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Focused ion beam imaging of grains in Al–Li–Cu quasicrystal

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Abstract. We report the observation of grain structures, as well as their evolution following annealing, in Al–Li–Cu quasicrystal single-phased samples. The investigation is performed by using scanning ion microscopy employing focused ion beam imaging from secondary electrons. On annealing, the grain sizes increase through the recrystallization process. Regular grain boundaries are observed. Their orientation and stability are discussed in relation with the Al–Li–Cu quasiperiodic structure.

1. Introduction

The structure quality is a major concern in quasicrystal elaboration. The fabrication of large mono-crystalline samples requires the possibility of monitoring, controlling and understanding their growth process. For this purpose it is essential to be able to characterize in a simple and direct way, at various stages of the sample growth, the evolution of the microstructure—grain morphology, grain size and grain orientation—that will provide information for the understanding of the growth mechanism. This in turn will determine the optimal choice for the thermal treatment corresponding to the best sample quality.

Focused ion beam (FIB) imaging can be used to observe microstructures in crystals (Gupta *et al* 1992, Barr *et al* 1992). It has been shown that FIB imaging has the ability to produce highly contrasted images of fine grains that can hardly be resolved using conventional scanning electron microscopy (Gupta *et al* 1992). The high image contrast is related to the ion channelling effect (Franklin *et al* 1988). When the direction of the incident ion beam approaches the direction of a dense plane, ions are deflected between rows of atoms and they follow an oscillatory trajectory along the channelling direction (Lindhard 1965). Secondary electron yield is then strongly decreased (Colombie *et al* 1969). As a consequence, different grain orientations relative to the incident beam direction lead to large variations in ion-induced secondary electron emission.

Quasicrystal structures are strictly non-periodic but perfectly ordered. A computer study showed well defined lattice rows and planes, as well as the possibility of channelling for quasicrystals (Kupke *et al* 1991). As far as experiments are concerned, electron-induced x-ray emission angular variations along major symmetry axes have been reported and attributed to channelling effect (Shindo *et al* 1989). Direct observations of channelling in quasicrystals by measuring back-scattered ion yield variations around symmetry axes have

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been reported as well (du Marchie van Voorthuysen *et al* 1992, Carstanjen *et al* 1992). This demonstrated clearly that ion channelling can occur in a non-periodic quasicrystalline structure.

Here we report the observation of micro-grains, as well as the effect of annealing on the grains, in single-phased icosahedral quasicrystal Al–Li–Cu samples using FIB imaging. We would like to emphasize that the basic difference between our observation and the channelling observations on quasicrystals quoted above is that, in our case, the observation is space resolved. The FIB is deflected to scan the quasicrystal sample surface. Images formed using secondary electrons allow us thus to determine the spatial distribution of the secondary electron yield. Then we can visualize the quasicrystalline grains in single-phased samples.

2. Experiment

The experiments are performed using an Orsay Physics Canion† system ion source, connected to an ultrahigh-vacuum chamber. The ion gun incorporates a focusing column, comprising two lenses in a condenser-objective configuration. A beam of Ga^+ ions, derived from a gallium liquid metal ion source (LMIS), can be focused at energies up to 30 keV, with a current density reaching 1 A cm^{-2}. The best spatial resolution is better than 40 nm. A system of diaphragms allows us to focus larger spots for rapid processing, such as milling and sputtering, that does not need great precision. The beam can be deflected to scan a maximum area of about 200 μm $\times$ 200 μm. The microscopic imaging is achieved by collecting the secondary electrons, through an electron detector built from a scintillator and a cooled photomultiplier. The beam scanning and imaging processes are controlled by a micro-computer (Wang *et al* 1998).

The Al–Li–Cu quasicrystalline seeds, of composition Al_6Li_3Cu, are obtained using the method described by Dubost *et al* (1986, 1988). They are obtained in the form of triacontahedral dendrites, embedded in eutectic phases (typically α-Al + Al_2LiCu). The samples, rich in quasicrystalline seeds, are taken from the mother ingot and cut in the form of cylinders 2 cm high and 1 cm in diameter. They are placed vertically in hermetically sealed stainless steel capsules. For the first stage of the process, they are heated just below the quasicrystalline phase melting temperature (about 615 °C) to melt the eutectic foreign phases, then solidified again through controlled slow cooling, up to several days, to favour the quasicrystalline phase growth. The mass density of the quasicrystalline phase is lower than that of the eutectic mixture but with a higher melting temperature, thus it floats on its eutectic liquid and solidifies preferentially at the top of the capsule. A negative temperature gradient is applied in the vertical direction to favour such solidification. So the samples grow vertically from the top to the bottom of the capsule.

