

Preparation of artificial turquoise pellets by hydrothermal hot pressing method

Hiroaki Onoda*, Ayaka Nishimura

*Department of Informatics and Environmental Sciences, Kyoto Prefectural University,
1-5, Shimogamo Nakaragi-cyo, Sakyo-ku, Kyoto 606-8522, Japan

Abstract

Phosphate materials based on Turquoise composition $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ were prepared using aqueous solutions. The light blue or green powders were obtained by heating at 500 or 700 °C. To obtain artificial Turquoise pellets, these were sintered by the hydrothermal hot press method at 150 °C. The amount of water, pressure, and milling as pretreatment were studied. Molded pellets were also prepared using oil as the solvent. The resulting pellets were evaluated in terms of density and hue. In addition, the effects of post-treatment, such as heating and beeswax coating, were also examined. There were several methods to improve the density of the molded product, including increasing the amount of solvent, increasing the pressure, using castor oil, and powder refining as a pretreatment. Castor oil and beeswax coating were also methods to improve product brightness. The pellets obtained in this study showed water resistance.

Keywords: turquoise, artificial ornament, hydrothermal hot pressing.

INTRODUCTION

Some natural ores are used as ornaments because of their beautiful luster and color [1, 2]. Although transparent natural ores such as diamonds are well known as ornaments, opaque ones are also used as ornaments [3, 4]. Turquoise is a blue to green natural ore, and the best ones are used as ornaments. Blue are generally considered more valuable, but green ones are more valuable in some regions. There is much demand for turquoise, but the supply of natural, high-quality products is limited. For this reason, artificial turquoise has been produced and supplied to the commercial market [5, 6]. However, problems have arisen, such as low quality products that are simply coated with other ores and sold as turquoise. These are inferior products, and there is a demand for better products, even as inexpensive imitations.

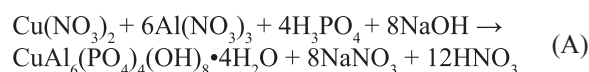
Natural ores have existed through exposure to wind and rain and have a certain degree or more of chemical stability. The authors have been developing new pigments without toxic heavy metals and have prepared inorganic phosphate pigments that mimic the composition of natural ores [7, 8]. In this context, we have successfully prepared blue and green pigments that mimic the composition of Turquoise ($\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$) by precipitation in aqueous solution [9]. Since this study involves the preparation of shaped artificial ores rather than powdered pigments, the method of preparing the compacts was considered. The most common sintering method, pressure-less sintering, requires high temperatures. On the other hand, phosphate volatilizes phosphorus oxide when heated to high temperatures, transforming it into an oxide [10, 11]. Thus, pressure-less

sintering is not suitable for sintering phosphates. We have previously prepared phosphate compacts by a hydrothermal hot pressing method to evaluate their conductivity [12, 13]. This method obtains compacts at relatively low temperatures by mixing a small amount of water with the sample powder and applying pressure [14, 15]. Thus, phosphate can be processed into molded products without decomposition.

In this study, the phosphate pigment was molded to create a high-quality artificial turquoise. Since turquoise composition powder turns green when heated, the light blue and green moldings were produced by varying the heating temperature as a pretreatment. It is expected to supply the market with high-quality artificial turquoise by applying a surface coating to the obtained artificial turquoise.

EXPERIMENTAL

Target material imitated of Turquoise, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, was prepared in the following reactions.



A total of 0.5 mol/L of copper and aluminum solutions were prepared from copper nitrate and aluminum nitrate in the ratio of Cu/Al=1/6. Then, 0.5 mol/L of phosphoric acid was added to this copper and aluminum mixed solution in the ratio of Cu/Al/P=1/6/4 (Turquoise ratio). The mixed solutions were adjusted to pH 5 with 8 mol/L of sodium hydroxide solution. The precipitates were filtered and then dried. The precipitates were heated at 500 or 700 °C for 1 hour under air conditions. All chemicals were of commercial purity (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) and were used without further purification. A part of the phosphate powder was treated with a ball mill (BALL

*h-onoda@kpu.ac.jp

<https://orcid.org/0000-0001-6267-2783>

MILL ANZ-10S, Nitto Chemical Co. Ltd., Tokyo, Japan) at 300 rpm for 1 hour. The polypropylene pot (47 mL) and 6 balls (alumina, 10 mm, average 2.1 g) were used for milling 4 g of sample powders.

