Flux-Aided Synthesis of Lu$_2$O$_3$ and Lu$_2$O$_3$:Eu—Single Crystal Structure, Morphology Control and Radioluminescence Efficiency

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**Abstract:** Li$_2$SO$_4$ or (Li$_2$SO$_4$ + SiO$_2$)-mixture fluxes were used to prepare a Lu$_2$O$_3$:Eu powder phosphor as well as an undoped Lu$_2$O$_3$ utilizing commercial lutetia and europia as starting reagents. SEM images showed that the fabricated powders were non-agglomerated and the particles sizes varied from single microns to tens of micrometers depending largely on the flux composition rather than the oxide(s)-to-flux ratio. In the presence of SiO$_2$ in the flux, certain grains grew up to 300–400 μm. The lack of agglomeration and the large sizes of crystallites allowed making single crystal structural measurements and analysis on an undoped Lu$_2$O$_3$ obtained by means of the flux technique. The cubic structure with $a = 10.393(2)$ Å, and Ia$\bar{3}$ space group at 298 K was determined. The most efficient radioluminescence of Lu$_2$O$_3$:Eu powders reached 95%–105% of the commercial Gd$_2$O$_2$S:Eu.

**Keywords:** lutetium oxide; flux synthesis; single crystal structure; radioluminescence
1. Introduction

At the end of 20th century, the Lu$_2$O$_3$:Eu X-ray phosphor became a subject of thorough research [1–19]. Also, other activators were used, especially for lasing in Lu$_2$O$_3$ sintered transparent bodies [20,21]. With its impressive density of 9.84 g/cm$^3$, high effective Z-number (63.7) and light yield similar to Gd$_2$O$_2$S-based phosphors [3,22–24] both lutetia powders and sintered ceramics were considered attractive for X-ray scintillator detectors [3,22,25]. Furthermore, with an energy band gap of about 5.85 eV [25], Lu$_2$O$_3$:Eu was recognized to have potential to produce as much as about 75,000 ph/MeV upon ionizing radiation excitation. This is well beyond the performance reported in literature [25], which gives hope that there still is room for significant improvement. The extraordinary absorption coefficient of X-rays by photoelectric effect rather than Compton scattering [26,27] allows using thinner Lu$_2$O$_3$:Eu phosphor layers, which translates into reduced light scattering, i.e., image smudging [27]. Clearly, Lu$_2$O$_3$:Eu may offer important advantages as X-ray phosphor if only its light yield could be improved and morphology well controlled.

High quality screens, with uniformly and densely packed grains, require spherical, rather uniform in size particles. It was shown that the spherical size of particles allows reducing the screen thickness by 1/3 [17,28]. Also, effective sintering of powders into translucent or transparent bodies, especially using pressureless techniques, is very much dependent on the starting powder morphology and its thermal history [17,29–32]. Yet, literature data on controlling the Lu$_2$O$_3$:Eu powders morphology are only scant [33–36] and those that are available were never confronted with the phosphors performance under X-rays. With this paper we try to partially fill this gap. We thus shall report on the evolution of morphology of Lu$_2$O$_3$:Eu powders produced using Li$_2$SO$_4$/(Li$_2$SO$_4$ + SiO$_2$)-flux-aided preparation technique. Since this fabrication procedure gave occasionally crystallites with sizes sufficient for single crystal structure determination, we took advantage of that and preformed such analysis. Up to now, the only direct determination of Lu$_2$O$_3$ structure was performed on single crystals obtained by a micro-pulling down (μ-PD) technique as well as a laser heated pedestal growth (LHPG) [37].

