ for the LBO growth was determined to be 90% ~94% (mass fraction)[34]. According to the dynamic viscosity of Li$_2$O-B$_2$O$_3$ solutions and the results of crystal growth experiments, the most suitable concentration for LBO growth, reported by D P Shumov et al. in 1994, was about 72% ~ 82% (mass fraction) LBO in solutions[35]. In this region, the viscosity of the solution was relatively low and the growth rate was stable, so LBO crystals can be grown with no inclusion and no crack. In the same year, S A Markgraf et al. investigated the growth parameters of LBO in detail, such as the solution composition, cooling rate, rotation, and obtained a 25 mm × 30 mm × 20 mm crystal from an excess B$_2$O$_3$ solution in N$_2$ atmosphere[36]. Observations concerning the occurrence of unstable growth were also discussed and methods to eliminate the unstable growth were suggested in that. In 1998, H G Kim et al. reported the growth of LBO from B$_2$O$_3$ self-flux solutions and discussed the effect of seed orientation, rotation speed, temperature gradient in solution and crystal polarity on crystal growth[37]. The solution composition with the molar ratio of Li:B =1:4.1 was preferable for inhibiting seed decomposition and decreasing the viscosity of the solution.

　　After the development of 10 years, with the efforts of researchers in various countries, remarkable progress has been made in the growth of LBO crystal using B$_2$O$_3$ as self-flux, which promoted the application of LBO crystal. However, the high viscosity and the resulting difficulty of the mass transportation of the solution of self-flux system made the growth rate of LBO crystal too slow, and the solution tended to super cool. In summary, large size LBO crystals with good quality were diffi-

cult to be obtained from the B$_2$O$_3$ self-flux.

4.2　Crystal growth of LBO with MoO$_3$ flux

　　In 1996, MoO$_3$ was reported as the flux for the crystal growth of LBO. The phase diagram for the LBO/MoO$_3$ system was shown by C Parfeniuk et al. and the viscosity of the solution was investigated[38]. The result showed that the viscosity of the solution was markedly reduced by MoO$_3$, and the growth condition of LBO with crucible rotation of 30 rpm, [312] direction seed and 40.8% (mass fraction) MoO$_3$ was suggested[39]. In 1999, the Li$_2$O-B$_2$O$_3$-MoO$_3$ ternary system was investigated by N A Pylneva et al. (as shown in Fig. 3[40]), and the region of growth of LBO crystals with good quality was determined[40]. With [001] direction seed, cooling rate of 0.1 ~ 0.5 ℃/d, LBO single crystals, up to 100 mm × 82 mm × 45 mm in size and 290 g in weight, were grown free of cracks, bubbles and inclusions without pulling and rotating. LBO crystals up to 570 g in weight were reported to be grown free of cracks, striations and growth sectory boundaries with MoO$_3$ flux by using thermal field configuration technique in 2005[41]. Lately, using the method of heat field symmetry control, LBO single crystal with the weight of 1 379 g and the dimensions of 148 mm ×130 mm × 89 mm was grown from the solution with the molar ratio of Li$_2$O:B$_2$O$_3$:MoO$_3$ as 1:1.29:1.71[42].

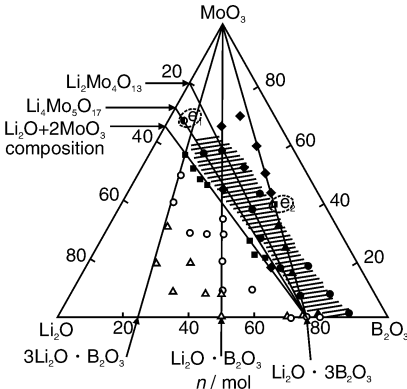Fig. 3　Li$_2$O-B$_2$O$_3$-MoO$_3$ ternary system reported by N A Pylneva et al.

　　Using MoO$_3$ as flux, the viscosity of the solution for LBO crystal growth was reduced significantly, which improved the mass transportation of the solution. The stability of crystal growth was enhanced, and the growth rate was accelerated, thus large scale LBO crystals could be obtained. Although spontaneous nucleation easily occurred due to serious volatilization of MoO$_3$, the flux used for the growth of LBO was mainly MoO$_3$ at present.

