Crystal-chemical effect of splat-cooling on a 30 mol % CeO_2 70 mol % La_2O_3 mixed oxide

In a recent paper [1] we have shown that several intermediate phases resulting from the addition of CeO_2 to La_2O_3 exist. They were observed in the range 0 to 35 mol% CeO_2. Their formation appears to be related to the method of synthesis used, i.e. co-fusion in air of oxides and an oxidizing anneal at 1500° C. Such phases have never been seen in this system after solid-state reaction in the range 1050 to 1600° C [2, 3].

In the present work, we used a liquid-quenching method, by splat-cooling a mixed oxide whose intitial composition was 30 mol% CeO_2 in La_2O_3. The results were compared with those obtained from samples melted, cast and annealed at 1500° C. These samples give X-ray powder diffractograms as shown in Fig. 1 (4). A possible indexing scheme has been reported [1] leading to a hexagonal crystal structure with cell parameters of a = 3.93 Å, c = 106 Å. A comparison with hexagonal $A(La_2O_3)$-type diffractograms gives the correspondence of Miller indices between diffraction lines as shown in Table I.

This intermediate phase is homologous to the other members of the series observed in the composition range 0 to 35 mol% and may be seen as a polytypic form of $A(La_2O_3)$ crystal cell.

A hammer-and-anvil type splat-cooling method was used (Fig. 2). The molten balls (at the focus of a solar furnace) were struck strongly by the hammer against a water-cooled support [4]. Two parts can be distinguished in the material quenched in this way. One is in the form of 250 to 500 μm thick plates remaining between hammer and anvil. The other consists of very thin lamellae (20 to 30 μm) very quickly splashed out of the shock zone against the water-cooled support. Results obtained in other work with the same device on alumina–lanthanum sesquioxide systems [4] showed that these projected lamellae were the most quickly cooled part of the sample.

The thick plates were dark and increased in weight after an oxidizing anneal at 600° C. These phenomena are associated with a dissociated cerium oxide with the approximate formula $CeO_{1.93}$. The powder diagrams obtained are characteristic of the A-type structure (Fig. 1, 2). The hexagonal cell parameters are a = 3.91 Å, c = 6.19 Å. The difference between these and the pure $A(La_2O_3)$ cell size is due to the large content of CeO_{2-x} in La_2O_3.

The projected lamellae were transparent and light in colour, no increase in weight was observed by T.G.A., therefore, it may be assumed that cerium oxide is stoichiometric (CeO_2). Diffraction patterns obtained from these lamellae and from annealed (1500° C) melted samples were very similar (Fig. 1, 3).

A surprising chemical and structural analogy is, therefore, apparent between the results of splat-cooling and oxidizing-annealing at 1500° C. As already shown, the quenching effect of a more moderate cooling process (thick lamellae) was quite different: hypostoichiometric cerium dioxide, hexagonal A-type solid solution. Interpretation of these phenomena is now under investigation. However, it may be noted that the splat-cooling process submits the sample to considerable thermal and mechanical stresses over a very short time. Consecutively, it may be assumed that the splat-cooling quench would cause a sufficiently strong undercooling effect to lead to a liquid $\rightleftharpoons$ cristalline solid transition, at a temperature compatible with the formation of the ordered intermediate phases. This effect does not exist in "thick lamellae".

The complete oxidation of cerium (CeO_2) after "splat-cooling" may be considered as a quenched state of the liquid stoichiometry. Another explanation would be that the undercooled liquid is particularly reactive with respect to oxygen in air, in a temperature range compatible with complete oxidation of cerium. On the other hand, it is of interest to note that in the case of other oxide systems (i.e. Al_2O_3–Ln_2O_3) [4], the same method of splat-cooling led to the formation of non-crystalline materials.