2. Results and Discussion

2.1. Structural Analysis

Let us start by presenting the X-ray diffraction (XRD) patterns of powders of Series I (Figure 1), which supposedly should/might provide Lu$_2$SiO$_5$ (LSO) powders, as the lutetia and silica were mixed in 1:1 molar ratio. Indeed, when the synthesis was only 1-h long (sample SI-1) a main fraction of the product was LSO, with Lu$_2$O$_3$ present as an impurity, readily detected but not a massive fraction. In the case of the sample heated for 2 h (SI-2), the powder was already largely composed of Lu$_2$O$_3$, while LSO existed only as an impurity phase. A 20-h prolonged heating at 1300 °C (SI-3) ended up with a single phase cubic Lu$_2$O$_3$ powder without any traces of LSO, as seen by the XRD technique. Hence, the XRD data of powders of Series I proves, that in the presence of significant amount of Li$_2$SO$_4$-flux, silica is effectively eliminated from the batch upon prolonged heating at elevated temperatures. Additional experiments, results of which we do not present here, proved that the process of removal of SiO$_2$ from the reacting mixture of Lu$_2$O$_3$ and SiO$_2$ was faster with increasing Li$_2$SO$_4$ flux content and with increasing temperature—at 900 °C it was much slower, while at 1400 °C it was even faster than at
1300 °C. This we took into account by proceeding with synthesis of samples of Series II–IV. The structural measurements of all powders of Series II–IV prove that each of the products is cubic Lu₂O₃. Yet, we noted that prolonged washing with hot water to remove the Li₂SO₄ flux may end up with slight contamination by LuO(OH). This should be taken into account when recovering the lutetia powder from the flux. Heat treatment at 900 °C for 2 h effectively eliminated the LuO(OH), and only Lu₂O₃ was seen in XRD patterns.

**Figure 1.** The measured XRD patterns of the powders of Series I: SI-1, SI-2, SI-3, together with simulated pattern of a cubic Lu₂O₃ (data from this work) and the pattern of a monoclinic Lu₂SiO₅.

In Figure 2, we present selected XRDs of samples of Series II–IV. They are representative of the other powders of the three series. Also, the powders of Series III, in which the most important change compared to Series II was addition of some SiO₂ to the flux, contain only cubic Lu₂O₃, and no silica or LSO was detected. Addition of 5 mol% of Eu₂O₃ to the reacting mixture (Series IV) did not affect the crystallization process and the product was a solid solution of Lu₂O₃:Eu. In this case, the diffraction lines were slightly shifted towards smaller angles due to the larger size of Eu³⁺ ion (0.947 Å) compared to Lu³⁺ (0.861 Å). Hence, already the structural measurements indicated that Eu₂O₃ dissolved in the Lu₂O₃ host during the synthesis process giving activated Lu₂O₃:Eu phosphor.
Figure 2. Representative XRD patterns of Lu$_2$O$_3$ powders of Series II, III and IV. (a) SII-1; (b) SIII-3; (c) SIV-2, together with simulated pattern of a cubic Lu$_2$O$_3$ (data from this work).

2.2. Flux-Stimulated Evolution of the Powders Morphology

In this section, we shall present and discuss differences in the morphology of Lu$_2$O$_3$ powders of the Series II–IV as well as evolution of the morphology within each series. For comparison, in Figure 3 we show scanning electron microscope (SEM) images of Lu$_2$O$_3$ starting material used in our synthesis processes. As we shall see, the morphology of the raw lutetia is much different from all morphology of the powders we synthesized using the flux. Figure 4 presents SEM images of Lu$_2$O$_3$ powders of Series II in which the flux consisted of Li$_2$SO$_4$ exclusively, and was used in different proportions to the Lu$_2$O$_3$. Clearly, alteration of the ratio of the flux against Lu$_2$O$_3$ did not affect the morphology to any significant degree. Basically, all powders of Series II consist of grains of similar sizes of 3–4 μm, though the largest of them are of about 20 μm in diameter. The grains are not very uniform when size is taken into account. The grains are mostly monocrystalline and form polyhedra of regular and similar shapes. Some granules consist of aggregated smaller crystallites (see the upper top image). These, though not very numerous, were seen in each specimen of Series II.

Figure 3. SEM images of the Lu$_2$O$_3$ starting materials (Stanford Materials Corporation).
Figure 4. SEM images of Lu$_2$O$_3$ were prepared using Series II synthesis for (a) SII-1; (b) SII-2; (c) SII-3.

