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Research Article

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Application of third-order nonlinear optical materials in complex crystalline chemical reactions of borates

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Abstract: In order to explore the application of third-order nonlinear optical (NLO) materials in complex borate crystalline chemical reactions, the laser light source with limited wavelength range can be extended to ultraviolet (UV) and deep UV region by using NLO crystal materials and frequency conversion technology, which has become a hot research direction of deep UV light source. The experimental results show that the UV cutoff edge of the grown $KLi(HC_3N_3O_3)\cdot 2H_2O$ crystal is 237 nm. The refractive index of the crystal was measured by prism coupling technique, and the Sellmeier equation of the refractive index of the crystal was fitted. The chemical bond of the crystal is a fundamental means to understand the relationship between structure and properties. With the emergence of a large number of hybrid functional crystals, the composition and structure of crystals become more complex, and the chemical bond theory has also been greatly developed, and then the chemical bond theory of meta crystals or complex crystals has emerged. Once proposed, the theory has been widely used, such as analyzing the eligibility of luminescent crystals, NLO crystals and high-temperature superconductor crystals. NLO materials are the dominant field of China in the world. Crystals with good nonlinear behavior have more complex crystal structures, due to the theory of amorphous structure, the exploration of this aspect is particularly difficult. For the first time, the influence of the composition of rare earth-doped bismuth borate glass on the crystal precipitation and glass microstructure of NLO materials was systematically studied, which laid a theoretical foundation for further development and understanding of new bismuth borate optical systems.

Keywords: borate crystalline, ultraviolet light, growth habit

1 Introduction

Nonlinear optical (NLO) materials are China's dominant field in the world. In order to maintain this favorable momentum, the development of new NLO materials is imminent. Crystals with good nonlinear behavior have complex crystal structures, and it is particularly difficult to carry out exploratory work in this area due to the amorphous theories. In the exploration of new crystals in nonlinear optics, the previous research work was qualitative exploration at the crystal level, using existing crystals for element substitution and doping to improve their properties.

At present, the research on new bismuth borate is in the ascendant, mainly focusing on the development and understanding of new glass systems and the change in optical properties by doping rare earth elements, the structure formation mechanism of bismuth borate glass and the influence on the structure of rare earth oxides. The aim of this study is to carry out research on the formation theory and microstructure control technology of new borate functions as soon as possible, to further reveal the influence of chemical composition on the structure and properties, and explain and predict the glass properties, which will be of great importance to the design and development of new borate functional materials.

From the point of view of material design and synthesis, NLO crystal materials used in deep ultraviolet (UV) all-solid-state lasers need to strictly meet the following performance requirements: first, the structure of non-centrosymmetric, only materials crystallized in non-centrosymmetric space group have second-order nonlinear effects; Second, wide transmission range, through the cutoff edge to reach deep UV (with a large band gap of

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E_g > 6.2 eV), which is the prerequisite for deep UV application [1]; Third, the larger effective NLO coefficient, according to the frequency doubling, optical conversion efficiency is proportional to the square of the crystal effective frequency doubling coefficient d_{eff}, so in order to effectively improve the crystal frequency doubling optical conversion efficiency, the crystal must have a large effective frequency doubling coefficient d_{eff}; Fourth, an appropriate birefringence ($\Delta n \sim 0.05$–0.10) is required, which not only meets the phase matching conditions of deep UV, but also avoids some bad effects (such as ionization effect, photorefractive effect, self-focusing, *etc.*) that affect the beam quality; Fifth, it is easy to grow large-size single crystal, ensuring that large-scale production can be achieved to meet the needs of industrial application [2]; Sixth, the raw material is non-toxic, stable physical and chemical properties, hardness, no deliquescence, easy to process, *etc.* However, only few existing deep UV NLO crystal materials can meet the above performance requirements. Therefore, the research and development of new NLO crystal materials for deep UV all-solid-state lasers is a key problem to be solved urgently in this field. UV (200 nm < λ < 400 nm) NLO crystal is the key element of all solid-state laser UV laser output. At present, the output of 266 nm (Nd: TAG quadruple) UV laser is mainly realized by β-BaB_2O_4 (β-BBO) and $CsLiB_6O_{10}$ (CLBO) crystals [3]. However, due to the large birefringence of β-BBO crystal and the deliquescence of CLBO crystal, these two crystals still cannot meet the demand of laser output in this band. Therefore, it is very necessary and urgent to explore a novel quadruple UV NLO crystal. $KBe_2BO_3F_2$ (KBBF) crystal can achieve Nd: YAG direct six octave deep UV laser (λ = 177.3 nm) output, and its excellent optical properties are due to the parallel arrangement of $[Be_2BO_3F_2]_\infty$ layers in its structure.