4.3　Crystal growth of LBO with other fluxes

　　To reduce the viscosity of the solution of self-flux system, additives were used. In 1990, Zhao et al. reported that addition of fluoride, such as LiF, into the self-flux system can re-

duce the viscosity of the system, but the detail was not reported[33]. And in 2001, the effect of NaCl additive on the growth and characterization of LBO crystal was reported[43]. The growth rate of LBO crystal increased observably with the NaCl concentration in solution increasing, but the crystals became more susceptible to cracking and a significant reduction in optical damage resistance was obtained when the level of Na$^+$ ions incorporated into the lattice exceeded approximately 250×10^{-6}[43]. Hao et al. reported that LiF and KF were used as additives in the growth of LBO crystals from self-flux system and the result indicated that KF was more suitable[44].

In conclusion, the growth of LBO crystal has been studied since this crystal was reported as a NLO crystal. Compared with other fluxes, MoO_3 flux was more suitable for crystal growth of LBO. Great progress was achieved by using MoO_3 as the flux. With advances in growth technology, the size of LBO crystal will be larger and larger, which will promote the application of this crystal.

5　Research on LBO crystal in our group

Research on the growth of LBO crystal has been going on in Beijing Center for Crystal Research and Development, TIPC, CAS since 1999. In the previous stage, the B_2O_3 self-flux was used, but no significant progress was achieved. This situation continued until the flux was changed to MoO_3. The phase diagram of LBO-MoO_3 and the viscosity of LBO-MoO_3 system had been investigated. In 2007, using a $\phi200$ mm $\times 180$ mm platinum crucible and a homemade three-zone resistively heated furnace (Fig. 4), a large LBO crystal, shown in Fig. 5, with the dimensions of 146 mm $\times$ 145 mm $\times$ 62 mm and the weight of 1 116.8 g was obtained. This was for the first time that LBO crystal up to 1 kilogram in weight was obtained. Based on this, the flux was optimized and a new flux system of MoO_3 and MX was used to avoid inclusions in LBO crystal, and the growth parameters were adjusted. To prevent large LBO crystals cracking, the

Fig. 4　Large homemade furnace with three-zone resistive heating for the crystal growth of LBO

anneal technique was explored. A high quality LBO crystal was grown, as shown in Fig. 6, with the size of 170 mm $\times$ 160 mm $\times$ 79 mm and the weight of 1 596 g. To grow larger LBO crystal, a growth equipment with a $\phi1$ 500 mm $\times 1$ 500 mm furnace and a $\phi310$ mm $\times 300$ mm platinum crucible was set up[45] and the technique of oriented growth was developed[46]. We have successfully grown a 160 mm $\times 150$ mm $\times 77$ mm LBO crystal with the weight of 1 988 g. The LBO crystal was free of cracks, striations and growth sectory boundaries, which makes possible to provide large NLO elements with aperture up to 100 mm $\times 100$ mm $\times 10$ mm for practical application.

The optical quality of as-grown LBO crystals was investigated

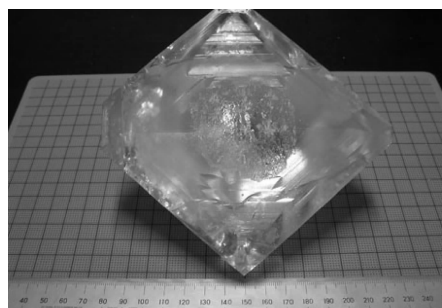Fig. 5　The as-grown LBO crystal with the dimensions of 146 mm $\times 145$ mm $\times 62$ mm and the weight of 1 116.8 g

Fig. 6　LBO crystal with the size of 170 mm $\times$ 160 mm $\times$ 79 mm and the weight up to 1 596 g

and the results showed that the optical homogeneity of LBO crystals was up to $10^{-6}/$cm. The experiment of SHG of LBO crystal was carried out with the cooperation of Prof. Y Z Xu's group in TIPC, ACS. A LBO crystal sample with the size of 4 mm $\times$ 4 mm $\times 50$ mm, yielded type-II phase matching with $\theta = 90°$ and $\varphi = 0°$ for frequency doubling 1 064 nm radiation of a Nd laser. The Nd laser can generate 1 064 nm radiation with 10 kHz and 100 ns. The stable 532 nm average output power of 200 W was achieved in 2006. Using LBO crystal, the third harmonic generation of high power Nd glass laser with 25 ns pulse width was also carried out. With 21 J of 1 053 nm input, 6.34 J of 351 nm radiation was obtained by using a 54 mm $\times 54$ mm $\times 14$ mm LBO sample. This work was accomplished with the cooperation of Prof. Z Wei's group in IOP, ACS. If the aperture of LBO sample becomes larger, the output power will increase.

