Nd-Sialon Microcrystals with an Orthogonal Array

Saifang Huang, Zhaohui Huang,* Minghao Fang, Yan-gai Liu, Jun tong Huang, and Jingzhou Yang

School of Materials Science and Technology, China University of Geosciences (Beijing), Beijing 100083, People’s Republic of China

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ABSTRACT: Nd-Sialon microcrystals with a novel orthogonal array morphology were developed by inducing catalysis of Fe for the first time, via a combination of vapor−liquid−solid (VLS) and vapor−solid (VS) growth mechanisms. The chemical composition of Nd-Sialon crystals was determined to be NdSi₆₃Al₂O₄N₀.₉₄. The morphology of the tips strongly depended on the relative position of the liquid droplet to the crystal. Furthermore, the crystal growth process of Nd-Sialon microcrystals with the novel morphology was discussed. The Nd-Sialon single crystal shows UV-to-blue emission when it is excited by a wavelength of 325 nm. Nd-Sialon is envisioned to have potential in many functional applications, such as white LEDs, detector arrays, MEMS, and optical components. This work shines a light on the growth of Nd-Sialon single crystals for potential laser application.

Sialon ceramics¹ are widely used in structural applications because of their excellent mechanical properties, high temperature oxidation resistance, and corrosion resistance.² Lots of outstanding work³ has been performed to improve their toughness. Lanthanide doped Sialon with a chemical formula of Ln(Si₆₋ₓAlₓ)₀(OₓN₁₀₋ₓ) (orthorhombic crystal system, space group Pmn2₁) was found in 1995 as an intergranular phase during the investigations⁴ into phase stability of Ln-doped α-Sialons (Ln = Nd, La, and Ce) along the join line Si₆N₆-Ln₂O₃.⁵ AlN was found in 1995 in Ln-Si-Al-O-N systems. Recently, Ln(Si₆₋ₓAlₓ)₀(OₓN₁₀₋ₓ) phosphors doped by La and Ce and their application in white light-emitting diodes (LEDs) were reported by the National Institute for Materials Science (NIMS) in Japan.⁶ And this report reveals that Ln-Sialon phosphors are suitable for solid-state lighting, especially for home illumination, which would promote energy conservation for the world, considering their high color rendering index (CRI), wide range of correlated color temperatures (CCTs), and high luminous efficiencies.

It is well-known that high efficiency and high power Nd-based solid-state laser materials⁷ (such as Nd:YAG, Nd:YAP, and Nd:YLF) were used widely in medical applications, laser guidance, materials processing, and even future nuclear-fusion applications.⁸ This motivates us to consider whether Nd(Si₆₋ₓAlₓ)₀(OₓN₁₀₋ₓ) can also be used as a new Nd-based laser material. Due to the difficulty of preparation of single-phase Nd(Si₆₋ₓAlₓ)₀(OₓN₁₀₋ₓ) polycrystalline ceramic,⁹ however, study on the growth of single-crystal Nd(Si₆₋ₓAlₓ)₀(OₓN₁₀₋ₓ) becomes very meaningful.

Some monocrystalline materials with micrometer size have been reported, including SiC,⁹ Al₂O₃,¹⁰ and Si₃N₄¹¹ growing via a vapor−liquid−solid (VLS) mechanism¹² by using transition metals as the catalyst. To the best of our knowledge, however, few works about preparation of Sialon single crystals with micrometer dimension were reported in the literature.¹³ In this paper, Nd-Sialon microcrystals with a novel orthogonal array morphology, which were developed by inducing catalysis of Fe using Nd₂O₃, Si₃N₄, and AlN as starting materials at 1700 °C for 3 h in flowing nitrogen atmosphere with a controlled pressure of 0.9 MPa, are reported. (Detailed preparation and characterization were described at the end of the paper.)¹⁴ These Nd-Sialon microcrystals grew across in three dimensions with diameters ranging from 5 to 10 μm and lengths up to 200 μm or even longer (Figure 1a and Figure S1 in the Supporting Information).