In this study, the non-equilibrium thermodynamics and crystallization kinetics of low-melting borate sealing glass system are systematically studied, the main factors and control mechanisms affecting the glass structure stability are proposed, and the effects of optimized composition on glass sealing temperature, mechanical properties, expansion performance, *etc.*, are discussed.

2 Literature review

After years of research, Joshi *et al.* conducted systematic research on the structure design, crystal growth and other aspects of UV crystal borate system from simple borate to composite borate, and continued to find that it was increasingly difficult to develop new borate NLO crystal materials, so it was particularly urgent to develop new material systems [4]. Zong *et al.* determined from the relationship between borate structure and NLO effect that borates containing plane conjugated groups (BO_3 and B_3O_6) have large frequency multiplier coefficient, appropriate birefraction index, short UV cutoff edge, *etc.* Plane conjugated groups are the core functional units of borate NLO crystal materials [5]. Parol *et al.* expanded the study of plane conjugated groups, which is a key step in exploring new UV NLO materials. However, there are few units with planar conjugated electronic structures in inorganic compounds [6]. In addition to borates, carbonates and nitrates are more common. In this study, in order to explore the application of third-order NLO materials in complex borate crystalline chemical reactions, the laser light source with limited wavelength range can be extended to UV and deep UV region by using NLO crystal materials and frequency conversion technology, which has become a hot research direction of deep UV light source. In the exploration of new NLO crystals, previous research work is qualitative exploration at the crystal level, using the existing crystal for element substitution and doping, so as to improve their properties. There is no mature theory to explain the nonlinear behavior of existing crystals. In the study of nonlinear phenomena, in the research process, anionic group theory is usually used to calculate and analyze the nonlinear behavior of crystals, the differences between groups are difficult to explain satisfactorily, because we only consider one group, not the groups of crystals as a part.

3 Carbonate UV NLO crystal

Carbonate compounds occur in a large number of natural minerals, and the discovery and metallogenic mechanism of carbonate minerals have been reported in many geological journals. Natural mineralization is mainly under high temperature and high pressure. Synthetic carbonate compounds are rare, mainly including compound carbonate systems, such as $LaKOCO_3$, $LiNaCO_3$, $Na_2LiLn(CO_3)_3$, $Na_3Y(CO_3)_3{\cdot}6H_2O$, *etc.* And the fluorocarbon system, such as $K_4Ln_2(CO_3)_3F_4$, $A_2A'(CO_3)F$ (A, A′ = K, Rb, Cs), $BaZn(CO_3)F_2$, *etc.* Only a few of these compounds have centerless structures. In 1996, by studying the binary phase diagram of Li_2Co_3-Na_2Co_3, D’Akov *et al.* grew $LiNaCO_3$ crystal of volume larger than 4 cm^3, and measured that the UV cutoff edge of the crystal was about 200 nm. Further research shows that the crystal can achieve the harmonic output of the second, third and fourth octaves of the ND-YAG laser by phase matching. The phase matching angles of the second, third and fourth octaves are 20.2°, 24.7° and 34.6°, respectively, in the optical axis plane. In 2011, our team discovered a series of $ABCO_3F$ (A = K, Rb, Cs; B = Ca, Sr, Ba) crystal, all the six compounds in the system have centerless structure, and the frequency doubling coefficients are 1–4 times that of KDP. The excellent linear and NLO properties can be seen from the few carbonate NLO crystals. Therefore, it is necessary to carry out systematic research on carbonate NLO crystals [7].

Although carbonates, especially carbonates without alkali metals, are stable in air, they are easy to decompose at high temperature, and it is difficult to grow single crystals by molten salt method. Therefore, our team mainly adopts hydrothermal method to explore carbonate NLO materials. In order to obtain carbonate crystals with stable properties and UV transmission, the design idea adopted is to select carbonate systems containing full or half full shell rare earth ions (La, Sc, Y, Gd, Lu) or carbonate systems containing alkaline earth metals (Mg, Ca, Sr, Ba). Alkali metals or alkali metal halides are introduced, so that it forms double salt under subcritical hydrothermal conditions [8].

