

Structure of the $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films prepared by pulsed-laser evaporation

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The structure of $\text{Ln}_2\text{Ti}_2\text{O}_7$ thin films prepared by pulsed-laser evaporation was studied using X-ray diffraction and transmission electron microscopy. The dependence of structure upon substrate temperature and ionic radius of the rare-earth elements was investigated. The variation of the crystal structure with substrate suggests that the condensation mechanism proceeded within the framework of the vapour–liquid–crystal scheme.

1. Introduction

Rare-earth titanates with the common formula $\text{Ln}_2\text{Ti}_2\text{O}_7$ have interesting optical and dielectric properties, and high thermal and chemical stability. Therefore thin films of these compounds may be used in optical and microelectronic devices. Multi-compound films made by vacuum deposition are sometimes non-stoichiometric. Accordingly, we have chosen the method of pulsed-laser evaporation which permits the growth of films with the same chemical composition as the source materials.

It is well known [1] that the rare-earth titanates exist in two structural types. From lanthanum to neodymium they have layered perovskite-type structure (monoclinic, $P2_1/m$) and from samarium to lutetium, pyrochlore-type structure (cubic, $Fd3m$). $\text{Sm}_2\text{Ti}_2\text{O}_7$ is transformed from the cubic to monoclinic state under high pressure and temperature [2].

2. Experimental procedure

A stoichiometric blend of the titania and rare-earth oxide was used to fabricate targets which were annealed in air at 1000°C for 10 h. Films were deposited, under a vacuum of 10^{-3} Pa, the vacuum itself being created by an oil diffusion pump, on to molybdenum substrates at different substrate temperatures up to 1500°C . Laser radiation ($\lambda = 1.06 \mu\text{m}$, $E = 300 \text{ J}$, $\tau = 10^{-3} \text{ s}$) was focused on the surface of the prepared target by means of a quartz lens ($F = 5 \text{ cm}$). Owing to the high density of power (10^7 W cm^{-2}) on the target surface and the impulse energy, the single laser impulse resulted in film deposition. The thickness of the films ranged from $0.2\text{--}0.5 \mu\text{m}$, depending on the distance between the target and substrate (the average distance was 2 cm) and the accuracy of focusing.

The phases of all the samples were determined by X-ray diffraction, using CuK_α radiation ($\lambda = 0.154178 \text{ nm}$). The least square method was used for the calculation of the lattice constants. Transmission electron microscopy (TEM) was used for dir-

ect observation and the electron diffraction study of the films. The samples for TEM were prepared by dissolving molybdenum substrate in a mixture of the sulphuric and nitric acids.

3. Results

Fig. 1 shows the phase composition of the rare-earth titanates in the films. Only the phases belonging to the $\text{Ln}_2\text{Ti}_2\text{O}_7$ composition are shown. At substrate temperatures up to 800°C , all films were amorphous. Increasing the temperature to 900°C leads to microcrystalline films with diffraction indicating a fluorite-type structure. A higher temperature leads to phases that are typical of the bulk materials: monoclinic from lanthanum to neodymium and cubic from samarium to lutetium. Samarium titanate forms two modifications that coexist in the temperature range $1400\text{--}1500^\circ\text{C}$. TEM shows that the crystal size for the

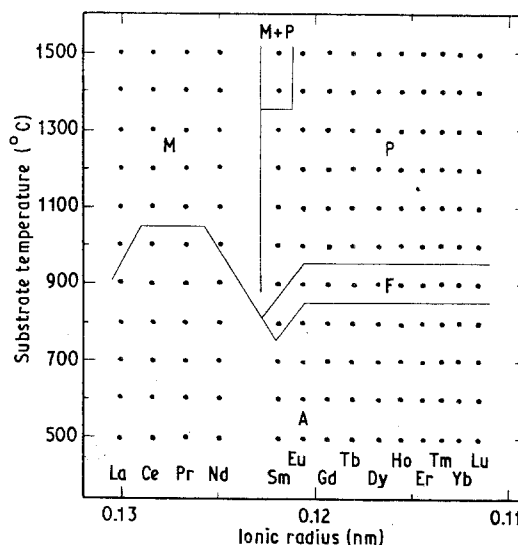


Figure 1 Phase identification in $\text{Ln}_2\text{Ti}_2\text{O}_7$ films versus substrate temperature and ionic radius. M, F, P, monoclinic, fluorite and pyrochlore phases, respectively; A, amorphous films.

all investigated titanates depends on temperature and could change from 10 nm at 900 °C to 1–1.5 μm at 1200 °C (see Fig. 2a, b). At lower temperatures, the crystal structure cannot be recorded by TEM.