TABLE I

$A(La_2O_3)$	Intermediate phase	$A(La_2O_3)$	Intermediate phase
(002)	(0.0.34)	(103)	(1.0.49), (1.0.53)
(101)	(1.0.15), (1.0.19), (1.0.21)	(112)	(1.1.34)
(102)	(1.0.32), (1.0.36), (1.0.38)	(201)	(2.0.15), (2.0.19)
(110)	(110)		

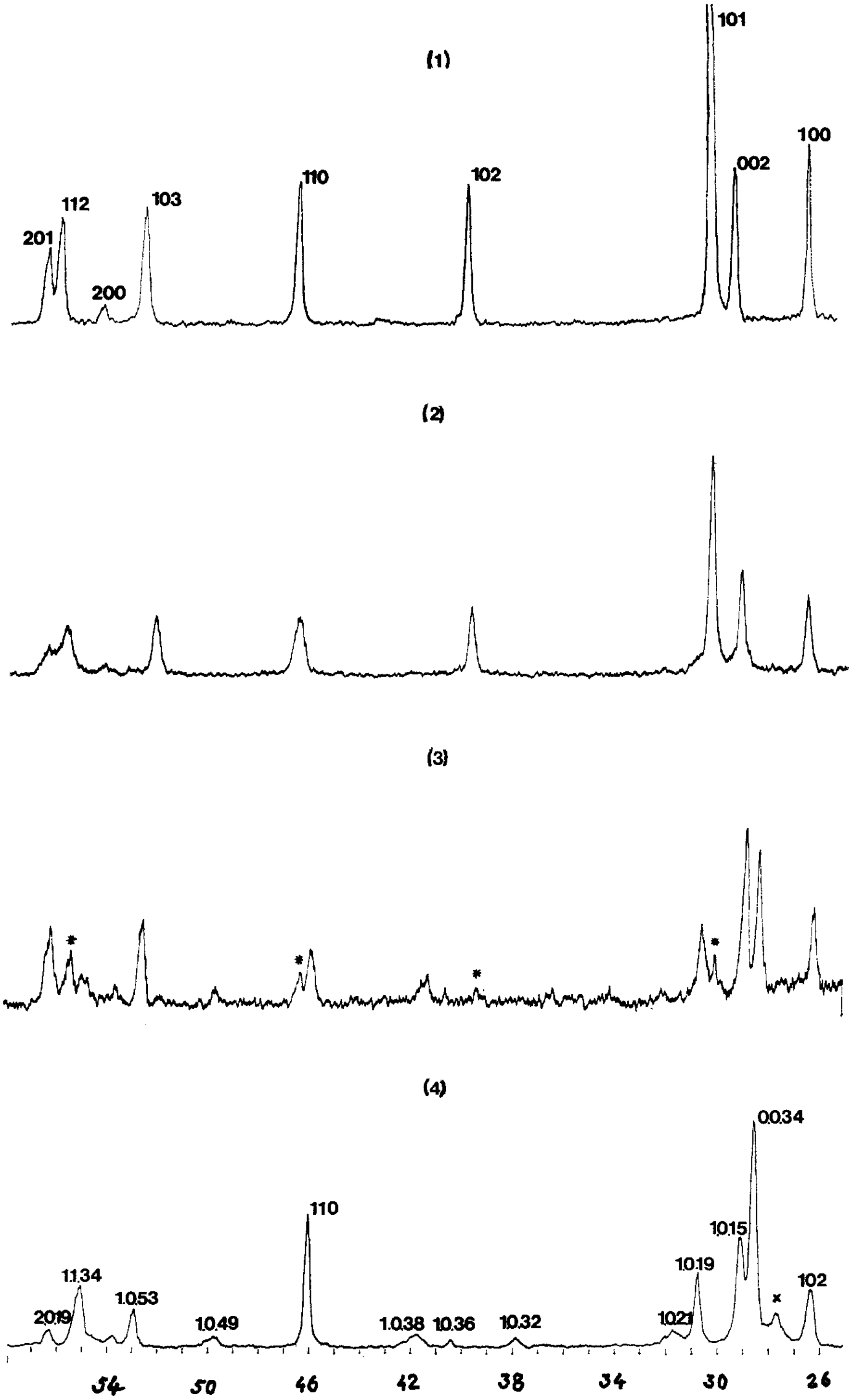

Figure 1 X-ray powder diffractograms (2θ – Cu$K\alpha$) of La_2O_3 samples containing 30 mol % CeO_2. (1) Hexagonal structure, A(La_2O_3). (2) Liquid-quenched, thick part: hexagonal A-type structure. (3) Liquid-quenched thin projected lamellae: hexagonal intermediate phase (*: A-type hexagonal lines). (4) 1500° C-annealed mixed oxide after air-melting: hexagonal intermediate phase obtained (X: fluorite type CeO_2 solution).