The mixtures of heated samples (1.0 g) and water (0-0.7 ml) were placed in a mold (inner diameter: 14 mm) and mechanically pressed with a uniaxial pressure of 15 - 35 MPa at 150 °C for 1 hour (Hydrothermal hot pressing process, HHP process). Because the mold had a slight excess of space, water could be volatilized in the sintering process. Since some natural ores contain mineral oil, castor oil was also used in the production of the moldings instead of water. The size of the obtained molded body was measured using a caliper, and the density was calculated from its volume and weight.

To evaluate the water resistance of the sample pellets, the petri dish was filled with water and the pellets were placed gently in it. The pellets did not decay even after being placed quietly for 5 minutes, confirming that they were sufficiently water-resistant. Since ornaments are not usually soaked in water for a long time, this time was judged to be sufficient for water resistance evaluation.

The chemical composition of these materials was analyzed using X-ray diffraction (XRD) and infrared (IR) spectra. XRD patterns were recorded on an X-ray diffractometer (MiniFlex, Rigaku Corp., Akishima, Japan) using monochromatic CuK α radiation (30 kV, 15 mA, 3°/min). The IR spectra of the samples were recorded by the KBr disk method (resolution: 4 cm⁻¹, 16 times scanned) using a HORIBA FT-IR 720 (HORIBA Corp., Kyoto, Japan). The particle size distributions of these materials were measured using a centrifugal precipitation particle-size distribution (SA-CP3L, Shimadzu Corp., Kyoto, Japan). The hue of pellets was estimated in L*a*b* color space with TES135 plus color analyzer (TES Electrical Electronic Corp., Taipei, Taiwan) (average of 5 times). The L* value refers to the whiteness of the powder, with 100 being white and the opposite being 0 being black. The a* value signifies the redness of the material, with positive and negative values corresponding to red and green, respectively [16]. The b* value denotes yellow intensity, in which positive and negative values correspond to yellow and blue, respectively.

RESULTS AND DISCUSSION

Powder materials: Figure 1 shows XRD patterns of samples prepared at various temperatures. Samples without heating had the peaks of Turquoise and CuO [17]. On the other hand, samples heated at 500 and 700 °C were amorphous. Figure 2 shows the IR spectra of samples heated at various temperatures. The IR spectrum of the unheated sample has a peak at 1650 cm⁻¹, which is due to water. This peak disappeared due to the volatilization of water in the sample by heating. The sharp peaks at 850 and 1390 cm⁻¹ were due to nitrate ions and disappeared by heating at 700 °C [18]. Samples contained nitrate ions because they were prepared using aqueous solutions containing nitrate ions.

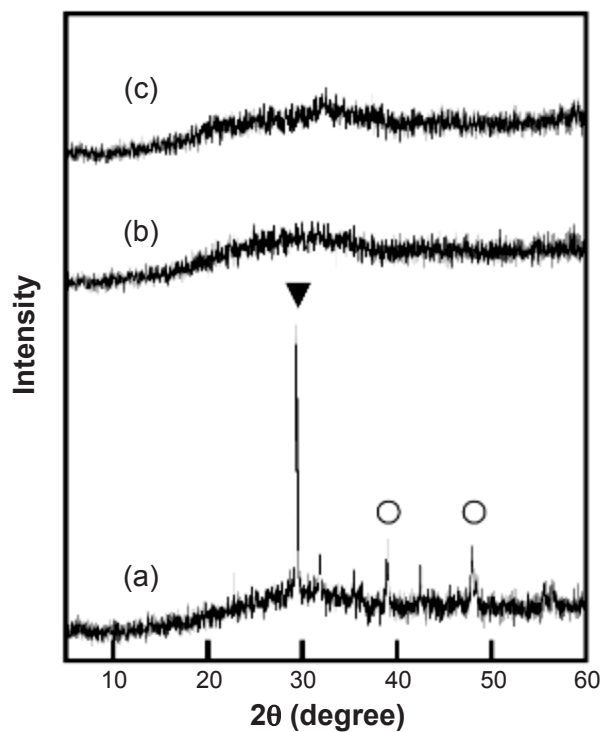


Figure 1: XRD patterns of samples heated at various temperatures, (a) without heating, (b) 500 °C, (c) 700 °C, ▼; Turquoise, ○; CuO.

