

# Chromium influence on rhombohedral twinning in sapphire

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**Abstract** Mechanical tests have been performed on sapphire doped with four different concentrations of chromium at temperatures between 800 and 1,000 °C. Samples were cut to favor rhombohedral twinning, which is the softest deformation mode of sapphire that inevitably leads to the failure of this material. We have investigated the effect of Cr doping on the rhombohedral twinning. The mechanical test results show that Cr atoms inhibit rhombohedral twinning, which appears to be athermal in the temperature range studied. An increase in the twinning-resolved stress is clearly observed. For 9,540 ppm Cr, the twinning-resolved stress becomes about three times higher than for undoped sapphire, potentially increasing its technological applications in the industry. The examination of lateral surfaces indicates that Cr atoms neither have influence on the twin width nor on the rhombohedral-twinning propagation. All these results have been properly explained within the model of Geipel et al.

## Introduction

Rhombohedral twinning in sapphire corresponds to the system  $K_1 = \{01\bar{1}2\}$ ;  $\eta_1 = \langle 0\bar{1}11 \rangle$ ;  $K_2 = \{0\bar{1}14\}$ ;  $\eta_2 = \langle 02\bar{2}1 \rangle$  and  $s = 0.202$ , and it is the easiest deformation mechanism [1]; it can be activated at temperatures as low as  $-196$  °C [2]. Above 500 °C, the resolved-twinning stress is close to 12 MPa, and it is largely independent of the temperature [1]. Such a low stress value for twinning is a problem for many applications of sapphire. This value is multiplied by a factor of 5 or 10 with the presence of a high dislocation density [3], then inducing a large hardening on this deformation mechanism. The rhombohedral-twinning stress depends on several factors, its somewhat scattered values [1], which may depend, for instance, on the quality of the lateral surface polish. Thus, in the case that surface defects because of mechanical polishing are removed by means of a chemical polishing, then the rhombohedral-twinning stress could increase by as much as one order of magnitude [4].

This twinning mechanism takes place below 1,300 °C [5] when the compression axis is between  $\langle \bar{1}120 \rangle$  and [0001], in particular at 45° from the latter, an orientation usually chosen for activation of basal slip [6]. Rhombohedral twinning has also been activated at temperatures below 1,250 °C in the “ab” orientation [6], where the compression direction is at 57° from the [0001] axis toward the  $\langle 0\bar{1}10 \rangle$  direction. Based on a model developed by Pirouz et al. [7] for silicon, Geipel et al. [8] proposed a model for rhombohedral twinning, where this mechanism originates from the glide and cross-slip of the partial dislocation  $b_t = 1/21.9\langle 0\bar{1}11 \rangle$  coming from the following dissociation process:

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$$\begin{aligned} 1/3\langle 01\bar{1}1 \rangle \rightarrow & 1/21.9\langle 0\bar{1}11 \rangle \\ & + (1/3\langle 01\bar{1}1 \rangle - 1/21.9\langle 0\bar{1}11 \rangle) \end{aligned} \quad (1)$$

The high mobility of the  $b_t$  dislocation leads to a faulted loop through the Frank–Read mechanism, expanding along the twinning plane  $K_1 = \{01\bar{1}2\}$ . Since another partial  $b_t$  cannot slip in the same plane, the  $1/3\langle 01\bar{1}1 \rangle$  pyramidal dislocation cross-slips to the adjacent  $\{01\bar{1}2\}$  plane, where again another  $b_t$  partial dislocation will be generated. Repeating this procedure along several  $\{01\bar{1}2\}$  adjacent planes, a rhombohedral twin is generated. Dislocation energetic calculations [9] indicate that the dissociation process shown in (1) could occur, generating a stationary and a twinning partial; their recombination being screw in character, the repeated cross slip of the latter produces the twin growth. This model also predicts that the two grains are mutually related by screw-rotation symmetry, verified by high-resolution transmission electron microscopy (HRTEM) observations [10]. Furthermore, by means of first-principles electronic-structure calculations based on the local density functional theory (LDFT) together with observation via HRTEM, it has been shown that the lowest-energy rhombohedral twin interface is terminated by interstitial vacancies [11].

Impurities are an obstacle for the dislocation glide so that their introduction into the crystal usually leads to a hardening of the deformation mechanisms. For instance, it has been observed that the addition of  $\text{Cr}^{3+}$  impurities impedes significantly the activation of the basal slip in sapphire [12], because of the interaction between  $1/3\langle 11\bar{2}0 \rangle$  basal dislocations and impurities. Since basal and pyramidal dislocations are similar in length, in the context of the Geipel et al. model [8], a similar Cr hardening could be found for basal slip and rhombohedral twinning, the two types of dislocations having similar interactions with impurities. In the present work, we have investigated the rhombohedral-twinning activation in sapphire doped with different concentrations of chromium. The aim of this work is to investigate if chromium also improves the mechanical strength of this material, relative to the rhombohedral twinning and show how the hardening can be explained within the Geipel et al. model [8].