In Series III (Figure 5), when synthesized using a mixture of Li$_2$SO$_4$ and SiO$_2$ as the flux, the grains become more uniform in size, compared to Series II. For the SIII-1 powder the sizes are typically 3–6 μm and only occasionally 20 μm grains are observed (Figure 5a). In the case of sample SIII-2 (Figure 5b), when the content of SiO$_2$ in the flux (compared to SIII-1) was roughly tripled, the grains become clearly larger. A six-fold increase of the SiO$_2$ in the flux (compared to SIII-1) further increases, though not significantly, the fraction of the largest grains (Figure 5c), among which we can easily select 70–100 μm monocrystals. Rarely, needle-shaped grains are observed as presented in Figure 5c. The needles are as long as about 200–300 μm. Their fraction gets larger with an increasing amount of the flux compared to Lu$_2$O$_3$ (compare Figure 5c,d). Since for cubic structures the needle-like shape of monocrystalline grains is unexpected, we decided to perform a full structural analysis of such a crystal to unambiguously resolve if Lu$_2$O$_3$ can crystallize in a different structure in the conditions we applied for the preparations. The results will be presented in the next section.

We already mentioned when discussing XRD patterns that by using a mixture of Lu$_2$O$_3$ and Eu$_2$O$_3$ it was possible to produce a Lu$_2$O$_3$:Eu phosphor by means of the Li$_2$SO$_4$-SiO$_2$ flux technique. The morphology of the material (see Figure 6) was not much different from its undoped counterparts presented above. Interestingly, it was routinely indicated by inductively coupled plasma (ICP) analysis that only about 60%–65% of Eu indeed entered the lutetia host during the flux-aided synthesis.
2.3. Single Crystal Structural Analysis

As we already saw, see Figure 5c,d, in some cases needle-shaped crystals could be selected within a batch. This observation encouraged us to verify the crystal structure of both the needles and the more
regular, polyhedral particles. Both types of crystals gave practically the same results and here we shall present those for the needle-shaped crystal selected from the powder SIII-3 (see Figures 5c and 7a). Below a detailed description of the results is given. It was unambiguously confirmed that this Lu₂O₃ crystal, despite its specific shape, crystallized in a cubic system, the space group is Ia̅₃ with \( a = 10.393(2) \) Å, \( V = 1122.6(6) \) Å³, \( Z = 16 \), \( T = 298 \) K. Other crystal data are listed in Table 1, together with refinement details. Complete crystallographic data for the structural analysis have been deposited with the Fachinformationszentrum Karlsruhe (FIZ), CSD No. 428012. Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany [38] on quoting the appropriate CSD number.

| Chemical Formula | Lu₂O₃ |
|------------------|-------|
| Formula Mass     | 397.94|
| Crystal system   | regular|
| \( a/\text{Å} \)  | 10.393(2) |
| Unit cell volume/Å³ | 1122.6(6) |
| Temperature/K     | 298(2) |
| Space group       | Ia̅₃ |
| No. of formula units per unit cell, \( Z \) | 16 |
| No. of reflections measured | 8753 |
| No. of independent reflections | 1789 |
| \( R_{int} \)     | 0.0425 |
| Final \( R_1 \) values (\( I > 2\sigma(I) \)) | 0.0287 |
| Final \( wR(F^2) \) values (\( I > 2\sigma(I) \)) | 0.0555 |
| Final \( R_1 \) values (all data) | 0.0307 |
| Final \( wR(F^2) \) values (all data) | 0.0560 |

The Lu₂O₃ represents the rare-earth sequioxide C-type of structure, isostructural to Y₂O₃. Figure 7c shows that the crystal structure of Lu₂O₃ offers two different positions for the metal ion (Lu1 and Lu2). Lutetium atoms are connected by bridging O1 and O1' oxygen atoms. Coordination numbers (CN) of both Lu1 and Lu2 are \( CN = 6 \). Lu1 occupies a perfectly centrosymmetric position (C₃i) in the lattice with all Lu1-O1 with symmetry codes: (i) \( -y + 1/2, -z + 1/2, -x + 1/2 \); (ii) \( y, z, x \); (iii) \( -x + 1/2, -y + 1/2, -z + 1/2 \); (iv) \( -z + 1/2, -x + 1/2, -y + 1/2 \); (v) \( z, x, y \); distances equal 2.2392(18) Å. Lu2 atom possesses non-centrosymmetric C₂ local site symmetry in the cubic structure of Lu₂O₃. The population of the Lu1 is 25% and the fraction of Lu2 is 75% of all metal sites. Figure 7b shows the packing of Lu₂O₃. Two types of layers of Lu sites are present. One of them contains only Lu2 atoms showing the non-centrosymmetric geometry (C₂), while the other consists of the same number of Lu1 (C₃i) and Lu2 (C₂) ions. The crystal structure of Lu₂O₃ is stabilized by bridging oxygen atoms between lutetium atoms. Table 2 presents all geometric parameters of the structure.
Figure 7. (a) The grain of the powder SIII-3 selected for the monocrystalline structural measurements; (b) a packing diagram of Lu$_2$O$_3$. For clarity, only two polyhedra were shown; (c) coordination environment of Lu1 and Lu2 in Lu$_2$O$_3$.