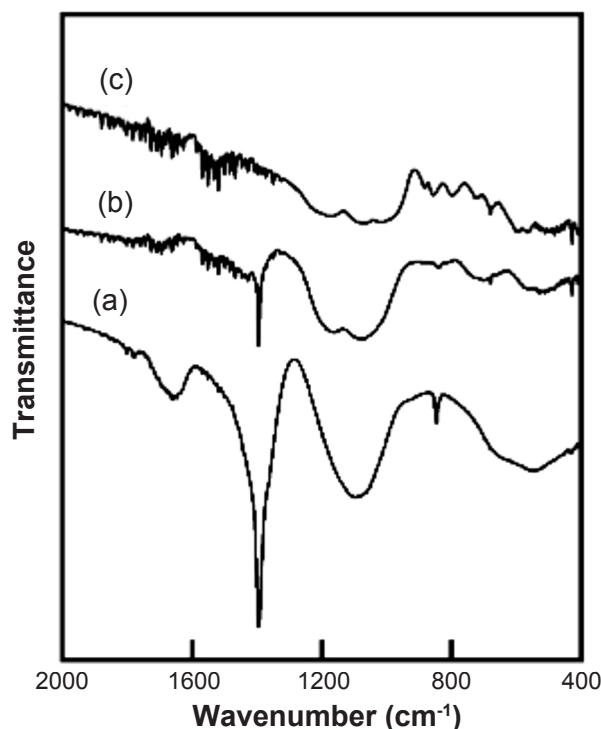


Figure 2: IR spectra of samples heated at various temperatures, (a) without heating, (b) 500 °C, (c) 700 °C.

The broad peak around 1080 cm⁻¹ was due to phosphate ions, indicating that the sample contained phosphate [17]. Figure 3 shows the photograph of samples heated at various temperatures. The sample without heating had a pale light blue color, which became darker with heating at 500° C. The



Figure 3 Photographs of samples heated at various temperatures, (a) without heating, (b) 500 °C, (c) 700 °C.

sample became green when heated at 700° C.

Pressing: Figure 4 shows the photographs of hydrothermally hot pressed samples. Samples heated

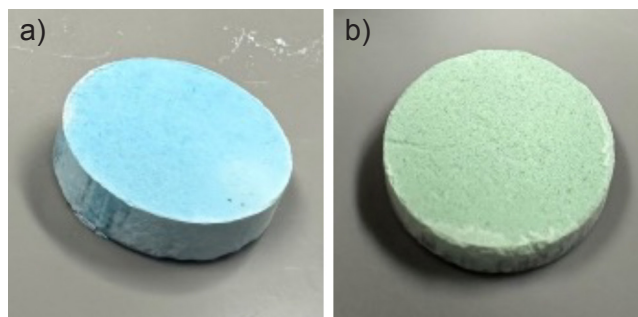


Figure 4: Photographs of typical samples pressed from powders heated at various temperatures, (a) 500 °C, (b) 700 °C.

at 500 °C and 700 °C formed light blue and green bulks, respectively. Table 1 shows the density and $L^*a^*b^*$ values of phosphate bulks prepared with various volumes of water. The increasing amount of water increased the density of the pellets. It was thought that the increased amount of water would allow the particles to move more easily, forming pellets with fewer gaps. The sample heated at 500 °C was able to form pellets even if a relatively large amount of water was added. For the samples heated at 500 °C, the addition of water during molding increased the L^* value, ie the color of the sample pellets became lighter. The a^* and b^* values decreased, indicating a greener and bluish tint, respectively. The formation of denser pellets corresponded to a decrease

Table 1 Density and $L^*a^*b^*$ values of phosphate bulks prepared with various volumes of water (150 °C, 20 MPa, 1 h)

Pre-heating	Water volume mL	Density gcm^{-3}	L^*	a^*	b^*
500 °C	0	1.26	68.3	-8.5	-10.6
500 °C	0.1	1.35	74.6	-15.5	-14.3
500 °C	0.2	1.37	76.8	-16.5	-16.0
500 °C	0.3	1.38	82.3	-18.4	-16.4
500 °C	0.4	1.40	78.9	-15.6	-15.5
500 °C	0.5	1.59	74.4	-23.7	-24.9
500 °C	0.6	1.63	76.5	-19.8	-21.8
500 °C	0.7	1.37	-	-	-
700 °C	0	1.52	73.5	-14.5	7.6
700 °C	0.1	1.53	74.0	-15.2	7.4
700 °C	0.2	1.76	61.6	-9.5	7.8

Table 2 Density and $L^*a^*b^*$ values of phosphate bulks prepared under various pressures (150 °C, 1 h)