X-ray diffraction shows complementary reflections at substrate temperatures near 1500 °C. They are related to the perovskite-type compounds LnTiO_{3+x} formed by partial oxygen loss from titania under vacuum and high temperature. The microstructure is represented by the large crystallites with the stoichiometric composition between which the perovskite phase is distributed with stacking faults evidently of nonstoichiometric origin (Fig. 2c).

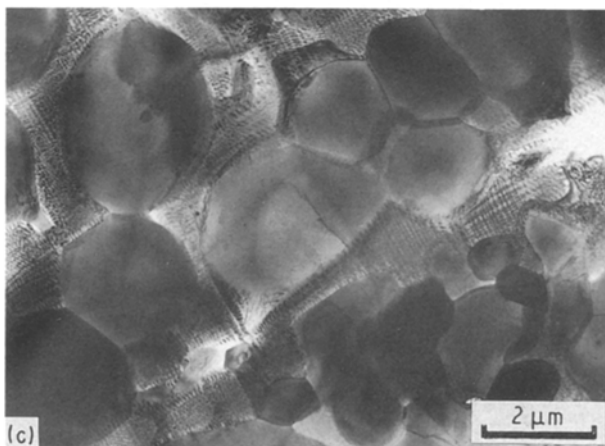
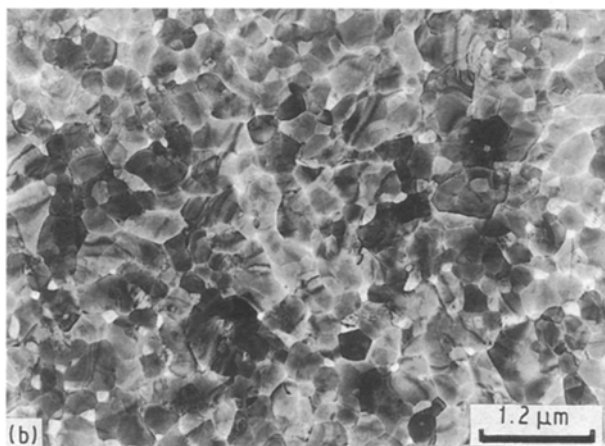
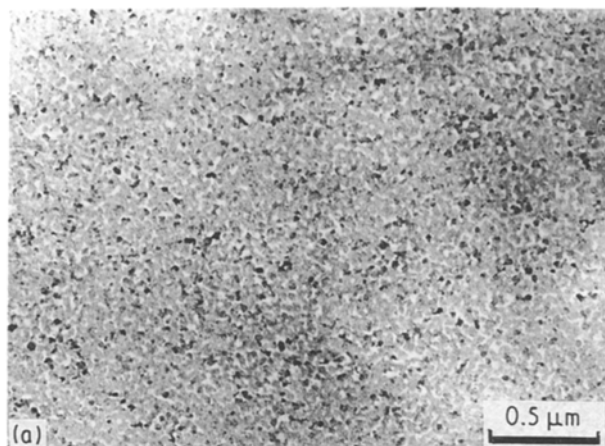


Figure 2 TEM images of the $\text{Ln}_2\text{Ti}_2\text{O}_7$ films at different substrate temperatures: (a) $\text{Tb}_2\text{Ti}_2\text{O}_7$, $T = 1000^\circ\text{C}$; (b) $\text{Lu}_2\text{Ti}_2\text{O}_7$, $T = 1200^\circ\text{C}$; (c) $\text{Er}_2\text{Ti}_2\text{O}_7$, $T = 1500^\circ\text{C}$.

The influence of oxygen nonstoichiometry is also noted for the cerium, praseodymium and terbium oxides. We used oxides CeO_2 , Pr_6O_{11} and Tb_4O_7 , but in films we obtained phases which are characteristic for the rare-earth elements with the oxidation number + 3. This was found using X-ray diffraction method. Only in the case of the cerium oxide was the ceria solid solution formed instead of amorphous films.

