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Formation of alkoxy-derived yttrium aluminium oxides

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Monoclinic $Y_4Al_2O_9$ and hexagonal $YAlO_3$ crystallize at low temperatures from amorphous materials prepared by the hydrolysis of yttrium and aluminium double alkoxides. Hexagonal $YAlO_3$ transforms to the cubic phase with a garnet structure as an intermediate product at elevated temperatures. The formation process of $YAlO_3$ is described. Solid solutions of hexagonal $YAlO_3$ crystallize between 50 and 62.5 mol % Al_2O_3. Yttrium aluminium garnet $Y_3Al_5O_{12}$(YAG) is formed by transformation of the solid solution.

1. Introduction

Three compounds exist in the system Y_2O_3–Al_2O_3: $Y_4Al_2O_9$, $YAlO_3$, and $Y_3Al_5O_{12}$ (e.g. [1]). The compound $Y_4Al_2O_9$ (monoclinic) was prepared by heating a stoichiometric mixture of Y_2O_3 and Al_2O_3 for a long periods of time above 1500 °C or by melting a specimen (mixture of Y_2O_3, $YAlO_3$ and $Y_4Al_2O_9$) obtained after heating for 2 h at 1400 °C [2–4]. Yttrium orthoaluminate, $YAlO_3$, has two modifications: orthorhombic (perovskite structure) [5], and hexagonal [6]. Although many investigations have been made of the formation of $YAlO_3$ by solid-state reaction, there have been conflicting results reported in the literature. Keith and Roy [7] reported the formation of $YAlO_3$ ($Y_3AlY(AlO_4)_3$) with a garnet structure ($3Y_2O_3 \cdot 5Al_2O_3 = Y_3Al_2(AlO_4)_3$ cubic) during the heating process. However, since their study, no further observation of this phase has been described. The formation of the orthorhombic modification is very complicated; it was formed as a first product [8, 9], one of the first products [3, 4] or an intermediate product [5, 7, 10]. On the other hand, the hexagonal modification was obtained only by coprecipitation; the hexagonal-to-orthorhombic transformation occurred at 950 °C [6].

Crystalline $Y_3Al_5O_{12}$ exists in the cubic form having a garnet structure. High temperatures are required to prepare pure $Y_3Al_5O_{12}$ as well as in other yttrium aluminates, by solid-state reaction. When the reactants were heated below 1600 °C, it could not be obtained as a single-phase but coexisted with $YAlO_3$ and Al_2O_3 [3, 4, 11]. Warshaw and Roy [9] reported the formation of $Y_3Al_5O_{12}$ only from hydroxides at 1700 °C. Viechnicki and Caslavsky [12] showed that Nd:$Y_3Al_5O_{12}$ was formed from mixed oxides after prolonged milling by heating for 3 h at 1650 °C. On the other hand, chemical methods permit the preparation of $Y_3Al_5O_{12}$ at lower temperatures. Yttrium-aluminium coprecipitates, which yield $Y_3Al_5O_{12}$ at 700 °C, have recently been prepared by the hydroxide precipitation method [13]. A systematic study of the formation of yttrium aluminium oxides was performed and is reported here, using amorphous materials prepared from alkoxides.

2. Experimental procedure

Aluminium isopropoxide $Al(OC_3H_7)_3$ was synthesized by heating aluminium metal (> 99.9% pure) in an excess of analytical grade 2-propanol with mercury (II) chloride (10^{-4} mol/mol metal) as a catalyst for 5 h at 82 °C [14]. Anhydrous yttrium chloride (99.9% pure) was dissolved in ethanol. As-received sodium was cleaned by removing a superficial crust; a known weight was dissolved in an excess of 2-propanol. The mixed solution was slowly added, with stirring, to the sodium isopropoxide solution. Under reflux for 3 h at 82 °C, a clear solution of yttrium aluminium isopropoxide and a precipitate of sodium chloride were obtained. After sodium chloride was removed by filtration, yttrium aluminium alkoxide was hydrolysed by adding a large quantity of aqueous ammonia (28 wt %) at room temperature. The temperature was slowly increased to 70 °C while the resulting suspension was stirred. The hydrolysis products of the various compositions shown in Table I were separated from the suspensions by filtration, washed more than ten times in water at 70 °C until the presence of chloride ions (tested by adding a silver nitrate solution) was no longer detectable, and dried at 120 °C under reduced pressure. The powders obtained are termed starting powders A–F. X-ray diffraction (XRD) analysis showed that all starting powders were amorphous. The particles were in the range 500–800 nm as measured by electron microscopy.