The Debye crystallogram of an Nd-Sialon single crystal with dimensions of about 50 μm × 50 μm × 200 μm was determined on a Bruker SMART APEX-CCD diffractometer by the Gandolfi method¹⁵ using Mo Kα radiation (λ = 0.71073 Å). The results showed that the Nd-Sialon crystal has an orthorhombic unit cell with a = 9.3060 Å, b = 9.7224 Å, and c = 8.8777 Å. And a digital X-ray powder diffractogram after proper background subtraction with 20 range from 3° to 58° (Figure 2) was transferred from the Debye crystallogram (Figure S2, Supporting Information). By matching the ICDD card, the single crystal was initially analyzed to be the phase of Nd(Si₆₋ₓAlₓ)₀(OₓN₁₀₋ₓ) (corresponding to JCPDS-52-0013). But it is found that the data in JCPDS-52-0013 was incomplete (only the 15th strongest lines were given). Thus, the simulated XRD pattern of LaSi₆₋ₓAlₓOₓN₁₀₋ₓ was used for comparison, which was generated from the crystallographic information file (CIF) with depository number CSD-081057 in the inorganic crystal structure database (ICSD). It shows that the powderlike XRD pattern of a Nd-Sialon single crystal matched the simulated XRD spectrum pretty well, except for a small shift of 0.24° to the low angle, which indicates that the Nd-Sialon crystal had a similar crystal structure to that of LaSi₆₋ₓAlₓOₓN₁₀₋ₓ. Therefore, the Nd-Sialon single crystal was verified to be the NdSi₆₋ₓAlₓOₓN₁₀₋ₓ phase.

The chemical composition of these crystals was determined by electron dispersive spectrometer (EDS) analysis, and the results (Table S1, Supporting Information) show that the mean atomic ratio of Nd/Si/Al/O/N in these Nd-Sialon crystals is 1:5.83:1.71:0:485:9:55, which indicates that the oxygen content is less than 2 wt %. Considering strong absorption of the O Kα and N Kα signals, the z value of NdSi₆₋ₓAlₓOₓN₁₀₋ₓ calculated according to (Si₋ₓAlₓ)₀(Oₓ)₀(N₁₀₋ₓ) is about 0.6, which is smaller than that (z ≈ 1) suggested by Shen and co-workers.¹⁶ In other words, the Nd-Sialon crystals prepared in this paper have a chemical formula of NdSi₆₋ₓAlₓOₓN₁₀₋ₓ.

Characteristic droplets were observed on the extremity of orthogonal oriented crystals (Figure 1b). As examined by EDS analysis (Figure S3), the results of semiquantification of element content in the liquid droplet marked “2” at the tip of the crystal showed that there are 63.20 wt % Fe and another 36.80 wt % Nd−Si−Al−O−N solution precursor (8.19 wt % Nd, 10.33 wt % Si, 5.32 wt % Al, 2.57 wt % O, 10.39 wt % N), while the crystal body marked “1” just contains Nd−Si−Al−O−N (33.74 wt % Nd, 38.03 wt % Si, 10.40 wt % Al, 4.68 wt % O, 13.16 wt % N). The atom ratio of Nd/Si/Al of about 1:6:1.7 suggests that the crystal body is NdSi₆₋ₓAlₓOₓN₁₀₋ₓ. It is known that iron-family

*To whom correspondence should be addressed. Address: No. 29 Xueyuan Road, Haidian District, Beijing 100083, P. R. China. E-mail: huang181@cumt.edu.cn. Telephone (Fax): +86-10-8232-2186.

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transition metal droplets act as catalyst in the VLS growth process. In order to study the effect of iron on the growth of Nd-Sialon microcrystals, a control test was taken, in which iron was not introduced and all other conditions were strictly controlled to be the same. The results showed that no Nd-Sialon crystal was obtained if iron was not added. Thus, the iron contained in droplets reveals that growth of a Nd-Sialon crystal might be catalyzed by Fe, behavior which needed to be further investigated and analyzed; and the VLS growth mechanism occurred at the tips of crystals along the growth direction. Moreover, diameters of droplets (0.5–2 μm) are much smaller than those of Nd-Sialon crystals (5–10 μm). This indicates that there might exist simultaneously a vapor–solid (VS) growth mechanism on the skew surface and the sidewall of crystals during the crystal growth process of Nd-Sialon, leading to radial growth. Therefore, Nd-Sialon microcrystals with an orthogonal array are suggested to grow via a combination of VLS and VS growth mechanisms.