3.1 Alkali metal-rare earth carbonate system

Under subcritical hydrothermal conditions, our team systematically explored alkali metal (Li, Na, K, Rb, Cs) and rare earth ion (La, Sc, Y, Gd, Yb, Lu) carbonate systems and alkali metal and halogen carbonate systems. Nine compounds with non-core structures were successfully synthesized: $Na_3Lu(CO_3)_2F_2$, $Na_8Lu_2(CO_3)_6F_2$, $RE_8O(CO_3)_3(OH)15X$ (RE = Y, Lu; X = Cl, Br), $Na_3Y(CO_3)_3$, $Na3Gd(CO_3)_3$, and $Na^4La_2(CO_3)_5$. Further characterization of the optical properties of these compounds showed that the series of compounds had large frequency doubling coefficients and short UV cutoff edges, which made them potentially excellent UV and deep UV NLO crystals (Table 1).

Table 1: Optical properties of alkali metal-rare earth carbonate crystals

Crystals	**Space group**	**Second-harmonic generation (SHG) coefficient (×KDP)**	**Cut-off edge (nm)**
$Na_3Lu(CO_3)_2F_2$	Cc	4.28	<200
$Na_8Lu_2(CO_3)_6F_2$	Cc	4.23	<200
$Na_3Y(CO_3)_3$	Ama_2	3.57	~220
$Na_3Gd(CO_3)_3$	Ama_2	3.53	~220
$Na_4La_2(CO_3)_5$	$P6_3mc$	3.00	~35
$Y_8O(CO_3)_3(OH)_{15}Cl$	$P6_3$	1.65	~266
$Lu_8O(CO_3)_3(OH)_{15}Cl$	$P6_3$	2.22	~266
$Y_8O(CO_3)_3(OH)_{15}Br$	$P6_3$	1.83	~254
$Lu_8O(CO_3)_3(OH)_{15}Br$	$P6_3$	3.00	~283

In this system, the alkali-fluorocarbonate system has been well studied, and the compound structure represented is $ABCO_3F$ (A = K, Rb, Cs; B = Mg, Ca, Sr, Ba), and the fluorine-free alkaline metal-alkaline earth carbonate system is rarely studied. Therefore, the exploration of alkaline metal-alkaline earth carbonate UV NLO crystals is the focus of research. In addition, it is also a research direction of our team to design and search for new alkali metal-fluorocarbon UV NLO crystals with high performance. The method we use to explore alkaline metal-alkaline earth carbonate is still hydrothermal method [9]. The exploration idea is to form insoluble alkaline metal-alkaline earth carbonate by introducing alkaline earth elements into soluble alkaline metal carbonate under hydrothermal condition. Under the guidance of this idea, a series of alkali-alkaline earth metal carbonates, $ANa_5Ca_5(CO_3)_8$ (A = Na, K, Rb, Cs) and $Ca_2Na_2(CO_3)_3$ with nonlinear effects have been found (Table 2).

Table 2: Optical properties of alkali metal-alkali earth carbonate crystals

Crystals	**Space group**	**SHG coefficient (×KDP)**	**Cut-off edge (nm)**
$Na_6Ca_5(CO_3)_8$	$P6_3mc$	~1	<200
$KNa_5Ca_5(CO_3)_8$	$P6_3mc$	~1	<200
$RbNa_5Ca_5(CO_3)_8$	$P6_3mc$	~1	~203
$CsNa_5Ca_5(CO_3)_8$	$P6_3mc$	~1	~210
$Na_2Ca_2(CO_3)_3$	$Amm2$	~3	~205
$Ca_2Na_3(CO_3)_3F$	Cm	~4	<200

In order to design a new high-performance alkali metal-fluorocarbon, we applied molecular engineering methods to the design of carbonate NLO crystals for the first time. Through literature research, we noticed that in calcium carbonate crystal, CO_3 plane group has high anisotropic polarization, the polarization of plane is $a_{||} = 4.2 \times 10^{-24}\ cm^{-3}$, and the polarization of vertical is $a\perp = 3.18 \times 10^{-24}\ cm^{-3}$. Therefore, we speculate that the CO_3 group may have more advantages in nonlinear coefficient and birefraction index than the BO_3 group with the same planar structure. Based on the above assumptions, our idea is to select the borate NLO crystal containing BO_3 group with excellent performance, and design a new carbonate NLO crystal by molecular engineering method, in order to improve the nonlinear coefficient and birefraction index of the designed crystal. According to this idea, we selected $YCa_4O(BO_3)_3$(YCOB) as the template compound, because the compound YCOB has a large frequency doubling coefficient and a wide transmission band, but its application in the UV region is limited due to its small birefringence. According to our design, the CO_3 group replaces the BO_3 group, and other equilibrium ions are replaced accordingly. We replaced Y ion with Na ion, not only because the radius of Na ion is similar to that of Y ion, but also because the introduction of Na ion does not cause "red shift" to the UV absorption edge [10]. In addition, the substitution of F ions for O may form compounds with low melting points, which is not only conducive to crystal growth by molten salt method, but also conducive to improving the optical properties of compounds. Because the polarization of F ion is very weak, the refractive index and birefringence of fluorine carbonate can be increased; At the same time, due to the strong electronegativity of F ions, the bandwidth of carbonic acid fluorination can be increased, and the resulting compounds have short UV cut-off edges. Finally, under the guidance of these ideas, we successfully synthesized a case of alkaline metal-alkaline earth fluorocarbon, $Ca_2Na_3(CO_3)_3F$, with a large frequency doubling factor, a wide UV transmission band and a large double fold rate (Figure 1).

