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High Quality $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Superconducting Thin Films Grown by MOCVD

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Abstract. YBCO thin films have been grown by Metal Organic Chemical Vapour Deposition in a cold wall type reactor. The β -diketonates of yttrium, barium and copper are used as precursors. Films have been deposited on (001) MgO and (012) LaAlO₃ single crystalline substrates. The morphology is very dependant on the gas phase composition. Different oxygen partial pressures have been investigated. An increasing oxygen partial pressure - at a fixed deposition temperature - is found to increase the growth rate and to promote the growth of a-axis grains (grains with the c axis parallel to the substrate's surface). In our standard deposition conditions, $T_{\text{substrate holder}} = 875^\circ\text{C}$, $P_{\text{Total}} = 5$ Torr, and $P_{\text{O}_2} = 2$ Torr, high quality films are obtained, exhibiting $T_c \sim 91$ K (10% -90 % of the resistive transition) and $J_c(77\text{K}) \sim 5 \cdot 10^6$ A/cm². A trilayer structure YBCO/Y₂O₃/YBCO (900Å/100Å/900Å) has been grown on LaAlO₃ substrate, with the epitaxial relationship : $\langle 110 \rangle (001)\text{YBCO} // \langle 100 \rangle$ or $\langle 010 \rangle (001)\text{Y}_2\text{O}_3$. No misorientations have been found in the (a,b) plane. The trilayer exhibits a sharp superconducting transition ($\Delta T_c = 0.4$ K), with $T_c = 82.5$ K, and $J_c(77\text{K}) \sim 10^6$ A/cm².

1. INTRODUCTION

Since the discovery of suitable source materials, the MOCVD process has been proved to yield YBCO thin films of same quality as those grown by PVD techniques, exhibiting high critical current densities and low surface resistances [1-3]. The OMCVD process offers some advantages over the PVD techniques, such as the possibility to cover complex shaped surfaces or to easily change the composition of the coatings. The counterpart is however the important number of parameters which have to be controlled. A crucial point is the control of the gas phase composition which determines the growth and the final composition of the films. The CVD technique has also the particularity to permit a wide range of oxygen activities. The influence of this parameter has often been studied for the purpose of lowering the deposition temperature. It has been demonstrated that the deposition temperature can be reduced by lowering the oxygen partial pressure [4-5]. However, few studies have been devoted to the effect of the oxygen partial pressure on the growth of YBCO films.

In this paper, we discuss the influence of the gas phase composition and of the oxygen partial pressure on the film quality. The superconducting properties as well as the microstructure (surface morphology, detection of secondary phases, texture...) have been studied with respect to the growth conditions.

Important applications of the high- T_c superconducting thin films are in the area of microwave components. Electronic devices often require layered structures involving insulating materials. Y₂O₃ is a potential candidate as an intermediate insulator. Its capability to be used as a substrate for YBCO growth, or as a junction barrier in YBCO / insulator / YBCO sandwiched structures has been reported [6-7] but such multilayers were obtained by PVD processes (laser deposition or evaporation) and not by CVD. Y₂O₃ is chemically stable towards YBCO, which is important to have a proper HTSC/insulator interface. This stability is supported by the fact that Ytria precipitates may be formed in yttrium rich YBCO films [8]. The Y₂O₃ dielectric constant has been reported to be 13-17 [9], which fullfills the requirement of a low dielectric constant in the perspective of microwave applications. Using the MOCVD process, it is easy to take advantage of the yttrium source to grow *in situ* Y₂O₃ films. A trilayer YBCO/Y₂O₃/YBCO has been grown and studied.

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2. EXPERIMENTAL

A sketch of the CVD reactor is shown in Figure 1. The β -diketonates $Y(tmhd)_3$, $Ba(tmhd)_2$, and $Cu(tmhd)_2$ are used as sources materials and are evaporated in three independent furnaces. The reactor (cold wall type) is a cylinder ($\phi = 15$ cm), thermostated at $250^\circ C$. The substrate holder is an Inconel cylinder of diameter 12 cm, which is resistively heated up to $900^\circ C$. Argon is used as a carrier gas and oxygen is separately introduced in a mixing chamber.