Pre-heating	Water volume mL	Pressure MPa	Density gcm^{-3}	L^*	a^*	b^*
500 °C	0.6	15	1.62	77.3	-18.7	-19.3
500 °C	0.6	20	1.63	76.8	-16.5	-16.0
500 °C	0.6	25	1.65	71.5	-24.1	-25.7
500 °C	0.6	30	1.61	70.5	-18.6	-15.9
500 °C	0.6	35	2.01	67.2	-26.0	-30.8
700 °C	0.2	15	1.71	56.2	-11.1	8.3
700 °C	0.2	20	1.76	61.6	-9.5	7.8
700 °C	0.2	25	1.82	59.6	-11.5	7.5
700 °C	0.2	30	1.84	70.4	-11.3	6.8
700 °C	0.2	35	1.90	61.2	-8.9	7.2

Table 3 Density and L*a*b* values of phosphate bulks prepared with various solvents (Heating; 500 °C, Pressing; 150 °C, 1 h, 20 MPa)

Solvent	Volume mL	Density gcm ⁻³	L*	a*	b*
water	0.2	1.37	76.8	-16.5	-16.0
water	0.3	1.38	82.3	-18.4	-16.4
castor oil	0.2	1.59	74.6	-22.2	-11.4
castor oil	0.3	1.61	76.8	-23.0	-12.9

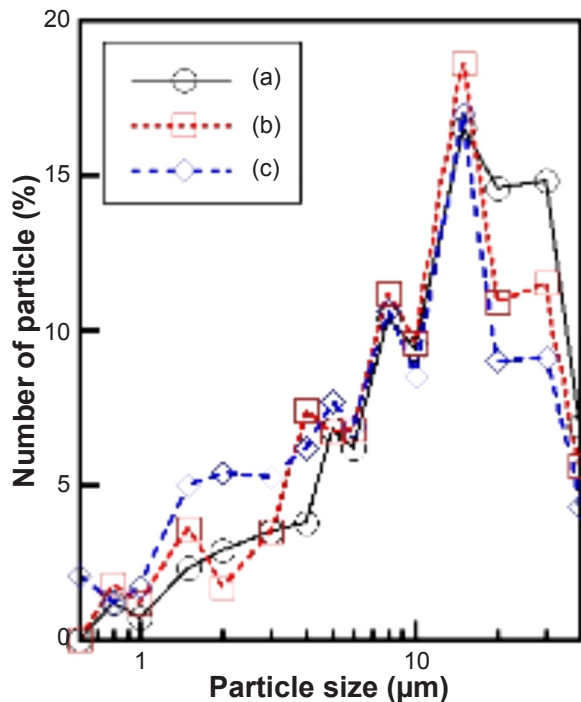


Figure 5 Particle size distribution of samples heated at 500 °C and then treated with ball-mill, (a) 0 h, (b) 1 h, (c) 6 h.

in the gaps within the pellets, which was thought to make the color appear more clearly. For the sample heated to 700 °C, a molded body could be obtained only up to the condition of 0.2 mL of water, and no regularity in color change was observed.

Table 2 shows the density and L*a*b* values of phosphate bulks prepared under various pressures. The amount of water was set to the condition where the density is the highest in Table 1. By increasing the pressure, the density of the pellet was improved. However, it was lower than the actual density of Turquoise (2.6-2.9 g/cm³). In the hydrothermal hot pressing method, it is known that the added water volatilizes, resulting in a somewhat low-density sintered body [15]. Among samples heated at 500 °C, the pellet molded at 35 MPa was the most greenish and bluish. The sample heated at 700 °C showed relatively little change in color due to pressure.

Since natural ore maintains its shape with mineral oil, the compact was produced using oil instead of water. Table 3 shows the density and L*a*b* values of phosphate bulks prepared with various solvents. The density of compacts was improved by using castor oil. The L* and a* values decreased, while b* values increased. The L* values closer to 100 are closer to white, and closer to 0 are closer to black. Therefore, further away from either value means a brighter color. In this study, the color became vivid by using castor oil. A decrease in a* value meant an increase in greenness, and an increase in b* value meant a decrease in bluishness. This color change may be related to the light yellow color of castor oil itself.

