

## Application Note SC-XRD 506

# Discovering the structure of a two micrometer-sized crystal of a lanthanide silicate

### Introduction

Zeolites and zeotype materials are the most common micro-porous inorganic materials employed in industrial processes. The three-dimensional network structure of these materials is well understood and is typically formed by tetrahedral  $\text{SiO}_4^{4-}$  building blocks. The idea to fine tune the material's properties while maintaining its robustness has impelled researchers to selectively replace the tetrahedral units by other building blocks. Among others, mixed-polyhedra materials with pentahedral and octahedral units are today established worldwide, combining the well-known tetrahedral  $\text{SiO}_4^{4-}$  building unit with mainly transition metal centers.

The research group at the University of Aveiro has pioneered these investigations focusing on the incorporation of rare-earth, preferably lanthanide, cations into inorganic networks. Similar to other zeotype materials the mixed-polyhedra materials are prepared using high temperature and high pressure techniques, mimicking nature's approach. Materials with fascinating photoluminescent properties are usually obtained. To understand the nature of the photoluminescence the knowledge of the newly synthesized material's crystal structure is of crucial importance. Sadly enough, despite many attempts, these synthetic approaches typically provide only very small crystals. Revealing a meaningful crystal structure from a micrometer-sized crystal is, however, a great and demanding challenge.

### A structural riddle

Recently, in our laboratories we prepared the new photoluminescent lanthanide silicate **1**, which systematically forms very small crystals.<sup>1</sup> The chemical formula of **1** was determined as  $\text{Na}[(\text{Gd}_{0.99}\text{Eu}_{0.01})\text{SiO}_4]$ . Photoluminescence studies indicated the presence of at least two crystallographically independent lanthanide sites that should be located in special positions within the unit cell. However, this requirement was in permanent contradiction with other preliminary structure elucidation studies, for example from powder data. In order to develop a coherent model we urgently demanded a single crystal structure analysis.



D8 QUEST with fixed-chi stage

## The New D8 QUEST

All our previous attempts to determine the crystal structure of **1** using the vintage single-crystal diffractometers we had installed at that time failed because of the weak diffraction properties of the sample. The installation of a new D8 QUEST instrument changed our laboratories capabilities. As one of the first samples on the new equipment we measured an extremely small, colorless single crystal with dimensions of only  $0.002 \times 0.010 \times 0.012 \text{ mm}^3$ .

Our D8 QUEST consists of the KAPPA goniometer and the PHOTON 100 CMOS APS detector. Furthermore, the system is equipped with a sealed tube Mo X-ray source ( $\lambda = 0.71073 \text{ \AA}$ ) and the new TRIUMPH focusing monochromator that provides a significantly increased flux density at the sample position. During the entire experiment the sample was kept at 100 K using a low temperature device, and the entire setup was controlled with the APEX2 software package.

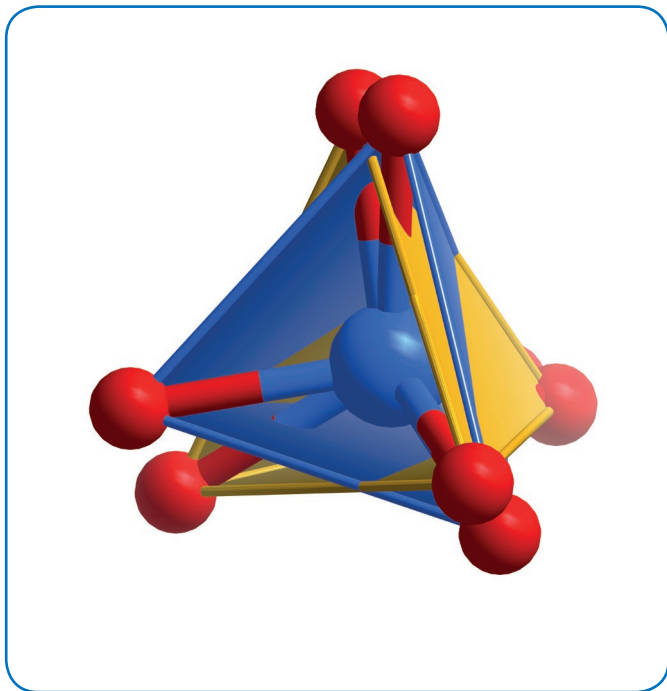


Figure 1: The two almost overlapping crystallographic positions for the  $\text{SiO}_4^{4-}$  tetrahedra composing the crystal structure of **1**. Each position has an overall rate of occupancy of 50%.