Figure 1 displays an optical micrograph showing an area of the vertical cross section of a sample. The upper part displays a homogeneous zone. As a matter of fact, x-ray diffraction experiments show that the upper part of the samples after slow cooling consists entirely of the quasicrystalline phase. We can thus obtain centimetre-sized single-phased samples by using this method.

The final stage of the process consists of annealing the samples at 575 °C for several days to favour the grain growth through recrystallization. In order to prevent lithium loss from evaporation, the samples are maintained in ^{4}He gas, whose pressure reaches about 45 bars at high temperatures during the whole treatment.

† Canion is a trademark of Orsay Physics, 29, rue J Rostand, 91400 Orsay, France.

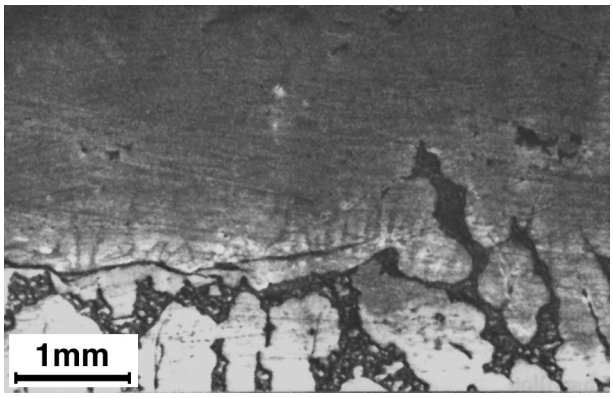

Figure 1. Optical micrograph showing the vertical cross section of a quasicrystalline Al–Li–Cu sample, obtained after slow cooling. The upper part is single phased.

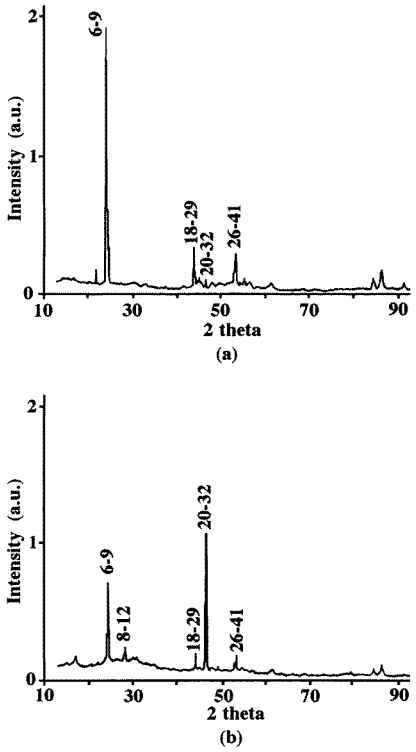

Figure 2. Two x-ray diffraction diagrams showing the reflections recorded on a Al–Li–Cu sample using Co Kα radiation. In (a) the incident x-ray beam scans a sample surface perpendicular to the sample cylinder axis. In (b) the incident beam scans a surface parallel to the cylinder axis. The Cahn–Shechtman–Gratias notation is used for indexing.

Finally, we notice that the quasicrystalline samples, both before and after the 575 °C isothermal treatment, are textured. X-ray diffraction displays pronounced threefold symmetry along the vertical (cylinder axis) direction. Two diffraction diagrams are presented in figure 2 (see also Degand 1992), where the Cahn–Shechtman–Gratias notation (Cahn *et al*

1986) is used for indexing. The diagram in figure 2(a) is obtained by recording the reflections when the incident x-ray beam is scanning a sample surface perpendicular to the cylinder axis, while the diagram in figure 2(b) is recorded when the beam is scanning a surface parallel to this axis. The experiments are realized in a diffractometer using the Co Kα radiation. The principal peak corresponding to the threefold axis (6–9) of the icosahedral symmetry is much stronger in figure 2(a) than in figure 2(b). One can also notice that the peaks corresponding to other major symmetry axes of the icosahedral group, 20–32 for twofold axes and 18–29 for fivefold axes, are very weak in figure 2(a), but the 20–32 peak, almost invisible in figure 2(a), is very strong in figure 2(b).