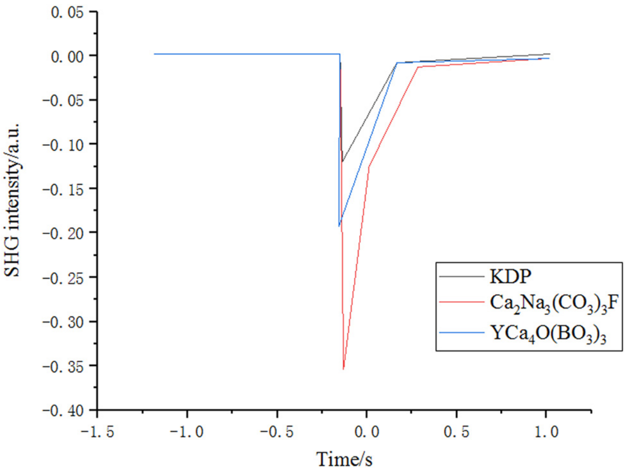

Figure 1: Comparison of optical properties of $Ca_2Na_3(CO_3)_3F$ and $YCa_4O(BO_3)_3$.

4 Nitrates UV NLO crystals

Compared with borates and carbonates, inorganic nitrate with the same planar triangular configuration $[NO_3]^-$ as NLO material is rarely reported. Nitrate compounds are rarely studied as NLO crystals due to their strong water solubility and unstable physical and chemical properties. However, in spite of this, there are some NLO crystals with low water solubility and stable properties in nitrate. Such as $K_2RE(NO_3)_5{\cdot}2(H_2O)_2$ (RE = La, Ce, Pr, Nd) and $Bi_2O_2(OH)(NO_3)$. However, due to the water solubility of most nitrate, there are few systematic studies on inorganic nitrate NLO crystal materials. Based on the successful development of inorganic borate and carbonate NLO crystals with planar triangular coordination groups, nitrate compounds with planar triangular structure are used as research objects to expand the exploration scope of NLO crystal materials. In 2014, our team carried out exploration of the Pb-containing nitrate system, during which we also found many cases of Pb-containing nitrate compounds with non-core structure. However, because these compounds contain heavy metal ion Pb, they will cause the band gap redshift of the compounds, which will affect the UV application of the crystals. To explore nitrate materials suitable for UV and deep UV applications, our team focused on nitrate systems containing alkaline metals, alkaline earth metals, or rare earth ions with full and half full shells. In order to find an appropriate method to explore water-insoluble nitrate crystals, our team summarized the previous work and did a lot of literature research, and proposed the idea of synthesizing water-insoluble nitrate by adjusting the solution pH, so as to carry out the exploration of UV nitrate crystals.

Based on the idea of synthesizing water-soluble nitrate by adjusting solution pH, our team carried out exploration and research on rare earth nitrate crystals, and successfully discovered a series of UV nonlinear nitrate optical crystals $Re(OH)_2NO_3$ (Re = La, Y, Gd). Further studies revealed how the NLO coefficients in this series of compounds are regulated by the radius of the rare earth cation. According to "anionic group theory," the arrangement of nitric acid radical group and group density directly affect the nonlinear coefficient of nitrate NLO crystal. We found that in this series of compounds, nitrate presents ABABAB. And there is an angle θ between the nitrate roots of layers A and B (Figure 2).

