

of climate change. Work such as that of Murphy *et al.* and other initiatives will reduce these uncertainties to a point where the dominating uncertainty remains the choice of emission path used in modelling. This is already the case for predictions that look at the second half of this century¹⁰. To shift that time horizon closer to the present will require improved climate models that can be compared in a systematic way¹¹, larger model ensembles for testing^{12,13}, and a systematic exploration of uncertainties in the radiative balance. ■

Thomas F. Stocker is in the Division of Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland.
e-mail: stocker@climate.unibe.ch

Materials science

Flame-broiled alumina

Paul F. McMillan

A method for preparing aluminate glasses and glass-ceramic composites opens up new possibilities for generating mechanically strong structural components and high-hardness coatings.

Shattered glass and cracked dinnerware: ceramics are brittle materials that fail catastrophically when they are stressed. However, strategies are being developed for creating ceramics, including glasses, that are toughened against fracture¹. The best of these techniques use nanometre-size crystals that are formed by devitrification of a glassy matrix² — that is, the formation of ordered crystalline regions throughout the amorphous, non-crystalline glass. On page 761 of this issue, Rosenflanz *et al.*³ describe a new method: micrometre-size beads of aluminate glasses are formed using a flame-spray technique; the glassy beads are then sintered into bulk glasses; further heating produces toughened, hard ceramics in which nanocrystalline alumina-rich phases are dispersed throughout a glassy matrix.

Alumina — aluminium oxide, Al₂O₃ — is the basis of many important ceramic systems, such as optical fibres. Alumina ceramics are also the industry standard for structural applications at high temperatures, especially in chemically reactive environments. Fracture-resistant aluminas are ideal for use in gas turbines, as protective tiles on space probes, and as supports for catalytic reactor systems. These applications all involve forming the ceramics into complex, dense shapes. The best way to do that is to first prepare the materials in an amorphous form, such as glass, and then devitrify them.

However, aluminate glasses form only within a narrow range of compositions because of their high melting temperatures, low viscosity on melting, and the competing

1. Houghton, J. T. *et al.* (eds) *Climate Change 2001: The Science of Climate Change* (Cambridge Univ. Press, 2001).
2. Murphy, J. M. *et al.* *Nature* **430**, 768–772 (2004).
3. Saltzman, B. *Dynamical Paleoclimatology* (Academic, London, 2002).
4. Stott, P. A. & Kettleborough, J. A. *Nature* **416**, 723–726 (2002).
5. Raper, S. C. B., Gregory, J. M. & Stouffer, R. J. *J. Clim.* **15**, 124–130 (2002).
6. Wild, M., Ohmura, A., Gilgen, H., Morcrette, J. J. & Slingo, J. *J. Clim.* **14**, 3227–3239 (2001).
7. Philippona, R., Dürr, B., Marty, C., Ohmura, A. & Wild, M. *Geophys. Res. Lett.* **31**, L03202 (2004).
8. Knutti, R., Stocker, T. F., Joos, F. & Plattner, G.-K. *Nature* **416**, 719–723 (2002).
9. Cubasch, U. *et al.* in *Climate Change 2001: The Science of Climate Change* (eds Houghton, J. T. *et al.*) 525–582 (Cambridge Univ. Press, 2001).
10. Zwiers, F. W. *Nature* **416**, 690–691 (2002).
11. Covey, C. *et al.* *Glob. Planet. Change* **37**, 103–133 (2003).
12. Allen, M. R. & Stainforth, D. A. *Nature* **419**, 228 (2002).
13. www.climateprediction.net

crystallization kinetics of their components. No one has yet prepared a bulk glass from pure alumina liquid using standard melt-quenching techniques (the same is true of water and silicon). But Rosenflanz and colleagues' flame-spray method yields glassy microspheres containing more than 80% alumina³. The flame-spray technique consists of feeding oxide powder into a high-temperature hydrogen–oxygen flame and then cooling it rapidly (quenching) to produce the glassy beads for sintering. The authors suggest that the technique could be extended to produce glasses in other 'reluctant' glass-forming systems.

Aluminate glasses formed in combination with calcium or zirconium oxides, or rare-earth oxides (REOs), are remarkable materials: they are mechanically strong and hard, and have some of the highest sound speeds of any glassy system⁴. Interestingly, devitrified samples containing mechanically weak REO components have hardness values that are almost as high as those of dense polycrystalline alumina. This reflects the importance of the interfaces between the components for toughening the glass-ceramics^{3,5}: the energy of a crack propagating through the material may be deflected or absorbed at such an interface, adding to its strength. So controlling the overall texture in these materials is the key to designing and developing composite ceramics that are both hard and strong.

Rosenflanz *et al.*³ present another important observation from their study of the REO-containing composite gadolinium

aluminate (Al₂O₃–Gd₂O₃); this observation is linked to the physical properties of alumina-rich liquids, rather than to materials research. Molten aluminates are highly 'fragile', in that the relationship between their temperature and viscosity does not follow Arrhenius' law⁵. This is correlated with the large configurational entropy in these systems, reflecting the wide variety of structural states that they can adopt: for example, Al³⁺ ions occur in multiple coordination environments (tetrahedral, octahedral, 5-coordinate, and so on), and rare-earth metal ions have coordination numbers ranging from 6 to 10. The result is a rapidly changing structure within the high-temperature liquids.

An intriguing consequence of this behaviour is that aluminate liquids and glasses can exhibit 'polyamorphism' — different liquid phases or glasses are possible that, although they have the same chemical composition, have different structures and thermodynamic properties⁶. This results in an unusual new phenomenon for the liquid state: density- or entropy-driven liquid–liquid phase transitions can appear as the pressure and temperature change. These transitions are analogous to the temperature- and pressure-driven structural transformations seen in crystalline solids, such as the diamond–graphite transition or the transitions between the quartz, cristobalite, coesite and stishovite polyamorphs of silicon dioxide.

When heating their gadolinium-aluminate glass, Rosenflanz *et al.*³ noticed an exothermic — heat producing — feature that could indicate the presence of polyamorphism in the supercooled aluminate liquid. Similar features have already been observed among yttrium-aluminate (Y₂O₃–Al₂O₃) liquids that are known to exhibit low- and high-density polyamorphs possessing different values of hardness and other physical properties^{7,8}. Controlling the polyamorphism in glassy aluminates and the resulting ceramic microtextures provides a new way to tailor the mechanical properties, including hardness, of families of composite materials. ■

Paul F. McMillan is at the Davy–Faraday Laboratory, Royal Institution of Great Britain, and in the Department of Chemistry, Christopher Ingold Laboratory and Materials Chemistry Centre, University College London, London WC1H 0AJ, UK.
e-mail: p.f.mcmillan@ucl.ac.uk

1. Morgan, P. E. D. & Marshall, D. B. *Mater. Sci. Eng. A* **162**, 15–25 (1993).
2. Yip, S. *Nature* **391**, 532–533 (1998).
3. Rosenflanz, A. *et al.* *Nature* **430**, 761–764 (2004).
4. Yeganeh-Haeri, A. *et al.* *J. Non-Cryst. Solids* **241**, 200–203 (1998).
5. Weber, J. K. R., Felton, J. J., Cho, B. & Nordine, P. C. *Nature* **393**, 769–773 (1998).
6. McMillan, P. F. *J. Mater. Chem.* **14**, 1506–1512 (2004).
7. Weber, J. K. R. *et al.* *J. Am. Ceram. Soc.* **83**, 868–872 (2000).
8. McMillan, P. F., Wilson, M. & Wilding, M. C. *J. Phys. Cond. Matter* **15**, 6105–6121 (2003).