Thermogravimetry (TG) and differential thermal analysis (DTA) were conducted in air at a rate of 10 °C min^{-1}; α-alumina was used as the reference for the DTA. Heated specimens, cooled at a rate of 10 °C min^{-1} from DTA runs, were examined by XRD

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TABLE I Chemical composition of starting powders and crystallization and transformation temperatures

Starting powder	Composition (mol %) Y_2O_3	Composition (mol %) Al_2O_3	Mole ratio $Y_2O_3:Al_2O_3$	Crystallization temperature (°C)	Transformation temperature (°C)[a]
A	66.67	33.33	2:1	900–940[b]	
B	55	45		900–945[b]	
				870–900[c]	1000–1060
C	50	50	1:1	870–900[c]	1000–1060
D	42	58		890–935[c]	970–1050
E	37.5	62.5	3:5	890–950[c]	950–1050
F	32.5	67.5		890–950[c]	950–1050

[a] Transformation of hexagonal $YAlO_3$ phase into $Y_3Al_5O_{12}$ phase.
[b] Crystallization of $Y_4Al_2O_9$.
[c] Crystallization of hexagonal $YAlO_3$ phase.

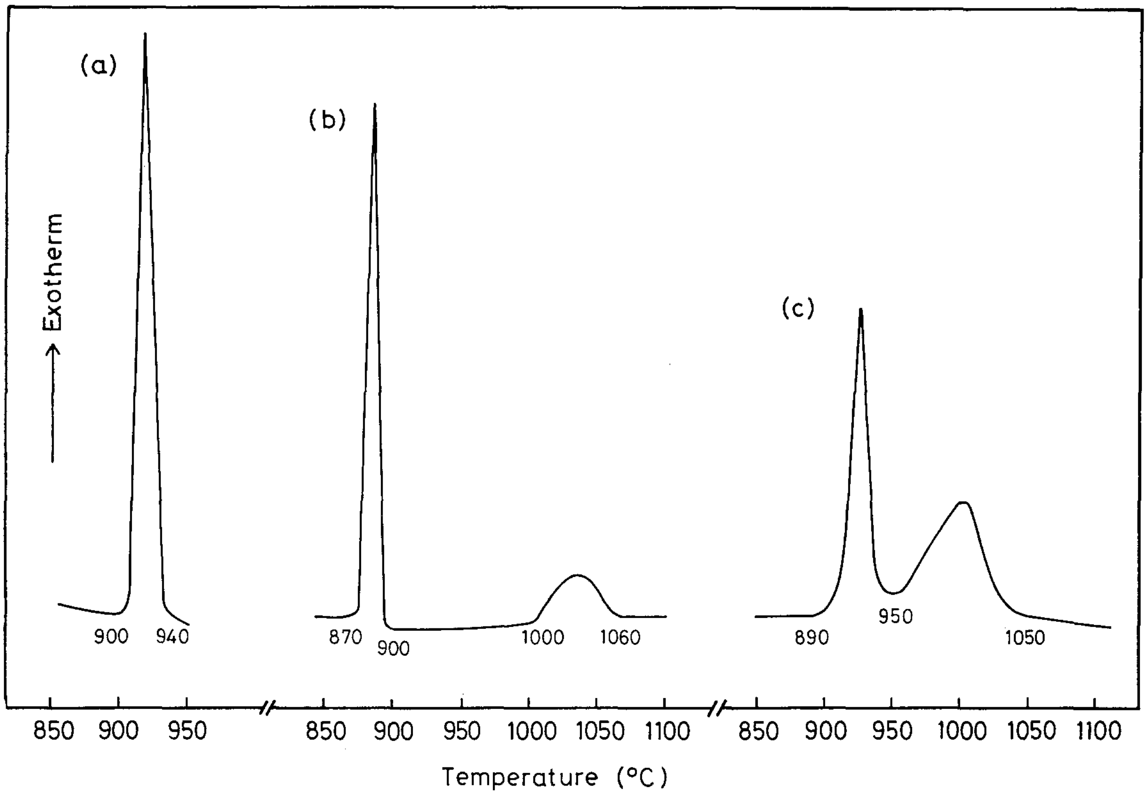

Figure 1 DTA curves for starting powders (a) A, (b) C and (c) E.

analysis using nickel-filtered CuK_α radiation. Interplanar spacings were measured with the aid of internal standard of silicon, and unit-cell values were determined by a least-squares refinement. Infrared spectroscopy was performed on a dispersion in potassium bromide, using the pressed-disc technique.

3. Results and discussion

3.1. Thermal analysis

Thermogravimetric examination for powders A–E showed weight decreases of 30.1%–33.5% at 460 °C. These can be attributed to the release of ammonia, absorbed water, hydrated water, and organic residues from the parent alcohol [15]. A weight decrease of 35.2% for powder F occurred to 535 °C. Although it was amorphous to X-rays, the specimen heated at 1200 °C showed the presence of α-Al_2O_3. Boehmite AlO(OH) gel was formed when $Al(OC_3H_7)_3$ was hydrolysed under the same conditions, followed by washing and drying; a weight decrease of the product occurred up to 560 °C. It seems reasonable to assume that powder F contains a small amount of AlO(OH) gel.

