$Gd_2F[CO_3][AsO_3]$: A Serendipitously Formed Gadolinium Fluoride Oxocarbonate Oxoarsenate(III)

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In an attempt to synthesize $Gd_5F_3[AsO_3]_4$[1–4] under high-pressure conditions from appropriate molar mixtures of GdF_3, Gd_2O_3 and As_2O_3, which were filled into a gold ampoule with a drop of deionized water, colorless lath-shaped crystals of what turned out to be $Gd_2F[CO_3][AsO_3]$ emerged. After seven days in a piston-cylinder high-pressure cell at 10 kbar and 850 °C, some CO_2 dissolved in the applied water must have served as source for the oxocarbonate formation. The mixed-anionic $Gd_2F[CO_3][AsO_3]$ crystallizes in the monoclinic space group $P2_1/c$ with the lattice parameters $a = 1015.04(6)$ pm, $b = 772.56(4)$ pm, $c = 775.85(4)$ pm and $\beta = 109.629(3)°$ for $Z = 4$ (CSD number: 2350405). Its crystal structure contains two positions for the Gd^{3+} cations, only one for F^-, C^{4+} and As^{3+} each, as well as six O^{2-}-anion sites, all at general *Wyckoff* positions $4e$. $(Gd1)^{3+}$ is surrounded by six O^{2-} and two F^- anions, while $(Gd2)^{3+}$ has only one F^-, but seven O^{2-} anions as coordination sphere, both in the shape of distorted square antiprisms (Figure 1, *left*). All oxygen atoms belong to either carbon (O1 – O3) or arsenic (O4 – O6) to form planar $[CO_3]^{2-}$ triangles or $[AsO_3]^{3-}$ ψ^1-tetrahedra (Figure 1, *right*). The fluoride anions reside in *quasi*-planar coordination of three Gd^{3+} cations and two of the resulting $[FGd_3]^{8+}$ triangles share a common edge (Gd1···Gd1) to assemble as discrete $[F_2Gd_4]^{10+}$ dimers (Figure 1, *mid*). A view of the complete crystal structure of $Gd_2F[CO_3][AsO_3]$ along [010] is shown in Figure 2. Wavelength-dispersive electron-beam X-ray microprobe analyses confirmed the composition and Raman spectra the presence of discrete $[CO_3]^{2-}$ and $[AsO_3]^{3-}$ anions as well as the absence of $(OH)^-$ groups, which could isomorphically replace part of the F^- positions easily.

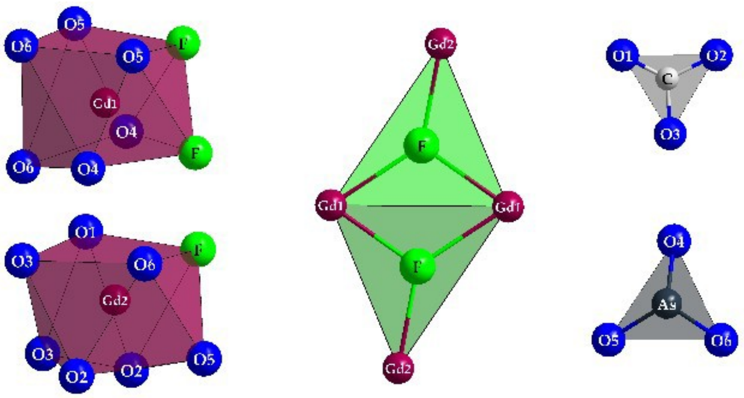

Figure 1. Distorted square antiprisms $[(Gd1)O_6F_2]^{11-}$ and structure of $[(Gd2)O_7F]^{12-}$ (*left*), congonial bitriangle $[F_2Gd_4]^{10+}$ (*mid*) as well as triangular $[CO_3]^{2-}$ and ψ^1-tetrahedral $[AsO_3]^{3-}$ anions (*right*) in the crystal structure of $Gd_2F[CO_3][AsO_3]$.

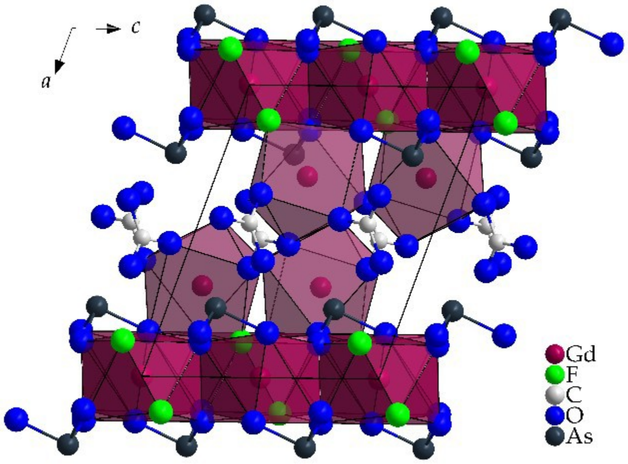

Figure 2. View at the monoclinic crystal $Gd_2F[CO_3][AsO_3]$ along [010].

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