4. Discussion

The theoretical examination of the laser deposition process [3] leads to the conclusion that the high evaporation rate and high energy of the condensed particles lead to the condensation process via the vapour–liquid–crystal scheme. Because of the considerable thickness of the films and the low heat conduction of the rare-earth titanates, a liquid layer is formed during condensation. Subsequent crystallization proceeds under conditions of high-speed cooling. This reasoning allows us to deduce that the role of the substrate temperature is the main factor influencing phase composition. At low temperatures (20–800 °C) the cooling rate of the liquid becomes so high that crystal nucleation cannot take place and the films are amorphous. At intermediate temperatures, nucleation predominates over crystal growth. In that case, dispersed films with disordered structures are formed. The pyrochlore structure can be considered as the ordered defect fluorite structure, and we have recorded the fluorite-type reflections instead of pyrochlore-type. Increasing the temperature further leads to the growth of more perfect crystallites with similar structure to the bulk material. Reflections belonging to the pyrochlore-type structure appeared, and their intensity increased with temperature. The unit cell of

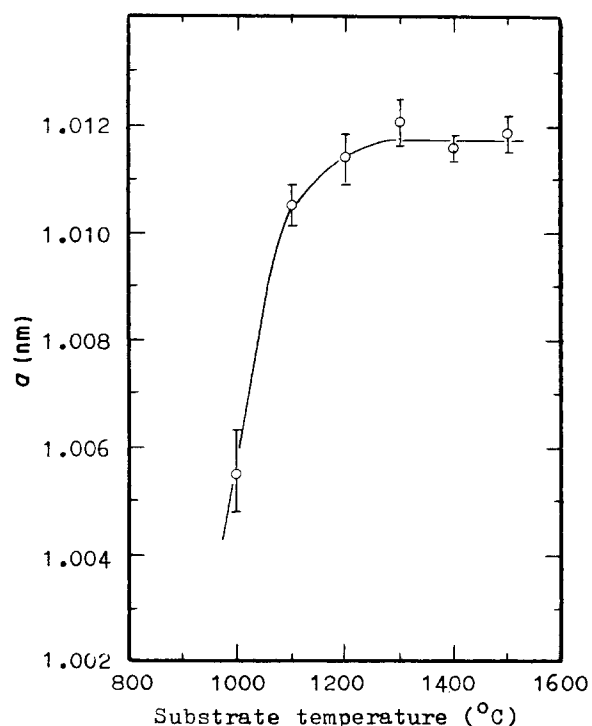


Figure 3 Unit cell of the $\text{Tb}_2\text{Ti}_2\text{O}_7$ films versus substrate temperature.

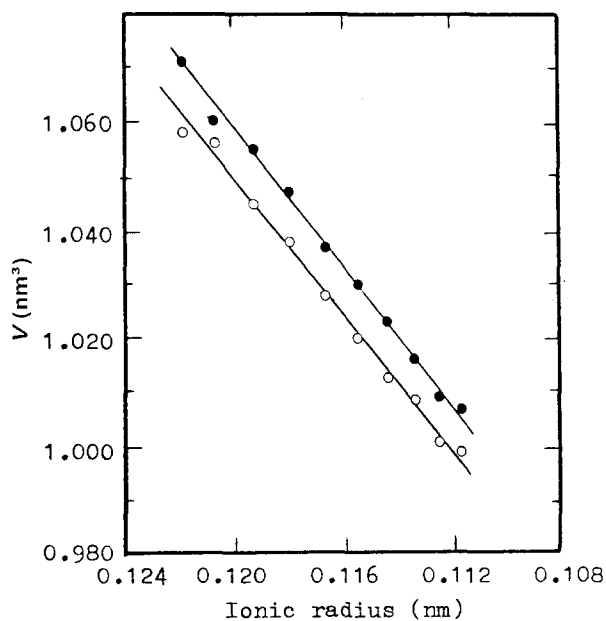


Figure 4 Unit cell volumes of the rare-earth titanates as a function of ionic radius: (○) present results, (●) Knop *et al.* [4].

the pyrochlores also grew and approached the equilibrium value at 1200 °C (Fig. 3).

Fig. 4 shows that the unit cell volumes of the titanates with pyrochlore structure are smaller in films than in massive materials. This is probably connected with the peculiarities of laser evaporation. The high-

velocity particle flow exerts considerable pressure on substrate and deposit. As a result, films can be more dense. A good confirmation of that assumption is the formation of the high-pressure phase – monoclinic $\text{Sm}_2\text{Ti}_2\text{O}_7$. Because the molar volumes of the cubic and monoclinic phases in films are equal, the phase transformation is made easier.

Finally, it should be mentioned that the non-stoichiometry of films is directly connected to the highest heat of oxide decomposition. The titania with the highest heat of decomposition among cerium, praseodymium and terbium oxides, loses oxygen at 1300 °C, and others form compounds with the oxidation number + 3 above 1000 °C.

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