The upper parts of the samples are cut from the cylinder and roughly mechanically polished. They are then cleaned in an acetone bath under ultrasound before being introduced into the FIB chamber. For imaging, the beam current is adjusted to about 10 pA, at a beam energy of 25 keV. The sample surface is adjusted normal to the beam axis, with a maximum deviation of less than $\pm 0.5^\circ$. The beam deflection angle variation due to scanning is below 0.02°.

One of the advantages of the FIB imaging is related to sample preparation. Because of the ion milling process, a very rough polishing is required only. It is difficult to observe the grains when the samples are scanned first, but contrasted zones appear after a short scanning time, due to the sputtering of the sample surface. The images are taken after a scanning of several minutes, when the microstructures are clearly visible. Scratch lines due to the sample mechanical polishing can be seen in some of the images, but it is clear that they do not prevent us from observing the grain contrast. On the contrary, this shows that well defined images can be obtained even on rough surfaces.

In order to check the possibility of imaging the channelling on Al–Li–Cu quasicrystal samples, we first localized a zone where we can observe two grains, clearly distinguished by a crack. The FIB scanning image (figure 3) shows a pronounced contrast between these two grains (the crack is indicated by two arrows). This indicates the difference in secondary electron yield, that is related to the grain orientations relative to the ion beam. The right part, darker in contrast, corresponds to the grain that is in a better channelling position with respect to the beam direction, compared to the left part that yields a higher density of secondary electrons. Indeed, the yield difference between these two grains reaches 10%.

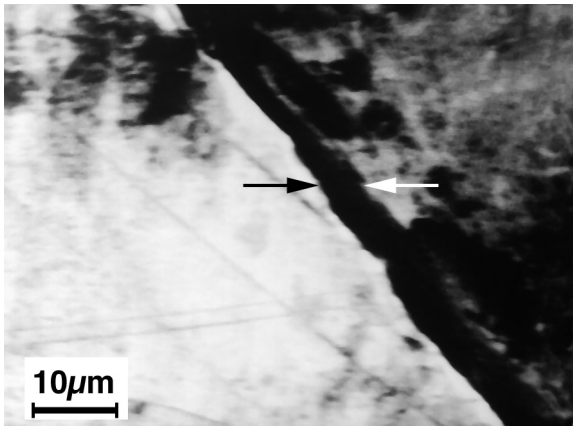

Figure 3. FIB scanning image showing the contrast between two quasicrystal grains, separated by a crack. The crack is indicated by two arrows.

3. Results

Figure 4 shows two images taken on single-phased samples obtained after slow cooling. The incident beam is aligned along the sample growth direction (parallel to the cylinder axis). The grain contour can be clearly defined. Figure 4(a) shows a distribution of small zones of about 30 μm in size, with different contrast levels. These zones are located in the intermediate region between two larger grains. This image suggests some remnants of the original dendritic growth. Figure 4(b) displays larger zones, whose sizes approach 100 μm. Besides, we can distinguish in this figure two regular boundaries between two zones, corresponding to two quasicrystal grains, as indicated by the arrows. The two boundaries form an angle θ, whose value is estimated as 120 ± 1 degrees. In a general way, for the slow-cooled samples, we observe that the grain size, for the most part, does not exceed 100 μm.