Table 2. Geometric parameters (Å, °).

| Atoms involved       | Distance (Å), Angle (°) |
|----------------------|------------------------|
| Lu1—O1               | 2.2392(18)             |
| Lu1—Lu2              | 3.4395(7)              |
| Lu2—O1               | 2.2277(19)             |
| Lu2—O1$^i$           | 2.2945(19)             |
| Lu2—O1$^x$           | 2.1954(18)             |
| O1—Lu1—O1$^i$        | 80.10(6)               |
| O1—Lu1—O1$^{ii}$     | 99.90(6)               |
| O1—Lu1—O1$^{iii}$    | 180.0                  |
| O1$^x$—Lu2—O1$^{xi}$ | 87.14(10)              |
| O1$^x$—Lu2—O1        | 99.66(6)               |
| O1$^{ii}$—Lu2—O1     | 109.94(8)              |
| O1—Lu2—O1$^{xii}$    | 138.89(9)              |
| O1$^x$—Lu2—O1$^i$    | 79.57(7)               |
| O1$^{ii}$—Lu2—O1$^i$ | 165.12(5)              |
| O1—Lu2—O1$^i$        | 79.15(9)               |
| O1$^x$—Lu2—O1$^{xiii}$| 165.12(5)             |
| O1—Lu2—O1$^{xiii}$  | 78.91(6)               |
| O1$^i$—Lu2—O1$^{xiii}$| 114.36(9)             |

Symmetry codes: (i) −y + 1/2, −z + 1/2, −x + 1/2; (ii) y, z, x; (iii) −x + 1/2, −y + 1/2, −z + 1/2; (x) −z + 1, −x + 1/2, y; (xi) −z + 1, x−1/2, −y + 1/2; (xii) x, −y, −z + 1/2; (xiii) −y + 1/2, z − 1/2, x.

The results presented here are generally very similar to the recently published data on the single crystal structure of Lu$_2$O$_3$ [37]. It may be surprising that for our crystal made with the Li$_2$SO$_4$ flux the final $R_I$ ($I > 2σ(I)$) value is even smaller than for the two crystals reported in [37], which were made by a μ-PD and LHPG techniques. The unit cell of the one obtained by the μ-PD showed a slightly smaller size of $a = 10.364(2)$ Å compared to that fabricated by LHPG, which was $a = 10.403(2)$ Å. The difference was suggested to result from O-vacancies supposedly present in the slightly yellow μ-PD crystal formed in a reducing atmosphere. The size of the unit cell obtained for our crystal made by the flux technique is much closer (10.393(2) Å) to the size of the LHPG crystal, and is almost identical with the size of the unit cell obtained for sintered ceramics (10.39120(6) Å) [37].
2.4. Radioluminescent Properties

As we mentioned in the Introduction, Lu$_2$O$_3$:Eu arouses interest mostly for its radioluminescent properties. Thus, having the possibility to control the morphology of its powders, we also were interested in testing their performance under excitation with X-rays. Figure 8 shows the X-ray excited luminescence (XEL) spectra of Lu$_2$O$_3$:Eu powders of Series IV. The spectral distribution of the emitted photons is typical for Lu$_2$O$_3$:Eu, with the main luminescence located at 610 nm and resulting from the $^5$D$_0$→$^7$F$_2$ transition. The overall XEL efficiencies of Lu$_2$O$_3$:Eu were related to the performance of a commercial Gd$_2$O$_2$S:Eu (GOS:Eu) measured at the same conditions. All as-made samples performed similarly and on average their light yield reached 70%–80% of the GOS:Eu efficiency. Thus, the phosphor performance was not affected by the particle sizes to any significant degree. When the raw powders were additionally heated at 900 °C (SIV-1-900 and SIV-2-900) and 1200 °C (SIV-1-1200), the XEL efficiencies increased to 95%–105% of the commercial phosphor (see Figure 8 and Table 3). An increase in the formal concentration of Eu from 5% to 8% (samples SIV-3 versus SIV-4) in raw Lu$_2$O$_3$:Eu did not further affect the phosphor performance. Since Lu$_2$O$_3$:Eu can be used in layers when at least 1.5-fold thinner—due to its higher absorption of X-rays than Gd$_2$O$_2$S:Eu—it provides some advantage over GOS. On the other hand, its significantly higher price reduces its competitiveness. Hence, only a further enhancement of the luminescence efficiency under X-rays might make Lu$_2$O$_3$:Eu a real competitor for GOS:Eu. While using the (Li$_2$SO$_4$-SiO$_2$) flux allows improving the phosphor morphology, the XEL efficiency, though high, is still too low to beat up the effective and reasonably priced GOS.