## Data collection in less than a day

Based on the initial scans the unit cell determination routine of the software suite indicated an orthorhombic unit cell. From the same scans the data collection strategy optimizer suggested 0.5 degree frames and the refined data collection strategy consisted of four scans composed of  $\omega$ - and  $\phi$ -rotations. A frame exposure time of 60 s was selected, appropriate for the small crystal size and the correspond-

ingly very weak diffraction signal of the sample. A total of 1142 frames were collected within just 19 hours.

The frames were processed using the integration plug-in of the APEX2 suite (SAINT) applying the 3D narrow-frame algorithm. Integration of the data gave a total of 3910 reflections to a maximum resolution of  $0.77 \text{ \AA}$  ( $\theta = 27.45^\circ$ ), of which 428 were independent (completeness = 99.1%,  $R_{\text{int}} = 3.21\%$ ,  $R_{\text{sig}} = 2.21\%$ ). 76 % of the reflections showed  $I > 2\sigma(I)$  and thus were conserved as "observed". The final unit cell constants of  $a = 6.816(1) \text{ \AA}$ ,  $b = 5.4758(9) \text{ \AA}$ ,  $c = 9.162(1) \text{ \AA}$ , were automatically determined by the SAINT engine and are based upon the refinement of 2131 reflections above  $2\sigma(I)$ . Data were corrected for absorption using the multi-scan method of the scaling plug-in (SADABS).

Using space group  $Pmna$  and four formula units in the unit cell ( $Z = 4$ ), the structure was solved using the new intrinsic phasing algorithm implemented in APEX2. The final mixed anisotropic and isotropic least-squares refinement on  $F^2$  with 44 variables (plus 12 restraints) converged at  $R1 = 2.10\%$ , for the observed data and  $wR2 = 4.46\%$  for all data. The goodness-of-fit (GoF) of 1.165 indicates the excellent quality of the obtained model.

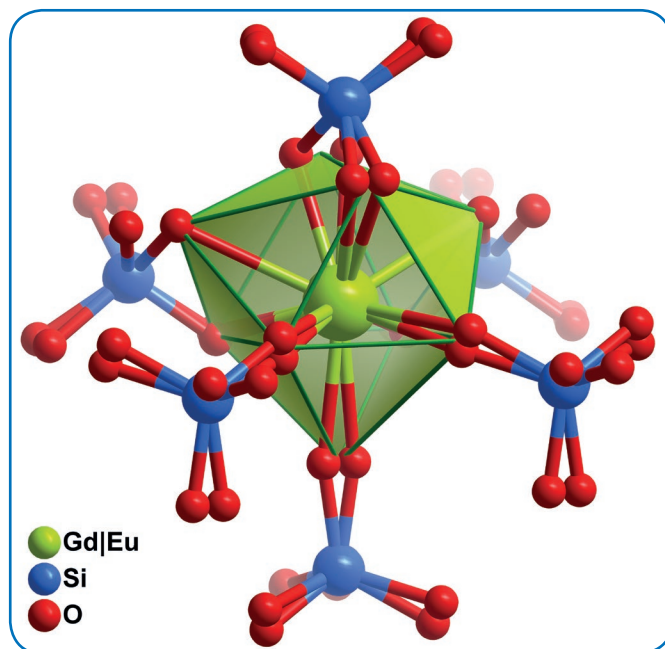
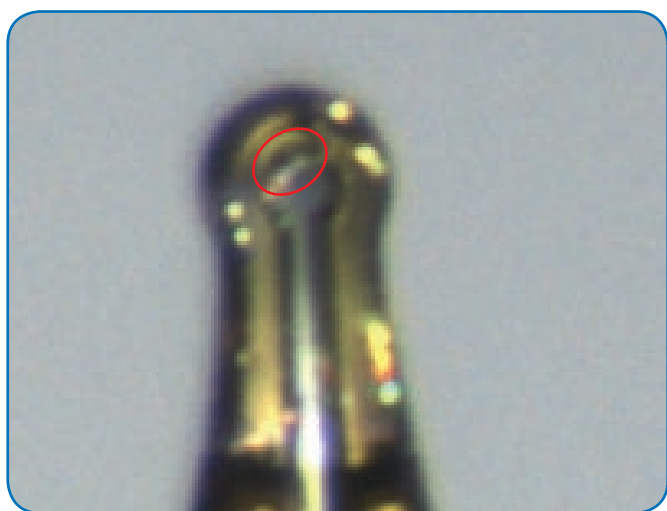


Figure 2: Lanthanide site in **1** showing the multiple coordination environments arising from the disorder of the  $\text{SiO}_4^{4-}$  tetrahedron. The distorted dodecahedral coordination environment is emphasized.