Pretreatment: to obtain higher densities, powder refinement was carried out by ball milling before molding [19]. Figure 5 shows the particle size distribution of samples heated at 500 °C and then treated with a ball mill. The

Table 4 Density and L*a*b* values of phosphate bulks prepared with various milling hours (150 °C, 1 h)

Pre-heating	Milling h	Density gcm ⁻³	L*	a*	b*
500 °C	0	1.63	76.8	-16.5	-16.0
500 °C	1	1.56	74.8	-24.4	-26.1
500 °C	6	1.76	74.2	-24.4	-26.0
700 °C	0	1.76	61.6	-9.5	7.8
700 °C	1	1.70	61.6	-6.5	9.6
700 °C	6	1.84	61.0	-5.8	9.3

Table 5 Density and L*a*b* values of phosphate bulks (150 °C, 1 h, 20 MPa) before and after sintering at 500 °C for 1 hour /gcm⁻³

Pre-heating	solvent	Volume of solvent mL	Density before sintering gcm ⁻³	Density after sintering gcm ⁻³
500 °C	water	0.5	1.59	1.49
700 °C	water	0.2	1.65	1.67
500 °C	oil	0.2	1.59	1.57

Table 6 L*a*b* values of phosphate bulks before and after coating with beeswax

Pre-heating	solvent	coating	L*	a*	b*
500 °C	water	before	76.8	-16.5	-16.0
		after	56.0	-19.7	-22.9
500 °C	oil	before	75.6	-22.2	-11.4
		after	34.3	-15.3	-7.0
700 °C	water	before	61.6	-9.5	7.8
		after	50.4	-12.4	7.1

milling slightly decreased the percentage of larger particles than 10 μm and slightly increased the percentage of smaller particles than 4 μm . Samples heated at 700 °C showed little change due to milling. It was considered that this was because the particles were hardened by being heated to a high temperature.

Table 4 shows the density and L*a*b* values of phosphate bulks prepared with various milling hours. Samples milled for 6 hours formed denser compacts than unmilled samples. The L* values were almost unchanged by milling. Samples heated at 500 °C showed a significant decrease in a* and b* values by milling and increased greenish and bluish colors.

After treatment: sintering was attempted as a post-processing step after hydrothermal hot pressing to obtain denser pellets [20]. Table 5 shows the density and L*a*b* values of phosphate bulks before and after sintering at 500 °C for 1 hour. No densification due to sintering was observed.

To add luster and avoid hydrolyses, the pellets were dipped and soaked in melted beeswax [21]. Table 6 shows L*a*b* values of phosphate bulks before and after coating with beeswax. Pellets prepared with water had an L* value of about 50 and a distinct color due to beeswax coating. In particular, the pellets of a sample heated at 500 °C had lower a* and b* values, i.e., more greenish and bluish. Density is higher due to beeswax seepage; however, this was not measured as a comparison with turquoise is not meaningful.

CONCLUSIONS

The hydrothermal hot pressing method was used to obtain a molded product that mimics the Turquoise composition. The methods to improve the density of the compacts included increasing the amount of solvent, increasing the pressure, using castor oil, and powder refinement as a pre-treatment. In addition, castor oil and beeswax coating are methods to improve the vividness of the product. The pellets obtained in this study exhibited water resistance.

REFERENCES

[1] M. K. Cidade, J. T. Perini, F. L. Palombini. Bionics for Inspiration: A New Look at Brazilian Natural Materials for Application in Sustainable Jewelry. *Bionics and Sustainable Design*. 2022;195-223. doi:10.1007/978-981-19-1812-4_8.

[2] J. Ducrocq, M. Fossati, W. Marsangy, I. C. Maniere. The Pearls and Their Soul. *Sustainable Luxury and Jewelry*. 2021;75-85. doi:10.1007/978-981-16-2454-4_5.

[3] Y. Xue, X. Feng, S. C. Roberts, X. Chen. Diamond and carbon nanostructures for biomedical applications. *Func. Diamond*. 2021;1(1):221. doi:10.1080/26941112.2021.2013716.

[4] R. Giustetto, V. G. Mancusi, L. Barale, M. Venturino, R. Compagnoni. The Neolithic greenstone industry from Valgrana/Tetto Chiappello (Cuneo Province, Northwestern Italy); A combined archaeometric and archaeological study. *J. Archaeol. Sci. Rep.* 2021;40:103222. doi:10.1016/j.jasrep.2021.103222.

[5] D. Bootkul, S. Intarasiri. Development of glass-ceramics from Soda lime silica glass waste with addition of kaolin and coloring oxide for Turquoise's imitation. *Vib. Spectrosc.* 2022;123:013467. doi:10.1016/j.vibspec.2022.103467.

[6] B. Feodor, F. Emmanuel, S. Nicolas, K. Stefanos, D. Aurelien. A New Reconstructed Turquoise Imitation Composed of Turquoise Powder with a PMMA (Acrylic) Binder. *J. Gemmol. London*. 2023;38(5):443. doi:10.15506/jog.2023.38.5.443.