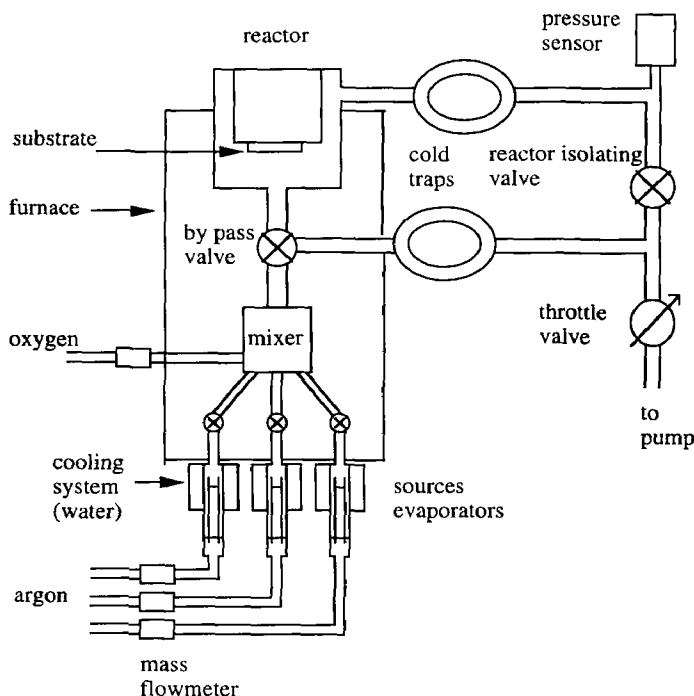


Figure 1 : Sketch of the CVD reactor

The amount of each material supplied in the reaction zone is controlled by the evaporation temperature in each furnace. Different gas phase compositions have been obtained by varying the evaporation temperatures in the yttrium and copper sources in the ranges $108.5^\circ C - 117.5^\circ C$ and $106.5^\circ C - 115.5^\circ C$ respectively. The barium source temperature has been set to $203^\circ C$. The composition of the gas phase has been determined from the precursor's weight-losses. Depositions have been made on 1 cm^2 (001) MgO or (012) $LaAlO_3$ substrates, using our standard deposition conditions :

Block heater temperature = $875^\circ C$

Total pressure = 5 Torr

Oxygen partial pressure = 2 Torr

Argon flow in each source = 40 cc/mn.

The deposition temperature has been estimated to be about $75^\circ C$ lower than the temperature of the block heater. After deposition, the films are cooled down to room temperature under atmospheric pressure of oxygen. The depositions at different oxygen partial pressures have been performed by using different oxygen flow rates during the growth.

The surface morphology of the films has been studied by Scanning Electron Microscopy. The microstructure has been studied by X ray diffraction analysis in the Bragg Brentano geometry ($\theta/2\theta$ scans). Rocking curves have been performed on the 007 peak of YBCO to check the quality of the epitaxy perpendicularly to the substrate surface. The in-plane orientation of the crystallites has been studied by

ϕ scans performed on the 102 /012 poles of YBCO. The thickness of the films deposited on MgO substrates is calculated from the intensity of the magnesium K_{α} peak via a calibration procedure, using Energy Dispersive X-ray spectrometry measurements. The superconducting properties have been studied with AC susceptibility measurements. The critical current density is measured as a function of the temperature, close to T_c , using the third harmonic response of the AC susceptibility [10].

3. Discussion with respect to the gas phase composition

The relative percentages of metallic elements - yttrium, barium and copper - in the gas phase are reported in this study as the gas phase composition.

The gas phase compositions are plotted in the diagram shown in figure 2. As evidenced by the X-ray diffraction patterns, all films contain the monoclinic copper oxide phase. The excess of copper in the films - even for a gas phase containing only 40 % of copper - indicates that the deposition of the copper element is more efficient than the deposition of yttrium or barium. The copper oxide phase results in precipitates, which are clearly visible on SEM micrographs. However the surface morphologies are very different according to the region of the diagram. Three typical morphologies are shown in figure 2. For a gas phase composition within : Y : 17% - 20%, Ba : 32% - 39%, Cu : 43.5% - 48.5%, the matrix is rather granular (photo 2-a). The morphology of figure 2-b with holes in a smooth matrix is typical of an yttrium rich film. A similar morphology is also observed on MgO substrates in case of yttrium excess. The high density of CuO lumps is due to the important excess of copper in the gas phase. The micrograph 2-c corresponds to a lower copper amount in the gas phase together with a high amount of yttrium. The CuO lumps are smaller in size and their density is lower. The matrix is rather smooth, with some holes and long shaped grains.