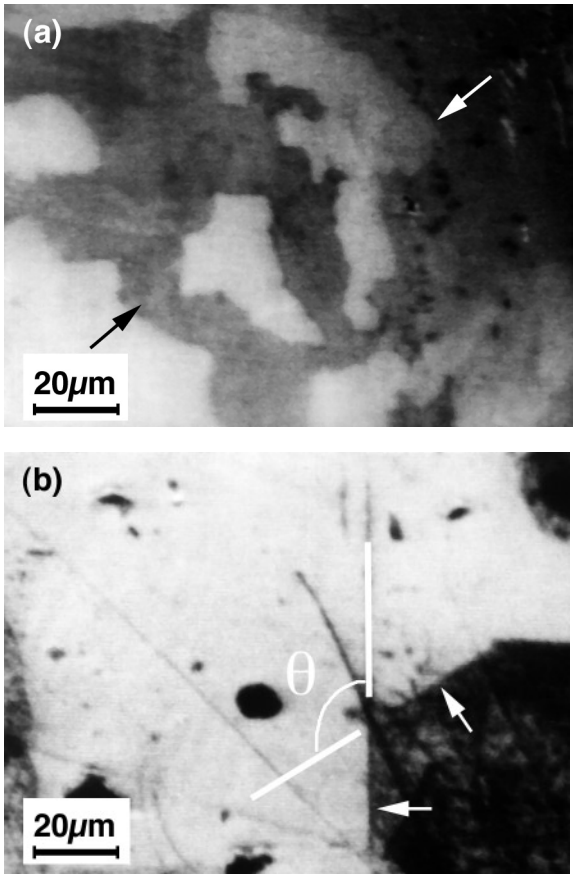

Figure 4. FIB scanning images taken on quasicrystal samples obtained after slow cooling. Arrows in (b) indicate two regular boundaries.

To characterize the effect of the final-stage isothermal treatment, we compared the slow-cooled samples with the ones obtained after an isothermal treatment of 10 days at 575 °C. Figure 5 shows the FIB images taken on these samples, always with the beam axis aligned along the sample growth direction. The images display much larger homogeneous zones

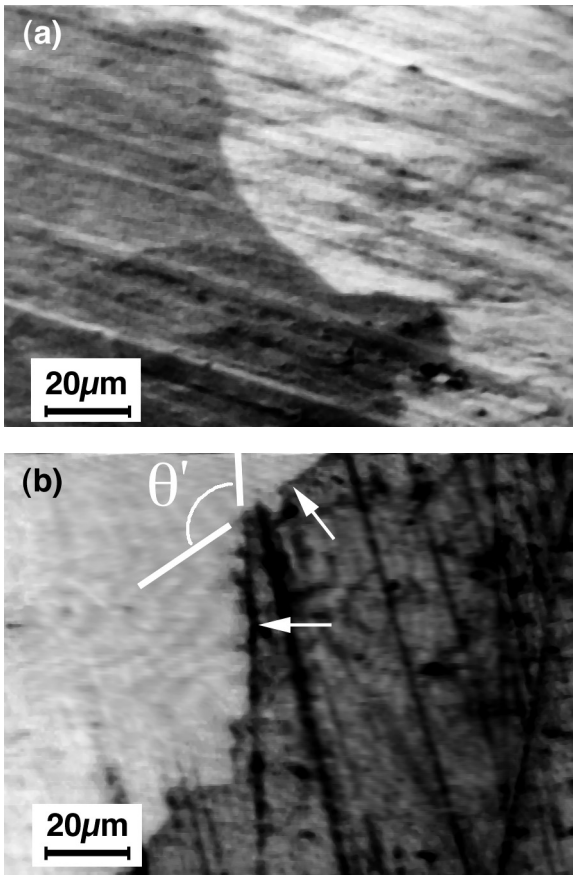

Figure 5. FIB scanning images taken on quasicrystal samples obtained after 10 days annealing. Arrows in (b) indicate two regular boundaries.

than the ones observed on slow-cooled samples. Intermediate zones, like those shown in figure 4(a), have not been found. It is clear that the annealing treatment favours the grain growth by recrystallization. Indeed, the grain size exceeds now several hundreds of μm. Regular grain boundaries can always be seen, as shown in figure 5(b), indicated by the two arrows. The boundary angle θ' can be estimated as 121 ± 2 degrees, which is the same as the boundary angle θ in the case of figure 4(b), in the limit of the experimental uncertainty.

In order to characterize the grain size evolution, we tried to follow the contour of a single grain that is in a better channelling position compared to the surrounding area. The zone covered by the beam deflection is much smaller than the grain size, so the image cannot be formed in a single beam scan. The contour can only be visualized by a series of successive FIB images. Figure 6 presents nine scan images that outline a 500 μm grain, where the scratch lines, resulting from mechanical polishing, have served as guide marks to determine the relative positions of the images.

We have not observed further details of the microstructures by tilting the samples, except contrast changes of the images. There can be two reasons for that. First, due to the mechanical constraints, the device allows only very limited tilting in its present configuration: the sample can only be tilted in a fixed position in restrained directions.

