Supplementary Information

Table S1. Bond lengths inside of different coordination polyhedra for various Ce_3O_3N modifications.

Ce_3O_3N-DM1	VIII 2.4161 O 2.4511 O 2.4595 O 2.5330 O 2.5590 O 2.5815 O 2.3611 N 2.4780 N Mean: 2.4799	
Ce_3O_3N-GS1	VII 2.2997 O 2.3643 O 2.3643 O 2.3856 O 2.7420 O 2.4369 N 2.4369 N Mean: 2.4328	VI 4 x 2.3437 O 2 x 2.5150 N
Ce_3O_3N-GS2	VI 2 x 2.4670 O 2 x 2.4115 O 2.2266 O 2.1871 N Mean: 2.3618	VI 2 x 2.3268 O 2 x 2.6067 O 2 x 2.3276 N Mean: 2.4204
Ce_3O_3N-GS3	VII 2 x 2.3774 O 4 x 2.4257 O 2.6800 N Mean: 2.4482	VI 2.2823 O 2.2860 O 4 x 2.3937 N Mean: 2.3572
Ce_3O_3N-GS4	VI 4 x 2.2907 O 2 x 2.3121 N Mean: 2.2979	VI 2 x 2.3351 O 2 x 2.4093 O 2 x 2.5117 N Mean: 2.4187
Ce_3O_3N-GS5	VII 2 x 2.2905 O 4 x 2.4481 O 2.7377 N Mean: 2.4445	VI 2.2501 O 2.3900 O 4 x 2.4106 N Mean: 2.3804

Ce_3O_3N-GS6	VI 4 x 2.2929 O 2 x 2.3145 N Mean: 2.3001	VI 2 x 2.3372 O 2 x 2.4108 O 2 x 2.5123 N Mean: 2.4201
Ce_3O_3N-GS7	VI 6 x 2.3756 O	

Table S2. Space group, unit cell parameters (Å), atomic positions, and total energy values in Hartrees (E_h) for eight optimized modifications found using the global search method.

Modification	Space group (no.)	Cell parameters (Å) and fractional coordinates	Total energy (Eh)
Ce_3O_3N-GS1	*P*2/*m* (10)	*a* = 5.89; *b* = 3.62; *c* = 5.04; β = 113.2º Ce (0 0 0) Ce (0.3017 1/2 0.6238) O (0.2702 1/2 0.0652) O (1/2 0 /2) N (0 0 1/2)	-1702.4813
Ce_3O_3N-GS2	*Amm*2 (38)	*a* = 3.59; *b* = 9.83; *c* = 5.78 Ce (1/2 0.1729 0.8911) Ce (0 0 0.3964) Ce (1/2 0 0.8038) O (0.5 0 0.1402) O (0 0.7712 0.1681) N (1/2 0 0.6528)	-1702.4685
Ce_3O_3N-GS3	*Imm*2 (44)	*a* = 3.38; *b* = 3.39; *c* = 17.39 Ce (0 0 0.7735) Ce (0 0 0.4276) Ce (0 0 0.0814) O (0 0 0.5589) O (0 0 0.2961) O (0 1/2 0.1775) N (0 0 0.9277)	-1702.4627
Ce_3O_3N-GS4	*Pmmm* (47)	*a* = 6.86; *b* = 3.53; *c* = 4.62 Ce (1/2 0 0) Ce (0.7607 1/2 1/2) O (0.2869 1/2 0) O (0 0 1/2) N (1/2 0 1/2)	-1702.4588
Ce_3O_3N-GS5	*Amm*2 (38)	*a* = 3.49; *b* = 3.32; *c* = 17.93 Ce (1/2 0 0.0970) Ce (0 0 0.4475) Ce (1/2 0 0.8038) O (0 0 0.5730) O (0 0 0.3143)	-1702.4576