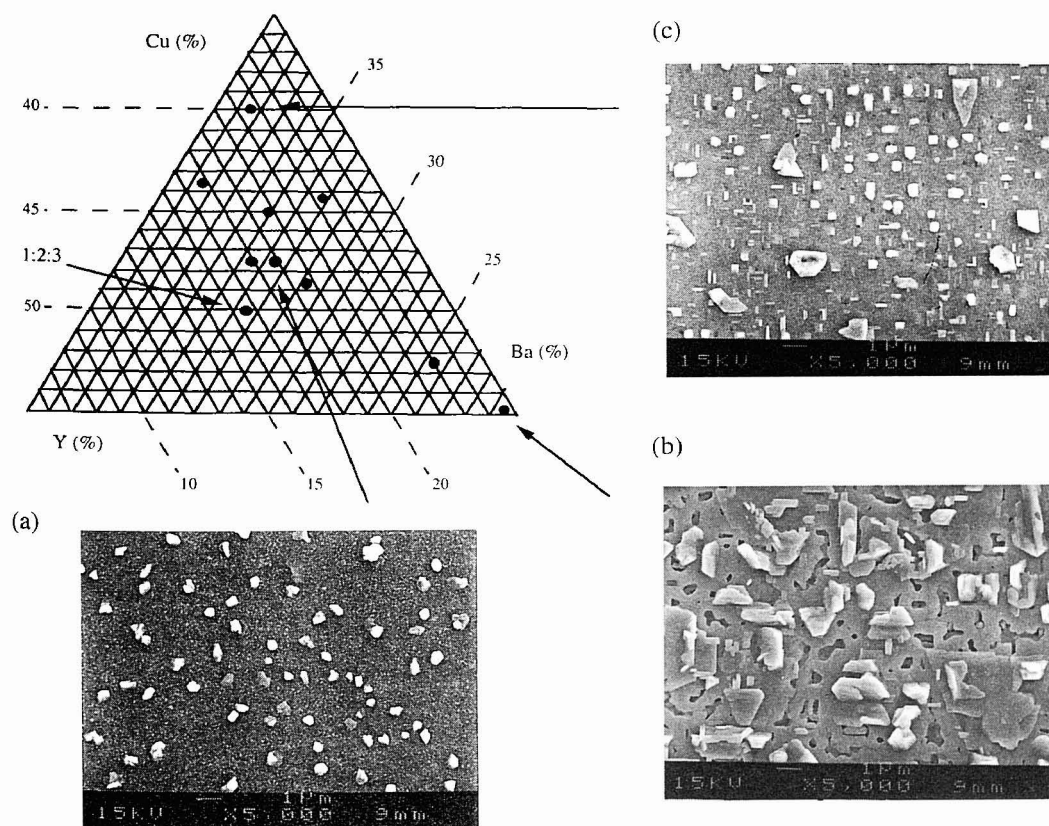


Figure 2 : Diagram of the gas phase compositions and SEM photos of typical related microstructures

The films are mainly oriented with the *c* axis perpendicular to the substrate surface but it was inferred from the ϕ -scans that all films contain some *a*-axis grains. The X-ray diffraction patterns of the films indicate the presence of secondary phases. For the case of yttrium and copper rich gas phases, the $Y_2Cu_2O_5$ phase is formed. It has not been possible to identify the minor extra-phases. Since the secondary phases are often textured, the recorded peaks do not necessarily correspond to the strongest lines of their powder diagram.