## Experimental procedure

Sapphire samples doped with four different concentrations of chromium, grown by the Verneuil technique, were provided by R.S.A. Le Rubis (Jarrie, France). Impurity concentrations were determined by PIXE at CNA (Seville-Spain) and at C2RMF-CNRS (Paris, France), being 60, 725, 3940, and 9540 ppm mol of  $\text{Cr}^{3+}$  as average values.

Ni, Cu, Ga, Co, Zn, and V impurities also were detected but in a much lower concentrations (below 11 ppm mol), although slightly greater for Ti. The content of all these elements has been determined by making use of two software packages (AXIL and Gupix-Win); for more details see [12].

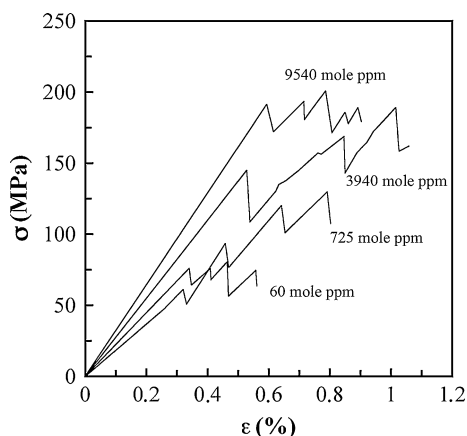
Specimens were oriented by Laue back reflection X-ray diffraction. They were cut in the form of parallelepipeds of  $2 \text{ mm} \times 2 \text{ mm} \times 4 \text{ mm}$  and they were given a final polish with a diamond paste less than  $3 \mu\text{m}$  in grain size. The compression direction was the so called “ab” orientation defined by Castaing et al. [6], with two faces parallel to  $(\bar{1}2\bar{1}0)$ . This orientation favors the activation of the two rhombohedral systems:  $S_1 \equiv \{K_1 = (01\bar{1}2); \eta_1 = [0\bar{1}11]; K_2 = (0\bar{1}14); \eta_2 = [02\bar{2}1]\}$  and  $S_2 \equiv \{K_1 = (1\bar{1}02); \eta_1 = [\bar{1}101]; K_2 = (\bar{1}104); \eta_2 = [2\bar{2}01]\}$ , with a Schmid factor of 0.15 and it avoids the activation of the rhombohedral system  $S_3 \equiv \{K_1 = (\bar{1}012); \eta_1 = [10\bar{1}1]; K_2 = (10\bar{1}4); \eta_2 = [\bar{2}021]\}$ .

Tests were carried out in air at temperatures between 800 and 1,000 °C at a constant cross-head speed of  $5 \mu\text{m}/\text{mn}$ , corresponding to an initial strain rate of  $\dot{\epsilon} = 2.0 \times 10^{-5} \text{ s}^{-1}$ , in an Instron machine model 1185. The load was transmitted to the specimens via SiC rods. After tests, lateral faces of each specimen were observed by optical microscopy (Leica DMRE) to analyze twins activated during deformation.

## Results and discussion

Figure 1 shows the strain–stress curves corresponding to the tests of sapphire doped with four different concentrations of  $\text{Cr}^{3+}$ , deformed at 1,000 °C. These curves clearly show the abrupt drops of the stress with the deformation of the material, which are a characteristic related to the twinning formation. Furthermore, there is a correlation between the drop amplitude and the width of the twin generated [1], where a major drop in the stress corresponds to a wider twin. In this work, we have taken the twinning stress as the value at which the first abrupt drop in the stress takes place. However, as we have mentioned before, the twinning stress depends on some factors, including the polished grade of surfaces; that leads to a high dispersion in this magnitude, and then several tests to get average values are required. We have performed at least three tests for each temperature and chromium concentration.