Fig. 1 shows the DTA curves for powders A, C and E. A sharp exothermic peak resulting from the crystallization of $Y_4Al_2O_9$ for powder A was observed at 900–940 °C. The starting powders C and E revealed two exothermic peaks. As will be described, the first exothermic peaks were found to result from the crystallization of hexagonal $YAlO_3$ ($YAlO_3$ solid solution) and the second exothermic peaks from the hexagonal-to-cubic phase transformation for powder C and from the hexagonal phase transforming to $Y_3Al_5O_{12}$ for powder E. The temperatures of crystallization and transformation of each starting powder are listed in

Table I. With increasing Al_2O_3 between powders C and E, the end temperature of crystallization was shifted to higher temperatures; on the other hand, the starting temperature of transformation moved to lower temperatures. No peaks for any of the starting powders were detected in the cooling process.

3.2. Formation of $Y_4Al_2O_9$

The starting powders A–F, being amorphous, did not exhibit significant change in structure up to the temperatures of the first exothermic peaks. The specimens from powder A heated to temperatures above the peak gave an XRD pattern characteristic of $Y_4Al_2O_9$. The X-ray data for the compound obtained by heating for 1 h at 940 °C were in good agreement with those reported [16]. The diffraction lines were indexed as a monoclinic unit cell with $a = 1.112$ nm, $b = 1.047$ nm, $c = 0.7392$ nm, and $\beta = 108.60°$. The compound $Y_4Al_2O_9$ was found to form at low temperatures from an amorphous material prepared by the alkoxy method.