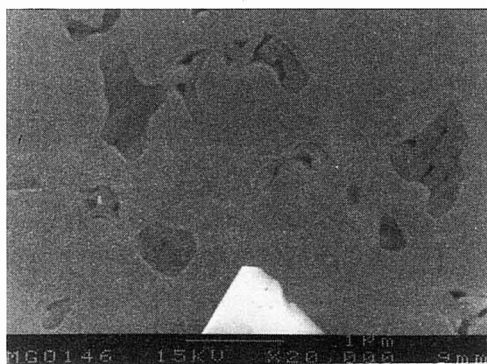
The critical temperatures (screening measurements) of the films range between 86.5 K and 89 K and the critical current densities at 77 K ranges between 10^5 A/cm² and $5 \cdot 10^6$ A/cm² except for one film (gas phase composition : Y : 17.9%, Ba: 38.6%, Cu : 43.5%) for which $T_c = 81$ K and $J_c(77K) = 2 \cdot 10^4$ A/cm². The X-ray profile analysis of the 00ℓ lines of this film shows broader diffraction peaks, which seems to indicate that this film was not fully oxygenated. This could explain its poorer superconducting properties.

This diagram emphasizes that a large range of gas phase compositions leads to superconducting films. However the richer yttrium and copper gas phases lead to the highest critical current densities. In such conditions, high critical temperatures (89 K) and high critical current densities ($5 \cdot 10^6$ A/cm² at 77 K) are obtained.

4. Effects of the oxygen partial pressure

The oxygen partial pressure has been varied between 0.2 Torr and 6 Torr, while keeping the deposition temperature constant ($T_{\text{subs. holder}} = 875$ °C) and the total pressure equal to 5 or 10 Torr. In this study, all films have been prepared with an excess of copper, since it has been shown that better transport properties are usually found in copper rich films. The depositions have been carried out on (001) MgO or (012) LaAlO₃ substrates for one hour. S.E.M. micrographs of YBCO films deposited at $P_{O_2} = 0.7$ Torr and 6 Torr are shown in figure 3. The surface morphologies of films deposited at 0.2 Torr and 0.7 Torr are very similar : the films exhibit a very smooth matrix (photo 3-a). As shown in figure 3-b, films grown at $P_{O_2} = 6$ Torr have a very different morphology, with "extra grains" on the matrix.

(a)



(b)

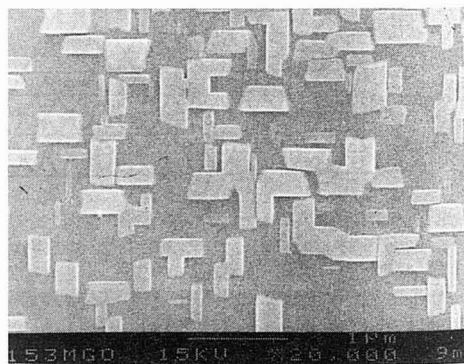


Figure 3 : SEM photos of films grown at different oxygen partial pressures (3-a : $P_{O_2} = 0.7$ Torr - 3-b : $P_{O_2} = 6$ Torr)

Texture analysis has evidenced an increasing amount of *a*-axis grains with increasing oxygen partial pressure. As inferred by the ϕ -scans performed on the 102/012 poles, no *a*-axis grains have been detected at low oxygen pressure (0.2 Torr and 0.7 Torr), whereas *a*-axis grains are found at 2 Torr and 6 Torr, in an increasing proportion. $\theta/2\theta$ scans have been performed on the two peaks 047 ($2\theta = 133.56^\circ$) and 407 ($2\theta = 136.64^\circ$) at both $\chi = 61^\circ$ and $\chi = 29^\circ$ (χ is the angle between the film normal and the incidence plane). Two peaks are observed at $\chi = 61^\circ$ but only the 407 peak is observed at $\chi = 29^\circ$, which means that

no b-axis grains (grains with the b axis perpendicular to the substrate surface) are detected. Hence, the increasing oxygen partial pressure only promotes a-axis growth.

The thicknesses of the films grown on MgO substrates have been measured. The growth rate as a function of the oxygen partial pressure is shown in figure 4. It is clear that the growth rate increases with increasing P_{O_2} , being multiplied by a factor of ~ 3 between 0.2 Torr and 6 Torr. Kanehori *et al.* [11] have reported a similar trend.