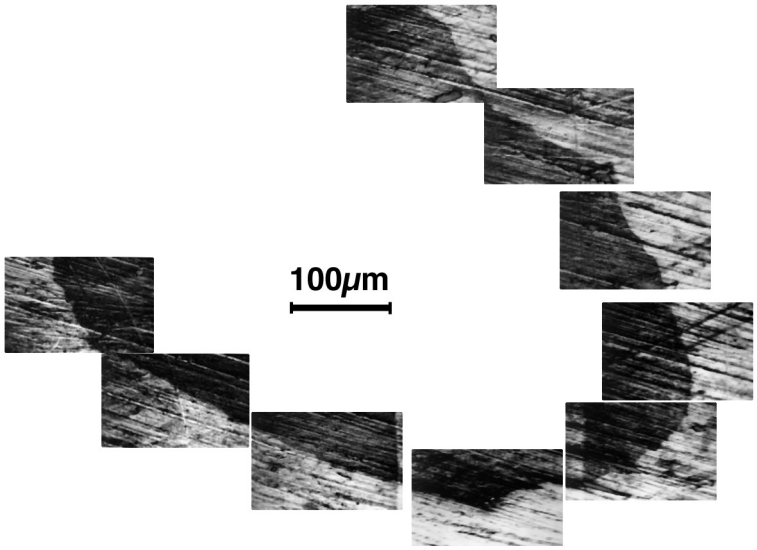

Figure 6. FIB scanning images showing the contour of a grain, of which the size exceeds 0.5 mm.

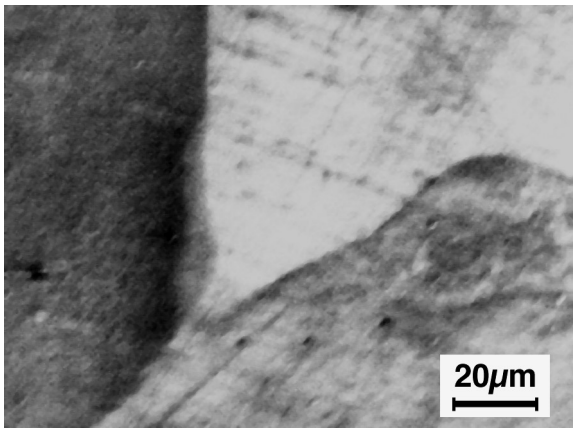

Figure 7. FIB scanning image showing a triple point.

Secondly, as shown by the x-ray diffraction measurements, most grains are oriented with the threefold axis along the ion beam (see discussion below), the probability for several differently oriented grains to meet can thus be weak. Indeed, very few triple points have been found. An example of that is shown in figure 7 from a sample after the final-stage annealing.

4. Discussion

This study demonstrates that the FIB imaging can give strong image contrast for quasicrystal grains, relative to the grain orientations, allowing a fast determination of the grain size, morphology and providing information about their relative orientation. Complementary

methods, such as the electron backscattered pattern (EBSP), will be necessary to determine the precise orientation of each grain in the samples.

It is shown that long-time annealing favours recrystallization, leading to grain size increase in the Al–Li–Cu quasicrystal samples. Quasicrystals are hoped to display particular behaviours in the recrystallization process. Two characteristics of the quasiperiodic structure can be evoked in this respect. On one hand, quasicrystals are characterized by their high symmetry order, which implies high multiplicity of equivalent orientations. For instance, the icosahedral point group $m35$ is of order 120, which is to be compared to the most symmetrical periodic (crystalline) group: the cubic point group (48 for cubic $m3m$). This may facilitate the quasicrystal grain coalescence, as compared to the situation of the periodic crystal, because the probability of finding two facets in close orientation increase with the degeneracy. On the other hand, it has been shown (Warrington 1988, Warrington *et al* 1997) that there are numerous possibilities to construct interfaces at the grain boundaries in quasicrystals, costing only low interface energy. It is hoped that coincidence lost by displacement shift, if any, can be recovered by phason flips, which do not change the local density and cost little energy. From this last point of view, some grain boundaries can be rather stable, and thus difficult to displace by thermal treatments. These two mechanisms can both affect the grain size evolution. The predominance of one over the other should depend on the initial relative positions and orientations of neighbour grains. Further investigations will be necessary to elucidate this point.