Figure 3 shows the scheme of the suggested growth process of Nd-Sialon microcrystals with an orthogonal array. NdSi₆₋ₓAlₓSiO₁₀₋₅ can easily form at low temperature (no higher than 1700 °C) in a Nd–Si–Al–O–N system. When the ambient temperature reached 1700 °C, iron powder placed in the graphite crucible melted (the melting point of iron bulk is 1538 °C) and partially gasified under a certain vapor pressure. Subsequently, iron-containing liquid droplets formed on the surface of crystals when the vapor pressure of iron saturated. Nd–Si–Al–O–N precursor atoms in the vapor phase were absorbed into liquid droplets which provided for crystal growth. Here, iron-containing liquid droplets might act as catalytic sites for absorption and dissolution of vapor-phase reactants. Once supersaturation occurred, Nd–Si–Al–O–N atoms precipitated from iron catalysts continuously, leading to nucleation and growth of Nd-Sialon crystals on the surface of the crystals’ base. Supersaturation was the thermodynamic driving force for crystal growth of Nd-Sialon.

The diameter of the Nd-Sialon crystals became smaller along the growth direction of the crystal, and it formed two kinds of tips, i.e. wedgelike morphology and needlelike morphology, marked “1” and “2”, respectively, in Figure 1a. The formation of different morphologies of tips was probably dependent on the relative position of the liquid droplet to the crystal. Formation processes of these crystals were illustrated by two models (Figure 3a and b). The tips with wedgelike morphology formed when the liquid droplets attached on the side of crystals at the beginning of crystal growth (Figure 3a), and others with needlelike morphology were generated in the case that droplets adhered on the center of the crystals (Figure 3b). In both cases, the growth speed along the growth direction (V₁) is much faster than that along the radial direction (V₄) due to the catalysis, i.e. V₁ > V₄, due to the rough surface of the crystal with some growth steps (Figure 1b). When liquid droplets formed on the body of crystals, new crystals grew perpendicularly to the surface of the crystals’ base. Therefore, a Nd-Sialon orthogonal array formed with oriented crystals containing both wedgelike morphology and needlelike morphology (Figure 3d). However, if the droplets adhered on the side surface with a slope angle of approximately 45° to the growth direction of the crystal body (see the crystal marked “3” in Figure 1a and the illustration of its growth process shown in Figure 3c), the situation became more complicated in that crystals could be divided into two sets of an orthogonal array with an angle of 45° (Figure 3e). Meantime, another small droplet marked “3” was found on the droplet marked “2” shown in Figure 1b with an inclination of about 45°, and it strongly suggests that a new crystal would be likely to grow along that direction. Thus, orthogonally oriented Nd-Sialon crystals were formed by introducing iron into the atmosphere as catalyst.

The Nd-Sialon (NdSi₆₋ₓAlₓSiO₁₀₋₅) crystals prepared with an orthogonal morphology can be repetitiously prepared in...
powder samples under the same experiment conditions and can also be observed obviously in bulk samples sintered via the same process. Images of these samples and Nd-Sialon crystals are shown in Figure S4. More specifically, the surface of bulk samples was covered with Nd-Sialon crystals with such a novel morphology (Figure S4b, e, and f).

An Nd-Sialon single crystal with dimensions of about 80 μm × 60 μm × 3000 μm (Figure S5, Supporting Information) was carefully selected from the powder samples and then investigated on a SPEX 1403 Raman Spectrometer using a He−Cd laser as excitation source with an output power of 2 mW. The photoluminescence (PL) spectrum of this crystal excited by energy of wavelength 325 nm is shown in Figure 4. It is obvious that the Nd-Sialon crystal shows an ultraviolet(UV)-to-blue emission under this excitation energy. The peak maximum at 405 nm (photon energy is 3.07 eV) is associated with the $^{2}I_{11/2}$ → $^{4}I_{13/2}$ transition of Nd$^{3+}$, and the energy level diagram is also shown in the inset of Figure 4. As shown in the inset, the Nd$^{3+}$ ions were pumped from the ground state $^{4}I_{9/2}$ to excitation state $^{4}I_{15/2}$ and transferred to metastable state $^{2}I_{11/2}$ with heat loss, then they returned to the $^{4}I_{13/2}$ energy level accompanied by the observed 405 nm emission. The PL spectrum indicated that the Nd$^{3+}$ emission center was formed in the present Nd-Sialon single crystal.