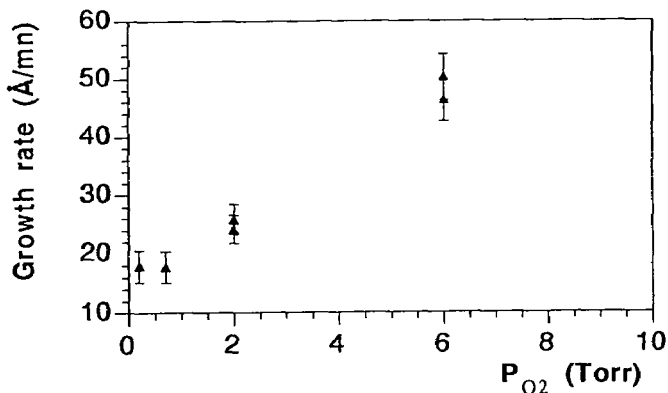


Figure 4 : Growth rate as a function of the oxygen partial pressure

The oxygen partial pressure may modify the decomposition process of the precursors during the growth, as well as the nature of the thermodynamical stable phases and the surface mobility of atoms or species. The increasing growth rate with increasing P_{O_2} may be explained by a more efficient decomposition process of the metal organic precursors with higher oxygen activity. The promotion of a-axis growth with increasing oxygen activity has been related to a decrease of the surface's mobility [12]. Chern *et al.* [13] have reported the same behaviour with N_2O used as an oxidizing agent.

All films exhibit a superconducting transition, with $\Delta T_c < 1$ K. However, a decrease of the critical temperature and an increase of the superconducting transition width are observed at high oxygen partial pressure. This decrease of the critical temperature with increasing P_{O_2} has been reported by other groups [5,11]. It may be related to the higher content of a-axis grains in the films prepared at high oxygen partial pressure. At P_{O_2} equal to 0.2 Torr and 0.7 Torr, critical current densities at 77 K above 10^6 A/cm² have been obtained.

5. YBCO/Y₂O₃/YBCO TRILAYER

We have grown an YBCO/Y₂O₃/YBCO trilayer on a LaAlO₃ substrate. The lower and upper YBCO layers, as well as the Y₂O₃ layer were deposited with the same conditions : $P_{Total} = 5$ Torr, $P_{O_2} = 2$ Torr and $T_{Subst. holder} = 900^\circ C$. During Y₂O₃ growth, the barium and copper sources were isolated from the reactor. Before depositing the upper YBCO layer, the copper and barium gas flows were firstly stabilized in the by-pass line before being switched to the reactor. After the deposition of the upper layer, the sample was cooled down to room temperature under one atmosphere of oxygen. The thicknesses of the YBCO layers are ~ 900 Å and the thickness of the Ytria layer is ~ 100 Å, as estimated from the growth rates.

The X-ray diffraction pattern of the trilayer is shown in figure 5. Only 00 l peaks of YBCO and Y₂O₃ are observed, which shows that the <001> direction is perpendicular to the substrate in both compounds. Rocking curves have been performed to check the quality of the alignment of the <001> direction along the substrate normal direction. The FWHM of the rocking curves performed on the 007 line of YBCO and on the 004 line of Y₂O₃ are 0.37° and 0.80° respectively, which shows the rather good quality of the epitaxy.

The in-plane epitaxy has been studied by ϕ -scans, performed on the 110 peak of LaAlO₃, on the 102/012 peaks of YBCO, and on the 222 peak of Y₂O₃. The ϕ -scans are shown in figure 6. It is apparent that very good in-plane orientation has been achieved, with the epitaxial relationship : YBCO <110> // Y₂O₃ <100> or <010>. The same relationship was found for an YBCO/Y₂O₃/YBCO trilayer grown on a MgO substrate

by activated reactive evaporation [7]. Y_2O_3 has a cubic structure, with the lattice constant equal to 10.70 \AA . The described orientation between YBCO and Yttria lattice may be related either to the Y-Y spacing (3.78 \AA), which matches within $\sim 3\%$ the YBCO lattice constants, or to the matching (within $\sim 2\%$) between half of the Y_2O_3 lattice constant $a/2 = 5.35 \text{ \AA}$ and the diagonal of YBCO lattice. The $\theta/2\theta$ diffraction pattern has also revealed the presence of Y_2BaCuO_5 phase ("211" phase) in the film, with several peaks, which are usually not observed in single YBCO layers.