As far as the grain morphology is concerned, some grains are observed with rather irregular forms. However, on several samples, both before and after the 10 days isothermal treatment at 575 °C, regular boundaries between quasicrystal grains are visible (figures 4(b) and 5(b)). This indicates the faceting of these grains. We note that in both cases the neighbour boundaries form an angle of about 120 degrees, and that the inner part of the angle is always darker. As far as their orientation is concerned, x-ray diffraction measurements show that the samples display preferentially a threefold symmetry axis along the vertical direction (figure 2). Due to the beam size (several millimetres), many grains contribute to the diffraction. So the pronounced threefold peak (6–9) in figure 2(a) shows that the majority of grains are oriented with the threefold axis along the sample cylinder axis (the growth direction), parallel to which the ion beam is aligned. This, of course, does not provide the orientation relation for each grain, but it allows us to suggest that grains having the weakest secondary electron yield are oriented with threefold axis close to the ion beam incident direction (vertical to the plane of observation), since the x-ray diffraction peaks corresponding to other symmetry axes (two- and fivefold) are very weak in this case (see figure 2(a)). As a matter of fact, as shown by du Marchie van Voorthuysen *et al* (1992), strong channelling occurs in quasicrystals along major symmetry axes (two-, three- and fivefold), which are parallel to dense atomic planes. For an icosahedral structure, a threefold axis is parallel to three families of twofold planes, which, in the case of the Al–Li–Cu quasicrystalline phase, are the densest planes (de Boissieu *et al* 1991). In this aspect, the dark grain boundary angle value—120 degrees—is particularly relevant. Indeed, for an icosahedral symmetry structure inspected along a threefold axis, two families of twofold planes, defined perpendicularly to two twofold axes that are perpendicular to the threefold axis, form an angle of 120 degrees, which is the same as the boundary angles θ and θ' in our observation. This relation is illustrated in figure 8: if a triacontahedron is projected along a threefold axis, the six twofold facets parallel to the threefold axis engender a regular hexagon. This orientation relation can again be compared to the x-ray diffraction measurements: the diagram obtained with the incident x-ray beam scanning a surface parallel to the cylinder axis (figure 2(b)) displays a strong twofold peak (20–32)

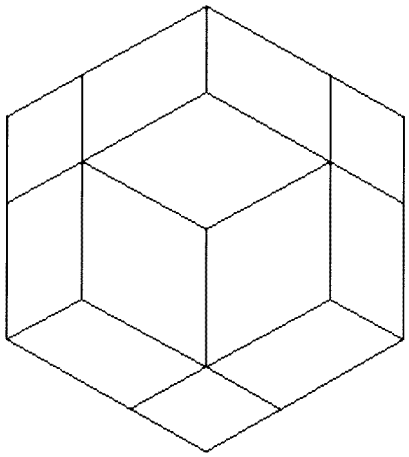

Figure 8. Projection of a regular rhombic triacontahedron along a threefold axis. Six twofold facets parallel to the threefold axis engender a regular hexagon.

which is almost absent in figure 2(a). This indicates that the majority of grains have their twofold axes perpendicular to the sample cylinder axis.

The specific boundary angle (120 degrees) can be understood in relation to the particular growth morphology of the Al–Li–Cu quasicrystalline phase—a rhombic triacontahedron with its facets perpendicular to the twofold axes—and the observation that the twofold planes are the densest for this phase. The fact that these boundaries are observed on samples both before and after the 10 days annealing suggests that the twofold planes can be stable grain interfaces for Al–Li–Cu, comparing the geometrical arguments and the x-ray diffraction analysis. Actually, this can be compared with some early works of Friedel *et al* (1953), who observed that a grain boundary in annealed metals costs little energy when the boundary plane is a plane of symmetry with low indices (high atomic density). In the case of an Al–Li–Cu quasicrystal, the twofold planes correspond to the same situation: low indices ({110000} in a six-dimension notation) and the highest atomic density. In a similar way, they can have low interfacial energy.

This work shows that scanning focused ion beam imaging can provide strongly contrasted and well defined images for quasicrystal grains, in relation with their relative orientations. This enables fast characterization of the quasicrystal sample microstructure, i.e. grain size, grain morphology. Moreover, this observation shows clearly the increase of the quasicrystal grain size following long-time annealing treatment, that favours the recrystallization. Geometrical analysis of the grain boundary orientation, compared to the x-ray diffraction results, suggests that the twofold symmetry planes form stable interfaces.

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