3.3. Formation and transformation of $YAlO_3$

Hexagonal $YAlO_3$ from starting powder C crystallized at 870–900 °C; only the hexagonal modification was observed up to 1000 °C. It was transformed to the cubic form between 1000 and 1060 °C. The specimen heated at 1060 °C showed the XRD pattern of the cubic form having a garnet structure whose ideal formula is $Y_3Al_5O_{12}$ ($Y_3Al_2(AlO_4)_3$). The X-ray data for the cubic form with $a = 1.211$ nm are presented in Table II and compared with those of $Y_3Al_5O_{12}$ [17]. Keith and Roy [7] reported that an equimolar mixture of Y_2O_3 and Al_2O_3 gave a phase with the same structure at 1600 and 1700 °C and suggested that this indicates a solid solution of the type $Y_3AlY(AlO_4)_3 = YAlO_3$. The present results also suggest that the garnet structure is tolerant not only to Al^{3+} in both six-fold and four-fold coordination [18] but also to replacement of half of the six-coordinated aluminium by yttrium, as represented by the formula $Y_3AlY(AlO_4)_3$. According to the data of Keith and Roy [7], the cubic form transforms into the orthorhombic modification after heating for 2 h at 1800 °C. However, although in the present study no thermal activity was detected in the DTA curve, the XRD lines of $Y_4Al_2O_9$ began to appear in the specimen heated at 1080 °C, and the intensity of the lines increased with increasing temperature up to 1200 °C; this result indicates that the cubic form decomposed into $Y_4Al_2O_9$ and $Y_3Al_5O_{12}$. After completion of the decomposition, the orthorhombic modification was formed by solid-state reaction between both compounds. Single-phase orthorhombic $YAlO_3$ was obtained by heating for 1 h at 1650 °C. From the above results, the formation process of alkoxy-derived $YAlO_3$ can be summarized as shown in Table III. When powder B was heated at 1060 °C, a mixture of $Y_4Al_2O_9$ and cubic $Y_3Al_5O_{12}$ phase was formed.

Table IV compares the infrared spectral data of the cubic form of $YAlO_3$ and $Y_3Al_5O_{12}$ [19]; these represent the same spectral pattern, although the absorption bands in the cubic form are located at lower frequencies than those of $Y_3Al_5O_{12}$. On the basis of the data of $Y_3Al_5O_{12}$ [19], the bands at 790, 730 and 697 cm^{-1} are due to the stretching vibrations of AlO_4

TABLE II X-ray diffraction data for the cubic form of $YAlO_3$ and $Y_3Al_5O_{12}$

$YAlO_3$ (cubic)[a]		*hkl*	$Y_3Al_5O_{12}$ (cubic)[b]	
d(nm)	I/I_0		*d*(nm)	I/I_0
0.494	40	211	0.4905	27
0.428	10	220	0.4247	7
0.324	20	321	0.3210	19
0.303	30	400	0.3002	27
0.2707	100	420	0.2687	100
		332	0.2561	< 1
0.2471	30	422	0.2452	20
0.2374	10	431	0.2355	6
0.2210	25	521	0.2192	23
0.2140	5	440	0.2122	5
0.1964	25	532	0.19474	26
		620	0.18994	< 1
		541	0.18536	< 1
0.1785	5	631	0.17705	2
0.1748	20	444	0.17330	17
		543	0.16988	< 1
0.1679	35	640	0.16652	31
0.1648	10	721	0.16338	9
0.1618	30	642	0.16046	28
0.1538	5	651	0.15247	4
0.1213	20	800	0.12006	10

[a] $a = 1.211$ nm.
[b] $a = 1.200\,89$ nm.

TABLE III Reaction process for alkoxy-derived $YAlO_3$

$$\text{Amorphous material} \xrightarrow[870\text{–}900\,°\text{C}]{\text{crystallization}} \text{Hexagonal} \xrightarrow[1000\text{–}1060\,°\text{C}]{\text{transformation}}$$

$$\text{Cubic (ss)} \xrightarrow[1080\text{–}1200\,°\text{C}]{\text{decomposition}} Y_3Al_5O_{12} + Y_4Al_2O_9 \xrightarrow[1200\text{–}1650\,°\text{C}]{\text{solid-state reaction}}$$

Orthorhombic

TABLE IV Infrared spectral data for the cubic form of $YAlO_3$ and $Y_3Al_5O_{12}$

Band	Wave number (cm^{-1})	
	$YAlO_3$ (cubic)	$Y_3Al_5O_{12}$ (cubic)
ν (AlO_4)	786 s	790 s
	718 s	730 s
	689 m	697 s
ν (AlO_6)	562 m	567 s
	510 m	514 s
	455 s	478 s
	427 m	434 m
δ (AlO_4)	389 m	397 m
or	368 m	380 m
ν (Y–O)	350 m	335 m

Note: s = strong and m = medium; ν = stretching vibration and δ = bending vibration.

tetrahedra, the bands near 500 cm^{-1} to stretching vibrations of AlO_6 octahedra, and the bands in the 300–400 cm^{-1} range to either bending vibrations of AlO_4 tetrahedra or Y–O streching vibrations. Accordingly, the absorption bands of the cubic form were assigned, as shown in Table IV, by reference to the data of $Y_3Al_5O_{12}$.