Theta range for data collection	3.73 to 27.45°
Index ranges	-8<=h<=6, -7<=k<=7, -11<=l<=11
Reflections collected	3910
Independent reflections	428 [ $R_{int} = 0.0321$ ]
Coverage of independent reflections	99.10%
Absorption correction	multi-scan
Structure solution technique	intrinsic phasing
Structure solution program	XT (Sheldrick, 2013)
Refinement method	Full-matrix least-squares on $F^2$
Refinement program	XL-97 (Sheldrick, 2008)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	428 / 12 / 44
Goodness-of-fit on $F^2$	1.165
$\Delta/\sigma_{max}$	0.000
Final $R$ indices	428 data; $R1 = 0.0210$ , $ >2\sigma(I)$ $wR2 = 0.0391$
	all data $R1 = 0.0329$ , $wR2 = 0.0446$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0162P)^2+1.7333P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.338 and -1.310 $e\text{\AA}^{-3}$



Picture 1: Crystal of 1 mounted on a 10 micron cryo-loop.

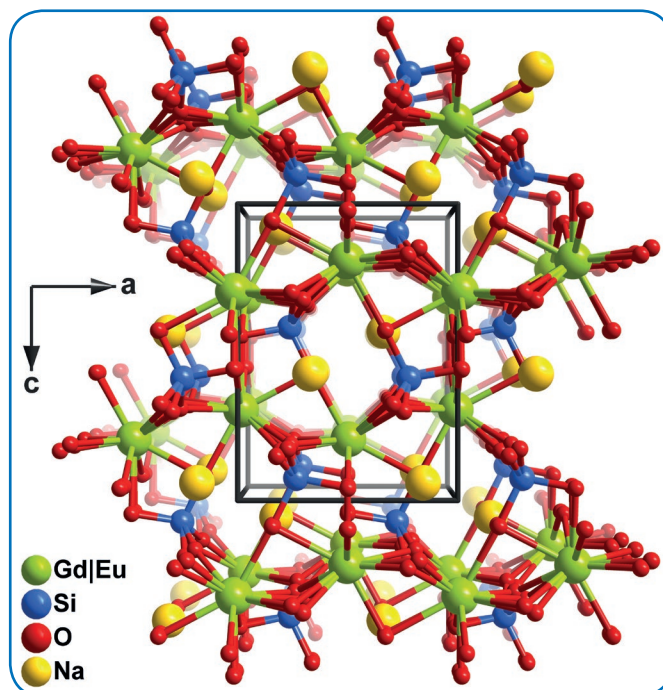


Figure 3: 3D arrangement of the building units in 1.

## Discussion

The single crystal structure confirms the presence of one single, crystallographically independent lanthanide center. Quite unexpectedly the single crystal analysis reveals a severe disorder of the tetrahedral  $\text{SiO}_4^{4-}$  building unit as depicted in Figure 1. The  $\text{SiO}_4^{4-}$  unit oscillates between at least two distinct crystallographic positions. This can be clearly determined from the refinement of some oxygen atoms to partial occupancies of 50%. This unusual disorder of the  $\text{SiO}_4^{4-}$  unit leads to a variety of possible coordination environments for the rare-earth cation, as shown in Figure 2. If the average of all possible coordination spheres are taken into account the rare-earth cation is coordinated to six symmetry-related  $\text{SiO}_4^{4-}$  tetrahedra with an overall coordination number of 8. The coordination of the rare-earth cation resembles thus a distorted dodecahedron (point symmetry  $D_{2d}$ ). Remarkably, and most importantly, these peculiar structural features unveiled from the single crystal X-ray diffraction analysis explain the observed photoluminescent properties of the material. As shown in Figure 3 the small voids present in the structure are filled with  $\text{Na}^+$  cations, balancing the charge of the three-dimensional zeotype network.

## Summary

The D8 QUEST and the superb APEX2 software suite enabled us to solve and refine the crystal structure of a tiny, very weakly diffracting photoluminescent lanthanide silicate with high quality. In particular the presence of the TRIUMPH monochromator combined with the sealed tube is the key factor for a successful treatment of this just 2  $\mu\text{m}$  sized sample. The increased flux density at the center of the beam provided by this new generation of focusing monochromator permitted the inspection of such a small crystal. We are very happy having this powerful D8 QUEST setup in the laboratory. It is a fast and very reliable alternative to other, much more expensive and time-consuming analytical methods. With our older instrument this type of analyses was not possible and a trip to a synchrotron source would have been our only option to obtain such high quality data. This is why the new D8 QUEST became very quickly the key tool in our daily research work on materials. The D8 QUEST allows an extraordinarily fast analysis of complex-material problems as well as the fast screening of our novel crystalline compounds. Thanks to the sealed tube setup the D8 QUEST is also the system of choice for our routine work in service crystallography.

## Author

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## References

<sup>1</sup> D. Ananias, F. A. Almeida Paz, D.S. Yufit, L. D. Carlos, J. Rocha (2014) Manuscript submitted for publication.

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