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Research

Advanced Materials and Materials Genome—Review

Recent Developments in Functional Crystals in China

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ABSTRACT Functional crystals are the basic materials for the development of modern science and technology and are playing key roles in the modern information era. In this paper, we review functional crystals in China, including research history, significant achievements, and important applications by highlighting the most recent progress in research. Challenges for the development of functional materials are discussed and possible directions for development are proposed by focusing on potential strengths of these materials.

KEYWORDS functional materials, laser crystals, nonlinear optical crystals, scintillation crystals, relaxor ferroelectric crystals, semiconductors

1 Introduction

Crystals are solid materials with long-range order. Those that exhibit functional properties, such as laser activity, nonlinear optical (NLO) properties, piezoelectric properties, and so forth, are called "functional crystals." Diamond is not only a well-known precious stone, but also a good functional crystal due to its extreme hardness and superior heat and electrical conduction. Silicon is the most widely used semiconductor crystal for creating the integrated circuits that have allowed computers to function as the foundation of our modern world. In 1900, corundum crystals were artificially grown in France, and were used to manufacture watch bearings, opening a new era for the application of functional crystals. Different from natural crystals, artificial crystals are high-tech materials with high purity and high perfection that are engineered for desired applications. Such applications mainly include functional properties that transform one form of energy, such as sonic, light, heat, electrical, magnetic, and so forth, into another. In modern science and technology, artificial crystals play key roles, and are called functional synthetic crystals. In this paper, we will give a brief review of some functional synthetic crystals, focusing on laser and nonlinear crystals that are related to the manufacture of solid-state lasers.

In 1960, Maiman invented the first laser using a ruby crystal (Cr^{3+}:Al_2O_3) as the laser medium; this device opened vast new horizons for quantum electronics [1]. The laser crystal is the core and foundation of the development of laser technology. In the 1970s, a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser crystal was developed and widely adopted due to its superior laser characteristics and high thermal conductivity. In the 1980s, a titanium-doped sapphire (Ti:Al_2O_3) was grown, and a tunable laser (with a range of 660–1100 nm) was developed. This tunable laser formed the foundation for ultra-fast, ultra-short-pulse high-intensity lasers, resulting in the development of femtosecond (fs)-pulsed lasers. The commercialization of the laser diode during the late 1980s caused the rapid development of all-solid-state lasers, which in turn promoted a great increase in laser applications and in laser technology itself. In the 1990s, the successful growth of a neodymium-doped yttrium orthovanadate (Nd:YVO_4) crystal made miniature pocket lasers possible.

A particular laser can emit only at a specific wavelength, which can in turn be converted to another wavelength by using NLO crystals. When laser radiation passes through the nonlinear medium, the nonlinear response to light-induced polarization of the electromagnetic field feeds back to the input light wave, resulting in the generation of harmonics at a particular wavelength by means of a nonlinear effect. This effect, which is related to the laser intensity, differs from linear optical effects and is referred to as a NLO effect. Crystals possessing NLO effects are called NLO crystals.

Functional crystals can be divided into several categories, such as laser media, NLO crystals, electro-optical (EO) crystals, piezoelectric crystals, pyroelectric crystals, and so forth, according to the principal effect of the crystal and its application. In addition, most of the substrates used as semiconductors are functional crystals. Although the crystal volume in most electronics equipment is small, their functional effect is quite important.

In this review, recent progress in the development of func-

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tional crystals in China is summarized.

Special attention has been paid to large, high-quality garnets, including neodymium and other rare earth ion-doped crystals that still maintain top priority in the development of laser media applications. The research and testing of transparent laser ceramics and micro-crystalline glasses are also going forward. A series of micro-chip laser crystals have been developed to meet the requirements of miniature lasers. Different kinds of NLO crystals that are suitable for use in the ultraviolet/visible/near-infrared (IR) spectral regions have been developed, and new NLO crystals that can be used in the far-IR to THz wave regions are topics of recent development in this field. To meet ever-growing needs in the mid-IR (e.g., near 2 μm) range, directly pumped laser crystals, Raman shift crystals, and mid-IR NLO crystals all fulfill the requirements. Along with the development of large potassium dihydrogen phosphate (KDP) and deuterated potassium dihydrogen phosphate (DKDP) crystals, large lithium triborate (LBO) and yttrium calcium oxyborate (YCOB) crystals have attracted a great deal of attention. Consequently, more research activity must also be devoted to improving crystal-growth technology in order to mass-produce high-quality crystals at low cost.

Scintillation crystals are very important in high-energy physics and medical diagnosis. Developments in this field are focused on the design and growth of new crystals that possess excellent scintillation response and that can expand the application of these crystals.

