

## Investigations into the Bi-Re-O and Bi-Ir-O Systems

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The Bi-Re-O and Bi-Ir-O systems are being investigated to find phases that may exhibit geometrically frustrated magnetism or interesting structural properties. Here we report the discovery and initial characterisation of a new phase in the Bi-Re-O system that exhibits rare three-dimensionally incommensurate structural and compositional modulations. This phase has the cubic fluorite-type substructure of the high-temperature form of bismuth oxide,  $\delta$ -Bi<sub>2</sub>O<sub>3</sub>. Rhenium becomes the latest in a series of transition metal dopants known to give rise to 3-D incommensurate modulations in bismuth oxides, the others being Nb(V), Ta(V), Mo(VI), and Cr(VI)<sup>[1-4]</sup>. Electron and X-ray powder diffraction data indicate a modulation vector of  $\sim 0.29\langle 111 \rangle^*_F$ , and energy-dispersive X-ray analysis using scanning electron microscopy indicate a Bi-Re ratio of  $\sim 5.9:1$ . These results suggest that the new phase has more in common with the Mo(VI) and Cr(VI) doped bismuth oxides than with the Nb(V) and Ta(V) cases, suggesting an oxidation state of Re(VI) or Re(VII). The case for Re(VI) backed up by magnetic susceptibility data that shows a weak antiferromagnetic signal below  $\sim 150$  K, attributable to interactions among the single unpaired *d* electrons of Re(VI). The oxygen bonding environment of the Re cations are shown spectroscopically to be different to the tetrahedral environment reported in the Bi<sub>3</sub>ReO<sub>8</sub> species<sup>[5]</sup>. Recent work on single crystal synthetic procedures to obtain samples of this phase, as well as a number of new phase identified in the Bi-Ir-O system will be presented.

### References

1. R. L. Withers et al., *Z. Kristallogr.*, 1999. 214: p. 296-304.
2. C. D. Ling et al., *J. Solid State Chem.*, 1998. 137 : p. 42-61.
3. M. Valldor et al., *J. Solid State Chem.*, 2000. 152: p. 573-576.
4. S. Esmaeilzadeh et al., *J. Solid State Chem.*, 2001. 156: p. 168-180.
5. A. K. Cheetham et al., *Acta Cryst.*, 1985. B41: p. 225-230