Allotropes of sulfur

No other element forms more solid allotropes than sulfur. At present, about 30 well characterized sulfur allotropes are known of which the most common form found in nature is the greenish-yellow orthorhombic α-sulfur, containing puckered rings of S₈.

α-sulfur

When pure it has a greenish-yellow colour (traces of cyclo-S₇ in commercially available samples make it appear yellower). It is practically insoluble in water and is a good electrical insulator with poor thermal conductivity. It is quite soluble in carbon disulfide: 35.5 g/100 g solvent at 25 °C. It has a rhombohedral crystal structure. This is the predominant form found in "flowers of sulfur", "roll sulfur" and "milk of sulfur". It contains S₈ puckered rings, alternatively called a crown shape. The S-S bond lengths are all 206 pm and the S-S-S angles are 108° with a dihedral angle of 98°. At 95.3 °C, α-sulfur converts to β-sulfur.

β-sulfur

This is a yellow solid with a monoclinic crystal form and is less dense than α-sulfur. Like the α- form it contains puckered S₈ rings and only differs from it in the way the rings are packed in the crystal. It is unusual because it is only stable above 95.3 °C, below this it converts to α-sulfur. It can be prepared by crystallising at 100 °C and cooling rapidly to slow down formation of α-sulfur. It has a melting point of about 120 °C and decomposes at around this temperature.

γ-sulfur

This form, first prepared by F.W Muthmann in 1890, is sometimes called "nacreous sulfur" or "mother of pearl sulfur" because of its appearance. It crystallises in pale yellow monoclinic needles. It contains puckered S₈ rings like α-sulfur and β-sulfur and only differs from them in the way that these rings are packed. It is the densest form of the three. It can be prepared by slowly cooling molten sulfur that has been heated above 150 °C or by chilling solutions of sulfur in carbon disulfide, ethyl alcohol or hydrocarbons. It is found in nature as the mineral rosickyite.
Some allotropes of Sulfur

$S_6$ - cyclohexasulfur
S₁₂ - cyclododecasulfur

S₆ - cyclo-hexasulfur
This was first prepared by M.R. Engel in 1891 who reacted HCl with thiosulfate, HS₂O₃⁻. Cyclo-S₆ is orange-red and forms rhombohedral crystals. It is called ρ-sulfur, ε-sulfur, Engel's sulfur and Aten's sulfur. Another method of preparation involves reacting a polysulfane with sulfur monochloride:

\[ \text{H₂S₄} + \text{S₂Cl₂} \rightarrow \text{cyclo-S₆} + 2 \text{HCl} \text{ (dilute solution in diethyl ether)} \]

The sulfur ring in cyclo-S₆ has a “chair” conformation, reminiscent of the chair form of cyclohexane. All of the sulfur atoms are equivalent.

Cyclo-dodecasulfur
Thermodynamically, S₁₂ is the second most stable sulfur ring after S₈. Therefore, S₁₂ is formed in many chemical reactions in which elemental sulfur is a product. In addition, S₁₂ is a component of liquid sulfur at all temperatures. The same holds for S₁₈ and S₂₀ which are often formed together with S₁₂. Its structure can be visualised as having sulfur atoms in three parallel planes, 3 in the top, 6 in the middle and three in the bottom.

Liquid sulfur after equilibration contains sulfur homocycles of all sizes and some of these can be isolated by quenching, extraction, fractional precipitation and crystallization depending on their differing solubilities.

Cyclo-S₁₂ can be prepared by heating elemental sulfur to about 200 °C for 5-10 min and then allowing the mixture to cool to 140-160 °C within about 15 min. Once the melt has become less viscous, it is poured in as thin a stream as possible into liquid nitrogen in order to quench the equilibrium. Recrystallization of the yellow powder from CS₂ allows the isolation of an adduct which slowly loses the solvent to give the cyclo-dodecasulfur.
Note that both B and S form stable $E_{12}$ species but the structures (and coordination numbers) are quite different.