		O (1/2 0 0.6850) N (1/2 0 0.9444)	
Ce_3O_3N-GS6	*Pmmm* (47)	*a* = 3.53; *b* = 4.63; *c* = 6.85 Ce (0 0 0) Ce (1/2 1/2 0.7394) O (1/2 0 0.2132) O (0 1/2 1/2) N (0 1/2 0)	-1702.4509
Ce_3O_3N-GS7	*Pm-3m* (221)	*a* = 4.75 Ce (1/2 0 1/2) O (0 1/2 0) N (1/2 1/2 1/2)	-1702.4394

Data mining of the ICSD database gave us 19 candidates with the general formula A_3B_3C. Every candidate was used as the starting structure type for *ab initio* optimization of the Ce_3O_3N compound. The initial structures and their references are: Al_3ScC_3[1], Ba_3FeN_3[2], Ca_3PI_3[3], Ca_3InP_3[4], Cu_3SbS_3[5], Fe_3TlTe_3[6], Fe_3W_3C[7], Gd_3MnI_3[8], K_3AlSe_3[9], K_3BS_3[10], $K_6Sn_2Te_6$[11], KB_3H_3[12], Na_3AsS_3[13], Ni_3SmGe_3[14], $NiSc_3Si_3$[15], [2] (proustite)[16], $Rh_4C_{12}O_{12}$[17], Tl_3AsSe_3[18], Ag_3AsS_3 (xanthoconite)[19].

Table S3. Space group, unit cell parameters (Å), atomic positions, and total energy values in Hartrees (E_h) for three optimized modifications found using the data mining method.

Modification	Space group (no.)	Cell parameters (Å) and fractional coordinates	Total energy (*Eh*)
Ce_3O_3N-DM1	*R3c* (161)	*a* = 10.17; *c* = 6.15 Ce (-0.1996 -0.0378 0.2416) O (-0.0656 0.2200 0.3762) N (0 0 0.0066)	-1702.4875
Ce_3O_3N-DM2	$P6_3/m$ (176)	*a* = 7.21; *c* = 4.75 Ce (0.3715 0.3398 1/4) O (0.2747 0.9691 1/4) N (2/3 1/3 1/4)	-1702.4007
Ce_3O_3N-DM3	*I-43m* (217)	*a* = 10.49 Ce (1/2 0 1/4) Ce (0 0 0.2430) O (0.8876 0.6093 0.1124) N (0.1159 0.1159 0.8841)	-1702.2837

Table S4. Total energy ranking in eV for the best candidates from the global energy landscape and data-mining searches (Ce_3O_3N-DM1, and Ce_3O_3N-GS1) and literature data [20] calculated using the VASP code and the LDA functional.

Modification	Space group (no.)	Total energy (eV)
Ce_3O_3N-DM1	*R3c* (161)	-65.8541
Ce_3O_3N-GS1	*$P6_3/m$* (176)	-65.7261
Literature*	*$P2_1$* (no. 4)	-65.5338