Table 1 shows the twinning-resolved stress  $\tau$  for sapphire doped with four different concentrations of  $\text{Cr}^{3+}$ . It is worth emphasizing that the temperature seems to have no influence on the hardening, or if any, it is so small that it cannot be detected in our tests owing to the experimental



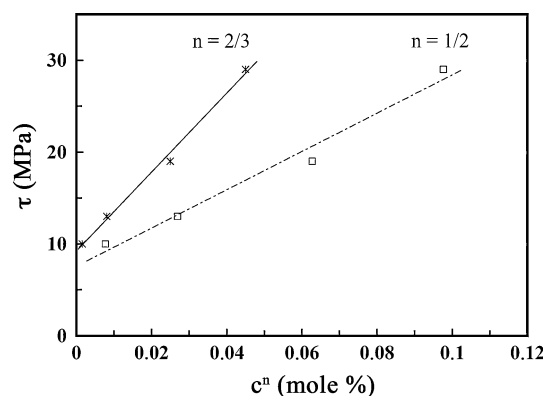
**Fig. 1** Strain–stress plot of sapphire doped with four different concentrations of chromium, deformed by rhombohedral twinning at 1000 °C

**Table 1** Average-resolved stresses for rhombohedral twinning in sapphire doped with four different concentrations of chromium

	Average-resolved stress $\tau$ (MPa)			
	60 ppm Cr <sup>3+</sup>	725 Cr <sup>3+</sup>	3,940 Cr <sup>3+</sup>	9,540 Cr <sup>3+</sup>
Temperature (°C)				
800	10 ± 4	13 ± 4	19 ± 5	28 ± 4
900	9 ± 3	15 ± 3	18 ± 4	29 ± 4
1000	12 ± 4	12 ± 3	20 ± 5	29 ± 4
Average	10	13	19	29

As it can be observed, this value increases with the concentration of this impurity. Average values used in Fig. 2 are shown in the last row

data dispersion. This athermal behavior is in agreement with the results of [1] for undoped sapphire. Here, we also show that, in our temperature range (800–1,000 °C), the twinning mechanism for Cr-doped sapphire is not thermally activated. For the less-doped one (60 ppm Cr<sup>3+</sup>), we obtain  $\tau \sim 10$  MPa in agreement with Scott et al. [1] who reported a value of  $\tau = 12.6 \pm 6.0$  MPa, with a standard deviation of 1.74 for 52 measurements between 500 and 1,244 °C, for undoped sapphire. This value increases with the chromium concentration and becomes three times higher for 9,540 ppm Cr<sup>3+</sup>. However, hardening  $d\tau/dc$  is about  $\mu/87$ , which is about half of the values found by Pletka et al. [13],  $\mu/28$  at 1,400 °C and  $\mu/39$  at 1,700 °C, for high temperature basal slip hardening by Cr. The origin of this difference could be because of the fact that samples used by Pletka et al. [13] contained a higher concentration of other impurities (Si, S, Cl, Ti, and Fe) besides Cr, leading to a higher hardening. The increase in the twinning-resolved stress can be justified using theories developed for solution hardening of metallic systems in the plateau regions. In these theories, the twinning-resolved



**Fig. 2** Average twinning-resolved stress  $\tau$  versus  $c^n$  ( $n = 1/2$  or  $n = 2/3$ ) for sapphire doped with 60, 725, 3940, and 9540 ppm mol of Cr<sup>3+</sup> (plotted in % mol). A better fit is obtained using  $n = 2/3$ , which corresponds to Labusch’s model

stress  $\tau$  of each Cr-doped sample can be written as a function of the impurity concentration  $c$ :