3.4. Formation of hexagonal $YAlO_3$ solid solution

Single-phase hexagonal $YAlO_3$ from powders C–E was formed at temperatures after each first exothermic peak, although the intensity of the XRD lines decreased with increasing Al_2O_3; this phase was present up to the temperatures of the second exothermic peaks. Although no transitional phases of Al_2O_3 were recognized in the heating process, as noted above, a small amount of α-Al_2O_3 contained in the specimen when powder F was heated at 1200 °C. It is clear that hexagonal $YAlO_3$ solid solutions were formed between 50 and 62.5 mol % Al_2O_3. The lattice parameters of pure hexagonal $YAlO_3$ obtained from powder C were $a = 0.3678$ nm and $c = 1.054$ nm; the values agreed with those ($a = 0.3678$ nm, $c = 1.052$ nm) reported by Bertaut and Mareschal [6]. Compositional changes result in a significant variation in the cell dimensions. Fig. 2 shows the variation of lattice parameters of the hexagonal $YAlO_3$ phases; the lattice parameter a was relatively constant (0.3678 nm) regardless of composition, whereas c decreased from 1.054 nm to 1.046 nm with increasing Al_2O_3.

3.5. Formation of $Y_3Al_5O_{12}$

Single crystals having a garnet structure have been drawing considerable attention since the early 1960s, as they are important crystals in the laser, microwave, and ultrasonic device fields. On the other hand, until recently little attention has been paid to the fabrication of the ceramics [20–22], because high temperatures are required to prepare pure $Y_3Al_5O_{12}$. The transformation of the hexagonal $YAlO_3$ solid solutions occurred at the temperatures of the second exothermic peaks. The XRD analysis confirmed that single-phase $Y_3Al_5O_{12}$ from powder E was formed at 1050 °C. The lattice parameter of the compound after heating for 1 h at 1650 °C was estimated to be $a = 1.202$ nm, agreeing with the value (1.200 89 nm) reported [17]. Thus $Y_3Al_5O_{12}$ could be easily prepared by transformation of the hexagonal $YAlO_3$ solid solution formed from alkoxides in the mole ratio $Y^{3+}:Al^{3+} = 3:5$.

The hexagonal $YAlO_3$ solid solution formed from powder D was transformed into the $Y_3Al_5O_{12}$ phase at 970–1050 °C. The lattice parameter of the phase was $a = 1.206$ nm. The values of lattice parameters for the $Y_3Al_5O_{12}$ phases decreased with increasing Al_2O_3. The specimen when heated at 1200 °C was a mixture of $Y_4Al_2O_9$ and $Y_3Al_5O_{12}$.

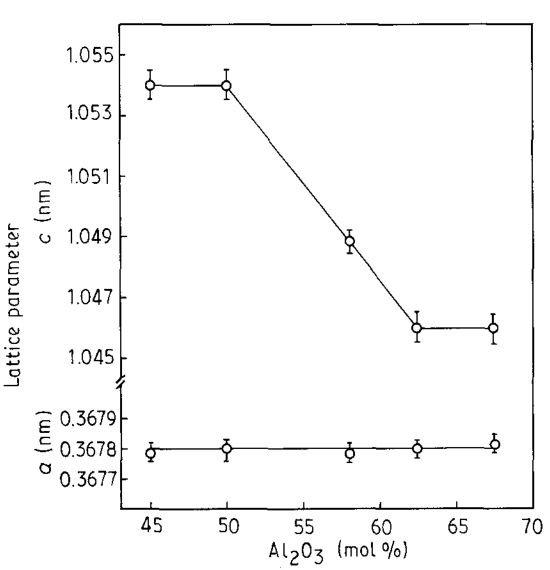

Figure 2 Lattice parameter for hexagonal $YAlO_3$ phases as a function of composition.

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