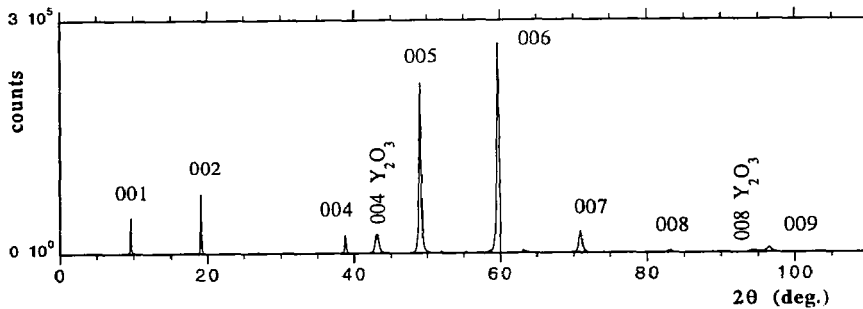


Figure 5 : X-ray diffraction pattern of the YBCO/Y₂O₃/YBCO structure using $FeK\alpha$ radiation (The diffraction ranges corresponding to the substrate lines - 012 line : $2\theta = 28^\circ - 31^\circ$ and 024 line : $2\theta = 60^\circ - 63^\circ$)

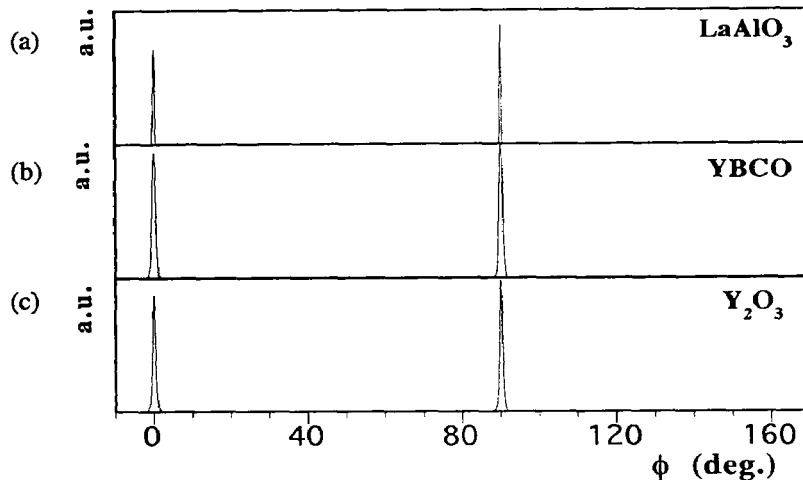


Figure 6 : ϕ -scans - (a) 110 peak of $LaAlO_3$, (b) : 102/012 peak of YBCO ($\chi = 56.7^\circ$), (c) : 222 peak of Y_2O_3

The trilayer exhibits a critical temperature of 82.5 K (screening measurement) but with a sharp superconducting transition, $\Delta T_C = 0.4 \text{ K}$, which shows that the oxygen content of the superconducting YBCO phase is homogeneous. The critical current density has been calculated to be $\sim 10^6 \text{ A/cm}^2$ at 77 K . This shows that high quality SIS layered structures can be grown by the CVD process. Recently, superlattices of YBCO/PBCO/YBCO have been successfully grown by this process [14].

6. CONCLUSION

High quality YBCO thin films have been prepared by MOCVD, exhibiting $T_C \sim 91 \text{ K}$ (resistive transition) and $J_C(77K) \sim 5 \cdot 10^6 \text{ A/cm}^2$. It has been shown that a large range of composition of the gas phase during

film growth leads to high quality superconducting films. Even with a low copper concentration in the gas phase (40%), a high copper content is observed in the layers, which is an indication of a higher deposition yield of the copper element compared with the yttrium and barium. This is related to the lower thermal stability of the copper compound. Different oxygen partial pressures have also been tested. An increase of the oxygen partial pressure is found to increase the growth rate and to promote the growth of a-axis grains. We finally reported the successful growth of an YBCO/Y₂O₃/YBCO trilayer, exhibiting a sharp superconducting transition ($\Delta T_c = 0.4$ K), $T_c = 82.5$ K and J_c (77 K) $\sim 10^6$ A/cm². The epitaxial relationship is : $\langle 110 \rangle$ (001)YBCO // $\langle 100 \rangle$ or $\langle 010 \rangle$ (001)Y₂O₃, with no misorientations in the (a,b) plane.

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