High temperature phase instability in yttrium orthoaluminate

Yttrium orthoaluminate doped with neodymium is of considerable interest as a potential laser material, but difficulties have been encountered in the Czochralski growth of single crystals suitable for this application. In particular, cracking is observed on cooling the crystals after growth and, on examination at room temperature the crystals are found to contain twins which impair their optical quality [1, 2]. This behaviour suggests that the crystals could undergo a structural transformation on cooling so it is clearly essential to characterize the high temperature behaviour of this material if it is to be successfully developed as a host lattice. The purpose of the present note is to report some preliminary results of an investigation into the high temperature structural properties of this oxide which indicate that phase decomposition occurs at high temperature under certain conditions.

Yttrium orthoaluminate, $YAlO_3$, is one of three congruent melting compounds reported to form in the mixed oxide system Y_2O_3-Al_2O_3 [3]. The garnet structure $Y_3Al_5O_{12}$ (YAG) having overall cubic symmetry has already proved highly successful as a laser material when doped with neodymium [4]. The third compound having the composition $Y_4Al_2O_9$ (hereafter referred to as YAM) is thought to have a monoclinic structure [5] but no attempt has yet been made to evaluate its potential as a laser host. The phase $YAlO_3$ (designated YAP) is orthorhombic and has a distorted perovskite structure with unit cell dimensions $a = 5.179$Å, $b = 5.329$Å and $c = 7.370$Å [6]. The main advantages of this compound in laser application are that the anisotropic optical properties associated with the low symmetry structure enable the laser gain and wavelength to be controlled by suitable choice of crystal orientation and that neodymium can be readily accommodated within the lattice during crystal growth [2, 7, 8].

In the present study, powdered samples from a neodymium-doped, Czochralski-grown single crystal of YAP were subjected to various heat-treatments and the subsequent room temperature X-ray patterns recorded. The heat-treatments were performed on a Netzsch DTA apparatus in a silicon carbide furnace. This equipment enabled the samples to be heat treated *in vacuo* or in a gaseous atmosphere at a controlled heating rate to preset temperatures and to be held there for given times. A heating rate of 5°C/min was used in all these experiments. The samples were subsequently furnace cooled at a cooling rate of approximately 25°C/min over the first 500°C.

The as-crushed material gave a well-defined X-ray pattern which indexed to the orthorhombic perovskite structure. Samples heated for ~ 2 h at temperatures up to 1290°C in vacuum, argon and air environments exhibited no change in the subsequent RT diffraction pattern. However, patterns taken from samples heated for a similar time above this temperature revealed extra reflections which became more numerous and more intense with increasing temperature; this was accompanied by a decrease in intensity of the YAP reflections with the eventual result that after a 2 h treatment at 1580°C, the YAP lines had virtually all disappeared. This behaviour was independent of the environment prevailing during the heat treatments. The *d*-spacings and relative intensities of the predominant reflections on the 1580°C pattern were in good agreement with those of the garnet structure YAG, and reflections from this phase could be identified on all the patterns from powders treated above 1290°C. However, not all the extra reflections corresponded to the YAG phase and the source of these new lines is at present unknown. Table I compares the *d*-spacings and intensities of the as-crushed YAP and YAG phases with those of the 1580°C pattern. Attempts to fit the extra reflections to the available data on the $Y_4Al_2O_9$ (YAM) phase, assumed to be monoclinic, have so far proved unsuccessful as has comparison with the well-documented compound Y_2O_3, which, if it was present, would imply a very extensive decomposition in order to produce one of the major constituents of the system. It thus seems likely that some previously unreported compound in the system is responsible for the observed extra reflections.

An examination of the kinetics of this thermal decomposition proves very interesting. The lack of any detectable thermal anomaly on the DTA trace during the heat-treatments suggests that the process is very sluggish, and it is clearly possible to prevent the reaction from occurring, since the starting material for the present study, grown in single crystal form, showed no evidence of other phases. The extent of the decomposition, which is apparently independent of the environment,

TABLE I Observed interplanar spacings and relative line intensities of YAP after heat-treatment at 1580°C for 155 min compared with those observed on as-crushed YAP and YAG. The intensities, determined from micro-densitometer traces, have been normalized to the strongest line (I = 100) on each film.

