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The preparation and structure of Ge_3F_8, a new mixed-valence fluoride of germanium, a convenient source of GeF_2

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Experimental Section

GeF_4 and Ge powder were obtained from Aldrich and used as received. The syntheses were carried out under rigorously anhydrous conditions, and all the solid germanium fluorides were handled in a glove box (water < 2 ppm).

Synthesis of Ge_3F_8: In a typical preparation, a 300 mL Monel autoclave (Autoclave Engineers Ltd.) fitted with a Autoclave Engineers Monel valve, was evacuated (10^{-3} mm) and heated at 400 K for 4 h, to remove surface moisture. It was then cooled, filled with dry N_2 and transferred to a glove box. The autoclave was loaded with Ge powder (3.1 g) in an alumina crucible, evacuated, and then filled to 4 bar pressure with GeF_4. The autoclave was sealed, and heated electrically to 390 K for 48 h, after which it was allowed to cool to room temperature. The residual GeF_4 was pumped away, the autoclave refilled with dry N_2 and opened in the glove box. The white crystalline deposit on the lid and upper walls was removed and stored in sealed containers in the glove box (2.8 g). Residual Ge powder was also present in the crucible.

Synthesis of GeF_2: The crystals obtained above (1.0 g) were transferred to a pre-dried glass apparatus and sublimed by heating *in vacuo* (390 K / 0.5 mm) onto a glass cold-finger. The white microcrystalline deposit was transferred to the glove box, collected and stored in a sealed container in the glove box. Yield: ~0.5 g, which corresponds to an overall yield of GeF_2 of ~30% based upon elemental Ge.

X-Ray data for Ge_3F_8: Formula weight = 369.77, temperature = 100(2) K, λ_1 = 0.71073 Å, crystal system = monoclinic, space group $P2_1/n$, Z = 2, with a = 4.9793(7), b = 5.0810(7), c = 11.814(2) Å, β = 90.974(6)°, V = 298.84(7) Å^3, μ = 15.093 mm^{-1}, F(000) = 336, reflections collected 2673, unique reflections 689, R_{int} = 0.0426, parameters 52, restraints 0, final R [I>2σ(I)]: R_1 = 0.0176, wR_2 = 0.0429; R (all data): R_1 = 0.0183, wR_2 = 0.0432.

Diffractometer: Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with VHF Varimax optics (100 µm focus). Cell determination, data collection, data reduction, cell refinement and absorption correction: CrystalClear-SM Expert 2.0 r7. (Rigaku Corporation, Tokyo, Japan, 2011) Structure solution and refinement were routine using WinGX and software packages within. (L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849)

Powder XRD data were collected with a Rigaku Smartlab diffractometer (Cu-$K_{\alpha 1}$ radiation, parallel beam, symmetric flat plate geometry, DTex250 1D detector, 5° soller slits), compared with patterns from ICSD and refined using the GSAS package. Polyhedral structure images were generated using the Vesta package. (K. Momma and F. Izumi, *J. Appl. Cryst.*, 2011, **44**, 1272)

The diffraction pattern from the mixture of germanium fluoride products obtained directly from autoclave reactions between Ge and GeF_4 is shown in Fig. S1. No correction for preferred orientation has been applied to the patterns of these highly crystalline samples, hence the intensities in the measured pattern do not exactly match the standards.

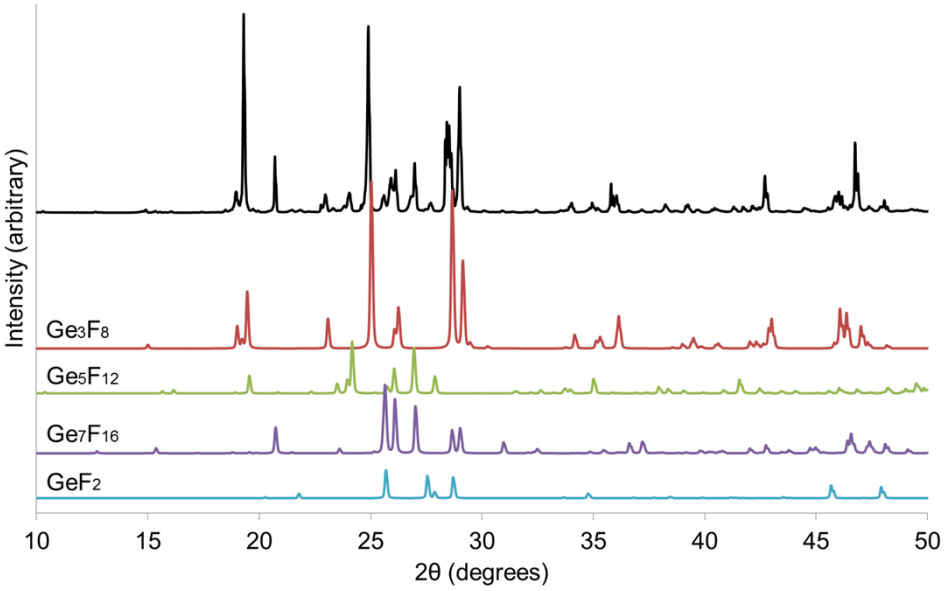

Fig. S1 The powder XRD pattern of the mixture of products obtained by reacting Ge with GeF_4 (black). Standard patterns generated from the single crystal structures of Ge_3F_8 (this work), Ge_5F_{12} (J. C. Taylor and P. W. Wilson, *J. Am. Chem. Soc.*, 1973, **95**, 1834), Ge_7F_{16} (J. Köhler and J.-H. Chang, *Z. Anorg. Allg. Chem.*, 1997, **623**, 596) and GeF_2 (J. Trotter, M. Akhtar and N. Bartlett, *J. Chem. Soc. A*, 1966, 30).

Sublimation of the above mixed-phase material resulted in GeF_2. This was fitted to the literature structure:

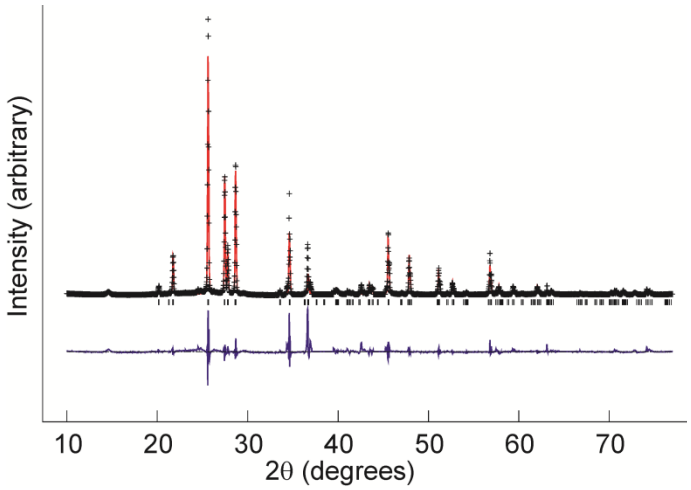

Fig. S2 Fit to the powder XRD pattern of GeF_2. Crosses mark the data points, the red line the fit and the blue line the difference. Black tick marks show the allowed reflection positions in $P2_12_12_1$; a = 4.6795(2), b = 5.1740(2), c = 8.3173(4) Å. Literature lattice parameters: a = 4.682(1), b = 5.158(1), c = 8.312(1) Å. R_{wp} = 20.1%, R_p = 13.9%. Spherical harmonic preferred orientation model refined (texture index = 1.42). Peaks from the Al sample holder were excluded at 38, 44 and 65°.