Recently, the extension of microstructure physics has become more pervasive, with a stronger influence on crystal technology than ever before. The microstructure of photoelectronic functional materials represents the intersection of materials science, condensed matter physics, and photoelectronic technology, and has profound scientific and technological significance. A great deal of progress in research on dielectric superlattices has been made in both fundamental and technological terms in recent years.

The progress made in this field will be reviewed in the following sections.

2 Present status of and progress in functional crystals

2.1 Laser crystals

A laser crystal is the fundamental material for constructing an all-solid-state laser. Laser crystals are crystals that can be electrically or optically pumped in order to produce efficient laser output. A laser crystal is normally composed of a matrix and an emitting light center, which can take the form of a rare earth ion, a transition metal ion, or some other sources such as a color center .

The earliest known laser output was obtained with chromium-doped ruby ($Cr:Al_2O_3$) in 1960. Since then, a variety of laser crystals with more than 350 different matrix materials and with more than 20 different kinds of emitting ions have been developed, and efficient laser output has been obtained at more than 70 different wavelengths. Laser crystals can be divided into three main groups: oxide crystals (e.g., Al_2O_3, $Y_3Al_5O_{12}$, $YAlO_3$, Y_2O_3, Sc_2O_3), fluoride crystals (e.g., CaF_2, BaF_2, SrF_2, LaF_3, MgF_2, $LiYF_4$, LiCAF, LiSAF), and metal oxysalt crystals (e.g., $Ca_5(PO_4)_3F$, Y_2SiO_5, YVO_4, $YAl_3(BO_3)_4$, $CaWO_4$). Among these, the most widely used crystals are the three basic laser crystals: Nd:YAG, Nd:YVO_4, and Ti:Al_2O_3. The Nd:YAG crystal is used to manufacture high- and medium-power output lasers; the Nd:YVO_4 crystal is used for miniature low-power output lasers; and the Ti:Al_2O_3 crystal is used for tunable ultra-fast output lasers. Apart from these three, some new laser crystals have been developed in recent years that hold promise for potential applications in meeting the growing requirements for all-solid-state lasers and the needs of the related high-tech industry.

2.1.1 Garnet laser crystals

Garnet is a natural mineral that has been studied for many years. Based on its internal structure, the garnet crystal belongs to the cubic system, with the general formula $A_3B_2C_3O_{12}$, where A is an atom such as Y, Gd, Lu, or La that occupies a site in the dodecahedron; B is an atom such as Sc, Al, Ga, or Fe that occupies a site in the octahedron; and C is an atom such as Al, Ga, or Fe that is located on a tetrahedral site. The important garnet crystals include YAG, yttrium gallium garnet (YGG), and gadolinium gallium garnet (GGG). YAG is one of the most widely used laser host crystals.

The Y—O bond in the YAG crystal is 0.245 nm in length. Since Y^{3+} and other rare earth ions have similar radii, the Y^{3+} ions at the dodecahedron sites can be replaced by other trivalent rare earth cations, including Nd^{3+}, Er^{3+}, Tm^{3+}, Ho^{3+}, and Yb^{3+}, as the active ions for lasing. In addition, ions at sites in the octahedron can be replaced by trivalent metal ions such as Cr^{3+}, V^{3+}, Mn^{3+}, and Fe^{3+} acting as sensitizers. Currently, Nd^{3+}:YAG, (Nd^{3+}, Ce^{3+}):YAG, (Nd^{3+}, Ce^{3+}):Tb^{3+}:YAG, and (Nd^{3+}, Ce^{3+}):Cr^{3+}:YAG are the most common laser materials in this class. To be classified as an excellent laser material, the host crystal should possess good mechanical, thermal, and optical properties. Table 1 lists the physical, chemical, and thermal properties of YAG [2], which is considered to be a model for laser crystals. The main disadvantage of Nd:YAG is the low doping concentration and the narrow absorption-spectrum peaks, both of which indicate that any further improvement in laser efficiency when pumped with a laser diode is difficult.

Since Geusic et al. first reported the laser output of the Nd:YAG crystal in 1964 [3], Nd:YAG crystals and the lasers built with them have attracted a great deal of research interest. Today, even kilowatt power level Nd:YAG lasers are available commercially; these have special applications in industrial processing [4]. With the recent development of high-power, high-heat capacity lasers, Nd:YAG has become a focus of current research. Compared with the widely used Nd:GGG crystal, the Nd:YAG crystal has advantages in its thermal and physical-chemical properties: For example, its thermal-lens effect is only one-half as much as that of Nd:GGG and lies below the thermal-stress limit; and its theoretical laser output is one-third higher [5].

A large-aperture, high-performance Nd:YAG crystal is the key material used in high-average-power solid-state lasers,