References

1. Tsokol, A. O., Bodak, O. I., Marusin, E. P., Baivelman, M. G., Crystal structure of the compound $ScAl_3C_3$. *Soviet Physics, Crystallography (=Kristalografiya)* **1986,** 31, 467-468.
2. Rabenau, A.; Kniep, R.; Höhn, P., $Ba_3[FeN_3]$: Ein neues Nitridoferrat(III) mit $[CO_3]_2$--isosteren Anionen $[FeN_3]_6$. **1991,** 196, (1-4), 153-158.
3. Lang, J.; Hamon, C.; Marchand, R.; Laurent, Y., Étude d'halogénopnictures. III. Structure de Ca_2PI et Ca_3PI_3. Surstructures de type NaCl. *Bulletin de Minéralogie* **1974**, 6-12.
4. Cordier, G., Schaefer, H., Stelter, M., Neue Zintlphasen: Ba_3GaSb_3, Ca_3GaAs_3 und Ca_3InP_3. *Zeitschrift fuer Naturforschung, Teil B: Anorganische Chemie, Organische Chemie* **1985,** 40, 1100-1104.
5. Machatsehki, F., XII. Präzisionsmessungen der Gitterkonstanten verschiedener Fahlerze. *Formel und Struktur derselben* **1928,** 68, (1-6), 204-222.
6. Klepp, K.; Boller, H., Die Kristallstruktur von $TlFe_3Te_3$. *Monatshefte für Chemie / Chemical Monthly* **1979,** 110, (3), 677-684.
7. Pollock, C. B.; Stadelmaier, H. H., The eta carbides in the Fe−W−C and Co−W−C systems. *Metallurgical Transactions* **1970,** 1, (4), 767-770.
8. Ebihara, M.; Martin, J. D.; Corbett, J. D., Novel Chain and Oligomeric Condensed Cluster Phases for Gadolinium Iodides with Manganese Interstitials. *Inorganic Chemistry* **1994,** 33, (10), 2079-2084.
9. Crystal structure of hexapotassium di-μ-selenido-bis(diselenidoaluminate), $K_6Al_2Se_6$. *Zeitschrift für Kristallographie* **1991,** 197, (1-2), 173-174.
10. Kuchinke, J.; Jansen, C.; Lindemann, A.; Krebs, B., Syntheses and Crystal Structures of the Novel Ternary Thioborates Na_3BS_3, K_3BS_3, and Rb_3BS_3. *Zeitschrift für anorganische und allgemeine Chemie* **2001,** 627, (5), 896-902.
11. Dittmar, G., Die KristallStrukturen von $K_6[Ge_2Te_6]$ und $K_6[Sn_2Te_6]$ und ihre kristall-chemische Beziehung zum $K_6[Si_2Te_6]$-Typ. *Zeitschrift für anorganische und allgemeine Chemie* **1979,** 453, (1), 68-78.
12. Kuznetsov, I. Y., Vinitskii, D. M., Solntsev, K. A., Kuznetsov, N. T., Butman, L. A., The crystal structure of $K_2B_6H_6$ and $Cs_2B_6H_6$. *Zhurnal Neorgnicheskoi Khimii* **1987,** 32, 3112-3114.
13. Palazzi, M., Structure cristalline de l'orthotrithioarsenite trisodique Na_3AsS_3. *Acta Crystallographica Section B* **1976,** 32, (12), 3175-3177.
14. Mruz, O. Y., Pecharskii, V. K., Sobolev, A. N., Bodak, O. I., Crystal structure of $SmNi_3Ge_3$. *Kristallografiya* **1990,** 35, 202-204.
15. Kotur, B. Y., Gladyshevskii, E. I., Crystal structure of scandium-nickel silicide (Sc_3NiSi_3). *Kristallografiya* **1983,** 28, 461-464.
16. Harker, D., The Application of the Three-Dimensional Patterson Method and the Crystal Structures of Proustite, Ag_3AsS_3, and Pyrargyrite, Ag_3SbS_3. *The Journal of Chemical Physics* **1936,** 4, (6), 381-390.

17. Wei, C. H., Structural analyses of tetracobalt dodecacarbonyl and tetrarhodium dodecacarbonyl. Crystallographic treatments of a disordered structure and a twinned composite. *Inorganic Chemistry* **1969,** 8, (11), 2384-2397.
18. Hong, H. Y. P.; Mikkelsen, J. C.; Roland, G. W., Crystal structure of Tl_3AsSe_3. *Materials Research Bulletin* **1974,** 9, (4), 365-369.
19. Engel, P.; Nowacki, W., Die Kristallstruktur von Xanthokon, Ag_3AsS_3. *Acta Crystallographica Section B* **1968,** 24, (1), 77-81.
20. Sharan, A.; Lany, S., Computational discovery of stable and metastable ternary oxynitrides. *The Journal of Chemical Physics* **2021,** 154, (23), 234706.