Figure 8. XEL emission spectra of the sample SIV-1 (black line) and SIV-1-900 (red line). See also Table 3.
Table 3. XEL efficiency of Lu₂O₃:Eu vs. commercially offered Gd₂O₂S:Eu.

| Lu₂O₃:Eu sample # | XEL Efficiency (%) |
|------------------|-------------------|
| SIV-1            | 72                |
| SIV-1-900        | 105               |
| SIV-1-1200       | 97                |
| SIV-2            | 66                |
| SIV-2-900        | 95                |
| SIV-3            | 80                |
| SIV-4            | 75                |

3. Experimental Section

Lu₂O₃ and Eu-doped Lu₂O₃ powders were prepared by means of a Li₂SO₄ or (Li₂SO₄ + SiO₂) flux (Li₂SO₄, Alfa Aesar, 99.7%, Karlsruhe, Germany; SiO₂, Sigma Aldrich, ~99%, St. Louis, MO, USA) method using a mixture of commercially offered Lu₂O₃ (Stanford Materials Corporation, 99.995%, Aliso Viejo, CA, USA) and Eu₂O₃ (Stanford Materials Corporation, 99.999%). Four series of compounds were prepared and details are given in Table 4. Powders of series I–III contain no activator. Taking advantage of the knowledge on the results of Series I–III, fourth Eu-activated powders, Lu₂O₃:Eu (5 mol%), were prepared using mixtures of Li₂SO₄ and SiO₂ as the flux (see Table 4 for details). These products gave Series IV of powders. To document the influence of Li₂SO₄ flux on the continuous removing of SiO₂ from the reacting mixture, three samples (Series I) were prepared using the molar ratio of Lu₂O₃:SiO₂ = 1:1, as in the Lu₂SiO₅, see Table 4 for other details. In typical synthesis, the mixture of the reagents and the flux was transferred to a Pt-Ir (90%–10%) crucible which was next heated up at 1400 °C for 50 h in air. In the case of Series I, the temperature was lowered to 1300 °C and the time varied from 1 up to 20 h. After heating, the mixture was cooled down to room temperature (RT). To recover the product, the Li₂SO₄ flux was washed out with hot water and finally the powder was dried at ~80 °C in air for a few hours. For radioluminescent measurements, fractions of samples SIV-1 and SIV-2 were additionally heated at 900 °C and 1200 °C to see how this treatment affects their performance. These samples are named SIV-1-900 and SIV-2-900.

The powder X-ray diffraction patterns were measured using a D8 Advance Diffractometer from Bruker (Billerica, MA, USA) with Ni-filtered CuKα radiation (λ = 1.540596 Å) in the range of 20 = 10°–100°, and with the step of 20 = 0.008°. Single crystal X-ray diffraction data for undoped Lu₂O₃ were collected at room temperature using the ω-scan technique on Xcalibur diffractometer (Agilent Technologies, Santa Clara, CA, USA) equipped with Ruby CCD-detector using graphite-monochromatized MoKα radiation (λ = 0.71073 Å) [39]. The data were corrected for Lorentz-polarization effects and for absorption. The structure was refined with the full-matrix least-squares procedure on F² by SHELXL [40] on coordinates of atoms were taken from a previously reported isomorphous crystal of Y₂O₃. All atoms were refined anisotropically. The products’ morphology was tested by means of SEM imaging with Hitachi S-3400N scanning electron microscope (Hitachi High-Technologies, Tokyo, Japan) equipped with an energy dispersive X-ray spectroscopy (EDX) EDAX analyzer. The room temperature X-ray excited luminescence—measurements of the Eu-activated powders of Series IV were performed using white radiation from a Cu X-ray tube working under the voltage of 40 kV and a current of 10 mA. The generated emission photons were collected with a 74-UV
lens connected to a QP600-2-SR-BX waveguide which transferred the luminescent light to an Ocean Optics HR2000CG-UV-NIR Spectrometer (Ocean Optics, Dunedin, FL, USA). Efficiency of the XEL was estimated using a commercially offered powder of Gd$_2$O$_2$:Eu as the benchmark kindly supplied by Phosphor Technology. The real content of Eu in Lu$_2$O$_3$:Eu powders was determined by means of Inductively Coupled Plasma (ICP) technique using an ARL 3410 ICP Spectrometer (Fisons Instruments, Ecublens, Switzerland).