In summary, Nd-Sialon microcrystals with a novel orthogonal array morphology, the chemical composition of which was NdSi$_{5.4}$Al$_{1.6}$O$_{0.6}$N$_{9.4}$, were developed by inducing catalysis of Fe. A combination of VLS and VS growth mechanisms was suggested during the formation Nd-Sialon microcrystals. Formation of Nd-Sialon crystals with wedgelike morphology and needlelike morphology developed due to the relative position of a liquid droplet on the crystal. The single crystal of Nd-Sialon showed a UV-to-blue emission when it was excited at 325 nm. This indicates that Nd-Sialon is envisioned to have potential applications for white LEDs, detector arrays, and optical components. Additionally, the micrometer-sized Nd-Sialon single crystal with a high aspect ratio could probably be used as a cantilever and switch in microelectromechanical systems (MEMS). This work also shines a light on the preparation of Nd-Sialon single crystals for applications as solid-state laser materials in the future.

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**Supporting Information Available:** SEM image of Nd-Sialon microcrystals with an orthogonal array, Debye Crystallogram of Nd-Sialon, EDS spectra of Nd-Sialon, EDS spectra of Nd-Sialon microcrystals, photos of samples and crystals with an orthogonal morphology, optical image of a Nd-Sialon single crystal with a cross morphology, luminescent spectra of the Nd-Sialon material, and table of chemical compositions. This information is available free of charge via the Internet at http://pubs.acs.org.

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**Figure 3.** Scheme of the growth process of Nd-Sialon microcrystals with an orthogonal array: (a) growth process of crystals with wedgelike morphology tips; (b) growth process of crystals with needlelike morphology tips, where $V_{g} > V_{r}$; (c) growth process of crystals with an angle of 45°; (d) crystals with an orthogonal array formed via the routes depicted in parts a and b; (e) crystals with an orthogonal array formed through combination of parts c and d. Nd-Sialon microcrystals with an orthogonal array were suggested to be catalyzed by iron-containing liquid droplets via a combination of VLS and VS mechanisms.

**Figure 4.** PL spectrum of an Nd-Sialon single crystal excited at 325 nm using a He−Cd laser as an excitation source. The inset shows a partial energy level diagram indicating the energy level transitions of the 405 nm emission.
References

(12) Preparation: Novel Nd-Sialon microcrystals with an orthogonal array were formed by mixing of Si3N4, AlN, and Nd3O8 during the preparation of Nd doped α-Sialon with overall compositions of Nd24.5Al12O35, Al12O35, N10–1.5 for x = 0.67, i.e., Nd24.5Al12O35. The starting materials used for the preparation of Nd doped α-Sialon were Si3N4 (99.7 wt %, a = 93.8 wt %), Shanghai Ansemi Advanced Ceramics Co. Ltd., China), AlN (99.7 wt %, Advanced Technology & Materials Co., Ltd, China), and Nd3O8 (99.9 wt %, Sinopharm Chemical Reagent Co. Ltd., China), with a composition of Nd3O8 17.098 wt %, Si3N4 64.156 wt %, and AlN 18.746 wt %, respectively. The starting mixture was milled in water-free ethanol for 24 h using agate balls as grinding media in a plastic jar and dried subsequently at 70 °C for 24 h. The dried powder agglomerates were put into a graphite crucible without special treatment, and iron powder (99.7 wt % of Fe) with a mass ratio of 1:20 to the powder agglomerates was also placed in it separately beside the sample as catalyst. Then the graphite crucible was placed into a high-temperature furnace. The sample was heated from room temperature to 1700 °C, holding for 3 h at a heating rate of 10 °C/min in flowing nitrogen atmosphere with a pressure of 0.9 MPa, and cooled down to ambient temperature by switching off the power after the scheduled dwell. Besides, a control test was taken, in which all other conditions were strictly controlled to be the same except that iron catalyst was not introduced. Characterization: The powderlike X-ray diffractogram of a Nd-Sialon single crystal was determined on a Bruker SMART APEX-CCD diffractometer using Mo Kα radiation with a wavelength of 0.71073 Å based on the Gandolfi method. Intensity data over the 2θ range 3–58° were generated from a Debye crystallogram of a Nd-Sialon single crystal. The microstructure of Nd-Sialon crystals was examined on a Philips-2004 XL30 ESEM-SEM scanning electron microscope equipped with an EDAX system. The PL spectrum of an NdSi0.5Al1.5O1.5N0.5 (≤ 0.6) single crystal with dimensions of about 80 μm × 60 μm × 300 μm was investigated at room temperature using a SPEX 1403 raman spectrometer with an HeCd laser (λ = 325 nm) as a light source.