YAP					YAG		
	As-crushed		After 155 min at 1580°C				
hkl	*d*Å	*I*	*d*Å	*I*	*d*Å	*I*	*hkl*
			4.897	25	4.897	30	211
			4.230	10	4.237	10	220
101	4.180	5					
			4.047	10			
			3.872	< 5			
110	3.709	40	3.705	≪5			
			3.532	< 5			
			3.362	5			
111	3.315	20					
			3.203	15	3.207	20	321
			3.110	10			
			3.053	10			
			2.999	25	3.000	25	400
			2.906	5			
			2.788	30			
			2.732	10			
			2.681	100	2.682	100	420
020	2.661	25					
112	2.612	100	2.606	10			
200	2.582	25	2.583				
021	2.500	15					
			2.444	20	2.446	25	422
			2.348	5	2.351	5	431
211, 103	2.218	10					
			2.187	30	2.190	30	521
022	2.156	30					
202	2.115	35	2.115	20	2.120	10	440
113	2.046	10					
			2.024	5			
122	1.990	< 5					
212	1.968	< 5					
			1.944	35	1.946	35	611
			1.921	10			
			1.870	10			
220	1.854	50	1.852	10			
004	1.841	20					
			1.811	15			
023	1.802	30					
			1.792	5			
			1.769	10	1.768	5	631

depends on the treatment temperature and on the time held at that temperature. Thus, 5 min treatment at 1580°C yields an identical pattern to that characteristic of a 2 h treatment at 1390°C, and longer treatments at 1580°C show a progressive strengthening of the new reflections attributable to YAG and the unknown phase. Prolonged annealing periods at 1580°C and 2 h treatments at temperatures up to 1800°C increased the intensities from the unknown phase at the expense of the others, and resulted in the detection of yet more lines; whether these correspond to the previously detected unidentified phase is not yet clear, but once again they were not attributable to YAM or Y_2O_3. In some cases reflections from the unidentified phase observed in the 1580°C pattern were no longer detected after these extreme annealing conditions indicating that the behaviour at very high temperatures could be even more complex.

Mizuno and Noguchi [3] also reported that the YAP phase was unstable when heated at temperatures below 1600° C for periods of the order of 20 h, and assumed its stable region to be above this temperature [9]. They did not specify whether powder or bulk material was used. The YAP phase is now usually assumed to be a congruently melting compound mainly because it has proved possible to produce single crystals by Czochralski growth. While the twinning and cracking found to occur in these bulk crystals may be related to this thermal degradation detected in powders, it seems more reasonable to attribute these effects to the observed anisotropic thermal expansion behaviour of this phase [10]. Bulk crystal chips of the present material showed no evidence of decomposition when subjected to similar heat treatments as the powdered samples, indicating that the reaction kinetics are strongly dependent on the surface to volume ratio of the sample. Thus, the reaction clearly proceeds much more slowly in the bulk than in the powdered material with the result that it has no significant effect during the time usually involved in the growth of single crystals by the Czochralski method. However, crystals deliberately held for prolonged periods at high temperature after growth tend to develop optical scattering centres and it is possible that the generation of these defects is related to the decomposition observed in the present material. This is one of the aspects of this reaction which is at present under investigation.

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Neodymium-doped glass-ceramic laser material

Since the time Maiman [1] demonstrated the first successful ruby laser, numerous transition metal and rare-earth-doped materials have been used as solid-state lasers. All these materials can be classified as either single crystals or as glasses. The reason for this, of course, is that most transparent inorganic materials fall into these two classifications.

This letter describes the first reported lasing of a transparent glass-ceramic host. The significance of this is the lasing of a two-phase material consisting of an anisotropic crystalline phase as well as a second isotropic glassy phase. The glass-ceramic host has some desirable physical properties for laser materials, such as the very low thermal expansion.

The glass from which the glass-ceramic was prepared has the following compostion in mol %: 73.14% SiO_2, 13.73% Al_2O_3, 8.69% Li_2O, 1.75% BaO, 1.51% TiO_2, 1.08% ZrO_2, and 0.10% Nd_2O_3. The glass was melted at 1600°C