[7] H. Onoda, K. Sugimoto. Synthesis of novel green phosphate pigments in imitation of natural ores. *J. Asian Ceram. Soc.* 2017;5(2):123. doi:10.1016/j.jascer.2017.03.004.

[8] H. Onoda, R. Sasaki. Preparation of novel blue phosphate pigments in imitation of copper lazulite. *Intern. J. Ind. Chem.* 2020;11(4):261. doi:10.1007/s40090-020-00221-1.

[9] H. Onoda, R. Sasaki. Preparation of novel blue phosphate pigments in imitation of turquoise. *Cerâmica*. 2019;65(376):641. doi:10.1590/0366-69132019653762807.

[10] Z. Zhan, W. Sun, S. Zhang, Q. Wen, H. Zhang, X. Xiong. Ablation and insulation behavior of magnesium phosphate cement composite in harsh environments. *Corros. Sci.* 2023;221:111326. doi:10.1016/j.corsci.2023.111326.

[11] Y. Zhou, H. Zheng, S. Zhao, C. Zhang, W. Bai, C. Sun, Y. Tong, J. Yang. Preparation, structural and mechanical characterization of ceria-added phosphate glasses. *J. Non-Cryst. Solids*. 2021;570:120878. doi:10.1016/j.jnoncrysol.2021.120878.

[12] H. Onoda, Y. Inagaki, A. Kuwabara, N. Kitamura, K. Amezawa, A. Nakahira, I. Tanaka. Synthesis and electrical conductivity of tetra-valent cerium polyphosphate bulks. *Phos. Res. Bull.* 2009;23:20. doi:10.3363/prb.23.20.

[13] H. Onoda, Y. Inagaki, A. Kuwabara, N. Kitamura, K. Amezawa, A. Nakahira, I. Tanaka. Synthesis and electrical conductivity of tetra-valent cerium polyphosphate bulks. *J. Ceram. Proc. Res.* 2010;11(3):344. doi:10.3363/prb.23.20.

[14] T. Kozawa. Microstructural development of MnCO_3

microsphere compacts through hydrothermal hot-pressing. *J. Europ. Ceram. Soc.* 2022;**42**(4):1530. doi:10.1016/j.jeurceramsoc.2021.12.022.

[15] B. Degraeve, B. Lefeuvre, N. Rocton, N. Herbert, N. Hamrouni, G. Hauss, A. Largeteau, M. Prakasam, H. Oudadesse, O. Merdrignac-Conanec. Processing of highly porous bioglass monoliths by hydrothermal hot pressing. *Ceram. Intern.* 2022;**48**(13):18190. doi:10.1016/j.ceramint.2022.03.078.

[16] S. Sattar. Characterizing Color with Reflectance. *J. Chem. Edu.* 2019;**96**:1124. doi:10.1021/acs.jchemed.8b00845.

[17] Turquoise R050554 - RRUFF Database: Raman, X-ray, Infrared, and Chemistry. RRUFF Project. Available at: <http://rruff.info/Turquoise/R050554>. Accessed June 17, 2024.

[18] H. Onoda, T. Funamoto. Preparation and Fluorescence

Properties of Crystalline Gel Rare Earth Phosphates. *J. Fluores.* 2015;**25**(2):247. doi:10.1007/s10895-014-1500-2.

[19] Z. Liu, W. Ye, Z. Zhang, Q. Wang, Y. Chen, Y. Cui. Particle size ratio and distribution effects on packing behaviour of crushed GMZ bentonite pellets. *Powder Tech.* 2019;**351**:92. doi:10.1016/j.powtec.2019.03.038.

[20] C. Yang, J. Ding, J. Ma, B. Zhang, F. Ye, Y. Wu, Q. Liu. Microstructure tailoring of high thermal conductive silicon nitride through addition of nuclei with spark plasma sintering and post-sintering heat treatment. *J. All. Com.* 2019;**785**:89. doi:10.1016/j.jallcom.2018.12.204.

[21] M. K. Reimann, R. K. Kremer, D. Chen, R. Dronskowski, J. Kösters, R. Pöttgen. Salt-flux growth of HoCuMg₄ single crystals. *Dalton Trans.* 2023;**52**:8893. doi:10.1039/d3dt01511d.

(*Rec.* 25/09/2023, *Rev.* 03/11/2023, *Ac.* 09/11/2023)

(*AE:* D. Z. de Florio)