Further study shows that the angle is affected by the radius of the rare earth cation, and the angle increases with the decrease in the radius of the rare earth cation. In order to establish the relationship between the angle and the nonlinear coefficient, we first conclude that the structure factor $C = \cos(\theta/2)$ (the structure factor C is a parameter that directly reflects the orientation of the anionic groups) of the nitric acid group in the crystal structure by using "anionic group theory." In combination with the group density of nitrate, the relationship between angle and nonlinear coefficient can be related (Table 3). It can be seen from Table 3 that the calculated

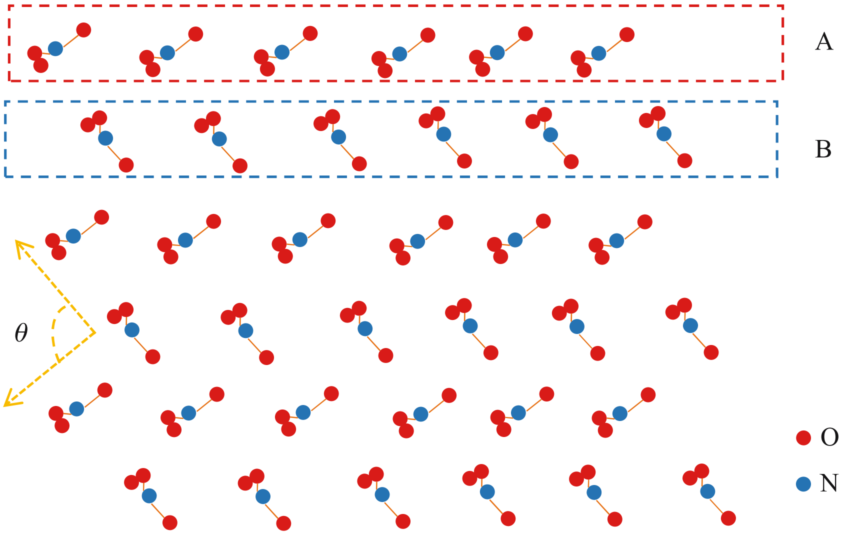

Figure 2: Arrangement of NO_3 groups in $Re(OH)_2NO_3$ crystal.

Table 3: The relationship between the crystal structure of $Re(OH)_2NO_3$ and NLO properties

Crystals	SHG coefficient (visible) (×KDP)	Structural criterion $C = \cos(\theta/2)$	Densities of the $[NO_3]$ (n/V) (nm^{-3})	(n/V) × C ($\hat{A}^{-3}$)	Angle (θ) of $[NO_3]$ groups (deg)
$La(OH)_2NO_3$	5.0	0.804	10.1	0.00812	72.863
$Gd(OH)_2NO_3$	5.5	0.767	11.0	0.00843	79.755
$Y(OH)_2NO_3$	5.6	0.754	11.3	0.00852	82.144

value is consistent with the change in the experimental value.

Experiments show that with the increase in rare earth oxide content, the crystallization tendency of the glass decreases and the stability increases. The greater the electric field strength of rare earth ions, the stronger the effect on inhibiting glass devitrification. When the rare earth oxide reaches a certain amount, the glass is relatively stable and difficult to crystallize. This amount decreases as the electric field strength of rare earth ions increases.

5 Conclusion and prospects

So far, through the joint efforts of scientists, a series of inorganic NLO crystals have been successfully designed and prepared from UV to deep UV region. However, there are few inorganic crystals that can realize phase matching and have appropriate frequency doubling coefficient at the same time. If we consider the difficulty of crystal growth, the size, physical and chemical properties, practical value and stability of the obtained crystals, the appropriate crystal materials will be less. It can be said that the targeted design of deep UV NLO materials with specific properties is still a great challenge. In view of the layered structure and crystal characteristics of KBBF, it is still one of the most favorable structures to generate deep UV harmonics so far. Moreover, with the in-depth study of the structure performance relationship of KBBF crystal, the development of KBBF borate structures may be a choice to optimize the next generation of deep ultraviolet nonlinear optical materials by using KBBF layered structure as a molecular engineering design template. Some design strategies have been proved to be effective by systematically studying the structure–performance relationship of A cation (K), B cation (Be) and anionic group replacement for KBBF.

However, lead-free is also the inevitable development direction of low melting point sealing glass. How to optimize the composition to obtain a lead-free borate sealing glass system with lower sealing temperature and stable performance is an important problem to be solved in the next research work. The influence of rare earth oxide content on the precipitation content of $BiBO_3$ optical crystals in tin borate glass and the corresponding optical properties also need to be further studied. Establishing an appropriate crystallization kinetic equation to better explain the growth mechanism of crystal precipitation in glass will be the focus of the theoretical part of this thesis in the next step.

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