Table 4. Exemplary amounts of starting materials for the four series of synthesized powders.

| Series | Sample # | Batch Composition (g) | Process Parameters | Product Composition |
|--------|----------|-----------------------|-------------------|--------------------|
|        |          | Lu$_2$O$_3$ | Eu$_2$O$_3$ | Li$_2$SO$_4$ | SiO$_2$ | Temperature (°C)/Time (h) |  |
| I      | SI-1     | 1.7585        | –            | 13.97     | 0.2661 | 1300/1 | Lu$_2$SiO$_5$, Lu$_2$O$_3$ |
|        | SI-2     | 1.7585        | –            | 13.97     | 0.2661 | 1300/2 | Lu$_2$SiO$_5$, Lu$_2$O$_3$ |
|        | SI-3     | 1.7585        | –            | 13.97     | 0.2661 | 1300/20 | Lu$_2$O$_3$ |
| II     | SII-1    | 2             | –            | 2         | –      | –      | Lu$_2$O$_3$ |
|        | SII-2    | 2             | –            | 4.77      | –      | –      | Lu$_2$O$_3$ |
|        | SII-3    | 2             | –            | 9.54      | –      | –      | Lu$_2$O$_3$ |
| III    | SIII-1   | 2             | –            | 4.77      | 0.045  | 1400/50 | Lu$_2$O$_3$ |
|        | SIII-2   | 2             | –            | 4.77      | 0.15   | Lu$_2$O$_3$ |
|        | SIII-3   | 2             | –            | 4.77      | 0.3    | Lu$_2$O$_3$ |
|        | SIII-4   | 2             | –            | 9.54      | 0.3    | Lu$_2$O$_3$ |
| IV     | SIV-1    | 1.9           | 0.0884      | 4.77      | 0.045  | Lu$_2$O$_3$ |
|        | SIV-2    | 1.9           | 0.0884      | 9.54      | 0.3    | Lu$_2$O$_3$ |
|        | SIV-3    | 1.9           | 0.0884      | 4.77      | 0.3    | Lu$_2$O$_3$ |
|        | SIV-4    | 1.84          | 0.1415      | 4.77      | 0.3    | Lu$_2$O$_3$ |

4. Conclusions

In this paper, we showed that Li$_2$SO$_4$-flux-aided synthesis of Lu$_2$O$_3$ and Lu$_2$O$_3$:Eu gives non-agglomerated powders with particles whose sizes may be controlled to some extent by addition of some SiO$_2$ to the flux. No traces of silica were detected in the final product. Large enough single crystals could be selected to perform structural analysis. This confirmed that lutetia is isostructural with cubic yttria and $a = 10.393(2)$ Å. This is in agreement with very recently published data on Lu$_2$O$_3$ structure determined on single crystals made by μ-PD and LHPG techniques. X-ray excited luminescence spectra were typical for Lu$_2$O$_3$:Eu and the light yield reached 95%–105% of the yield of commercial GOS:Eu, which is not enough to compete effectively with this phosphor in practical applications.

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Author Contributions

Justyna Zeler fabricated the powders, recorded the SEM images and measured the RL spectra, Lucjan B. Jerzykiewicz preformed the structural measurements and related calculations, Eugeniusz Zych directed the project. All authors analyzed the results and contributed to writing.

Conflicts of Interest

The authors declare no conflict of interest.

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