6　Applications of LBO crystal in future

In comparison with other NLO borate crystals, the applications of LBO mainly concentrated on SHG of near IR and optical parametric oscillator (OPO) in near-IR and visible ranges. For example, LBO crystal can be used for frequency doubling of Nd: YVO4 laser ($\lambda = 1$ 342 nm)[47], Nd: YAG laser ($\lambda = 946$ nm)[48], InGaAs diode-laser oscillator ($\lambda = 930$ nm)[49], and Ti: sapphire laser ($\lambda = 746$ nm)[50]. The 532 nm output power of 138 W was generated when the LBO crystal was employed for SHG of a Q-switched Nd: YAG laser[51]. Of course, LBO crystal can generate UV radiation though sum-frequency generation[52-53].

Recently, LBO crystal was reported to be used in optical parametric chirped-pulse amplification (OPCPA)[54]. OPCPA technique combines optical parametric amplification (OPA) with chirped pulse amplification (CPA) in a single process and has many advantages, such as high gain coefficient, broadband gain bandwidth, weakly thermal effect and high energy conversion co-

efficient[55]. By using OPCPA technique, PW(10^{15} W) level e-ven 10^{21} W peak power of laser pulse can be achieved, so this technique has good prospect in fields of inertial confinement fusion (ICF), particle acceleration and the physics of intense field. In 2003, using OPCPA technique based on LBO/LBO/KDP crystals, a final output pulse with a peak power of 16.7 × 10^{12} W was obtained[56], which means that LBO crystal can be used in the fast ignition in laser fusion.

With the development of diode pumped solid state laser (DPL) and laser display technology, laser display, especially laser projection display, becomes practical[57]. With LBO crystal, red laser (659 nm), green laser (515 nm) and blue laser (440 nm) can be obtained[58-60]. Based on this, a laser projection display prototype machine with 140 inches screen was fabricated and worked well[61]. This indicates that LBO crystal can be widely used in laser display in future.

7 Conclusion

As a NLO material, LBO crystal possesses excellent properties with high laser-induced damage threshold, large NLO coefficient, good chemical stability and good mechanical properties. It has been widely used in laser generation of visible and UV ranges and dominates the market of NLO borate crystals. In the near future, LBO crystal will be applied in the fields of laser display, OPCPA and nuclear fusion.

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机动车尾气污染控制技术与产业发展取得明显进展

　　2010 年 7 月 19 日，国家 863 计划资源环境技术领域办公室在无锡组织召开了"十一五""机动车污染控制技术研究"重点项目验收会。科技部王伟中副部长出席项目验收会并作重要讲话。针对机动车污染控制需求，科技部自"十五"以来对机动车尾气污染控制技术及产业发展进行了连续支持，"十一五"将"机动车污染控制技术研究"列为 863 计划重点项目，瞄准即将实施的国 IV 排放标准以及未来的国 V 以上排放标准，研制汽油车、柴油车、摩托车和替代燃料车等不同车型尾气控制技术与装置，并推动相关产业发展。经过 3 年多的努力，项目研发的汽油车及柴油车排放控制技术水平达到或超过国 IV 标准，部分接近国 V 标准，摩托车排放控制技术水平达到或超过国 III 标准，形成了具有自主知识产权的关键技术储备，打破了国外公司在该行业的垄断地位。项目累计申请国家发明专利 42 项，参与企业占据国内汽油车和摩托车净化器产品相当大的市场份额，部分净化器产品批量出口，使我国机动车尾气净化技术研发进入世界先进行列。主要技术成果荣获 2009 年国家科学技术进步二等奖。

（本刊通讯员）