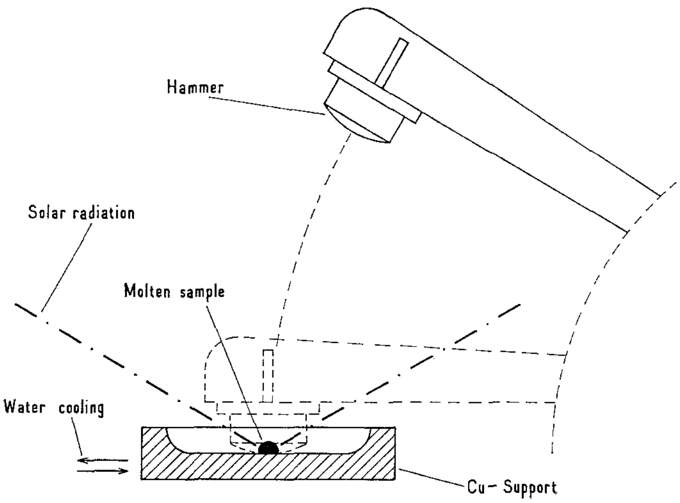

Figure 2 Splat-cooling apparatus associated with a solar furnace.

References

1. F. SIBIEUDE, D. HERNANDEZ and M. FOEX, *Compt. Rend. Acad. Sci. Paris* **278** **C** (1974) 1279.
2. C. BAUER and H. GRADINGER, *Z. Anorg. Allgem. Chem.* **276** (1954) 209.
3. T. C. PARK and D. M. J. BEVAN, *Rev. Chim. Min.* **10** (1973) 15.
4. J. COUTURES, F. SIBIEUDE, A. ROUANET, M. FOEX, A. RECOLEVSCHI and R. COLLONGUES, *Rev. Int. Hautes Temp. Réfract.* **4** (1974) in press.

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Growth of alumina by oxidation of amalgamated aluminium sheets

The work reported in this note developed from studies on aluminium amalgam to develop a technique for making ohmic contacts on ceramics and semiconductors. Various workers have reported the growth of alumina powder by exposing aluminium sheet wetted by mercury to moist air or to water. Usually mercury does not wet aluminium sheet. Watson *et al.* [1] have used 1% aqueous mercuric chloride solution for wetting aluminium sheet with mercury, while Bennett *et al.* [2] wet the aluminium sheet first with dilute HCl and then treated the HCl-wetted portion with a drop of mercury. Dilute hydrofluoric acid [3] has also been used to wet the aluminium sheet with mercury. Peri and co-workers [4-6] used a solution of glacial acetic acid and red mercury oxide in water to grow alumina powder from aluminium sheet. Bruce *et al.* [7] reported the instantaneous formation of alumina by wetting aluminium sheet with gallium and then reacting this gallium-wetted sheet with water. Numata [8] reported the growth of alumina on AlSb crystals in moist air or water. In the case of magnesium, Bennet *et al.* [2] observed an instantaneous formation of magnesium oxide powder by wetting magnesium with mercury and by exposing the mercury wetted magnesium sheet to moist air.

In the work reported here, we used both dilute HF and dilute HCl to wet the surface of aluminium with mercury and then left the amalgamated aluminium in moist air. Voluminous growth of fibrillar alumina was then observed. It was found that the completion of growth of alumina in moist air from the aluminium sheet wetted with dilute HF was faster than that from the aluminium sheet wetted with mercury with dilute HCl. The rate of growth at a particular humidity and temperature is shown in Fig. 1.

The growth of alumina powder for both the wetting agents HF and HCl, stopped after some time. Bennett *et al.* [2] attributed this to the formation of an intermediate phase at the