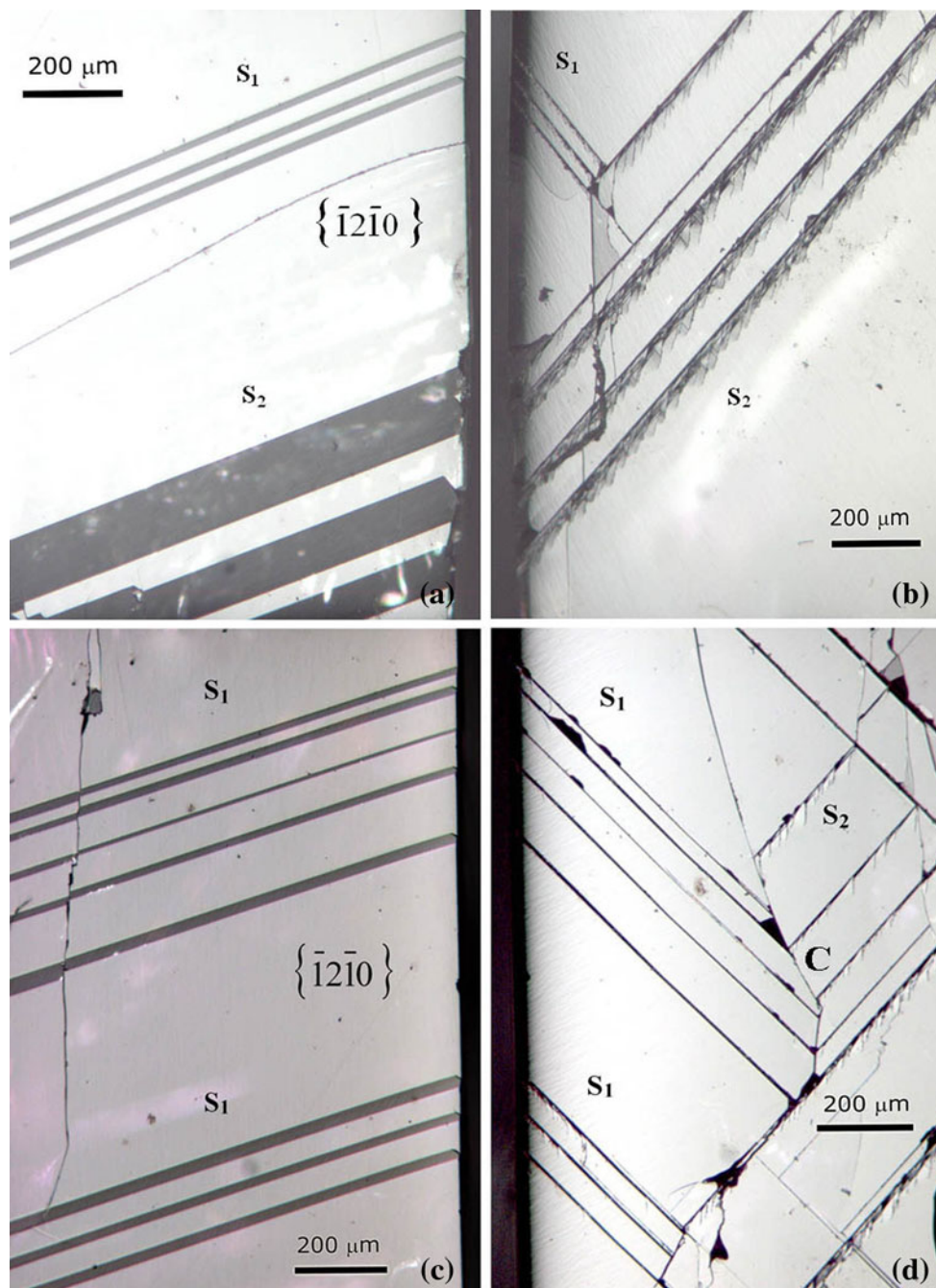
$$\tau = \tau_0 + Kc^n \tag{2}$$

being  $\tau_0$  the value for undoped specimen,  $K$  a constant and  $n = 1/2$  or  $n = 2/3$  depending upon whether we make use of the Fleischer [14] or the Labusch [15] model, respectively. Figure 2 is a plot of the twinning-resolved stress  $\tau$  versus the impurity concentration  $c^n$  ( $n = 1/2$  or  $n = 2/3$ ). Note that we have used average twinning-resolved stress values for each chromium concentration, shown in Table 1. It is observed that Labusch’s model ( $n = 2/3$ ) leads to a fit of better quality than Fleischer’s model ( $n = 1/2$ ), as also observed for basal slip [13]. Furthermore, the fit to our experimental data provides  $K = 0.4$  GPa and  $K = 0.2$  GPa for  $n = 2/3$  and  $n = 1/2$ , respectively. The parameter  $K$  value obtained using Fleischer’s model is very small and the fit using Labusch’s model provides a  $K$  value in reasonable agreement to the values for this parameter for basal slip. Castillo-Rodríguez et al. [12] found close values ( $K = 0.48$ – $0.62$  GPa) for dual basal slip activation at temperatures between 900 and 1,500 °C. Pletka et al. [13] reported a value for parameter  $K$  close to 1 GPa for ruby deformed between 1,300 and 1,700 °C. This fact could indicate that some interaction between dislocations and chromium impurities produces an increase in the twinning-resolved stress, i.e., a hardening similar to the one observed for basal slip.

As mentioned before, rhombohedral twinning is because of the glide on adjacent  $(01\bar{1}2)$  planes of the  $b_t = 1/21.9\langle 0\bar{1}11 \rangle$  zonal dislocation [8], which is generated by the dissociation of  $1/3\langle 01\bar{1}1 \rangle$  pyramidal dislocation as shown in (1). The changes to adjacent  $(01\bar{1}2)$  planes require a previous recombination into the  $1/3\langle 01\bar{1}1 \rangle$  pyramidal dislocation and afterward a cross slip process if it has a screw

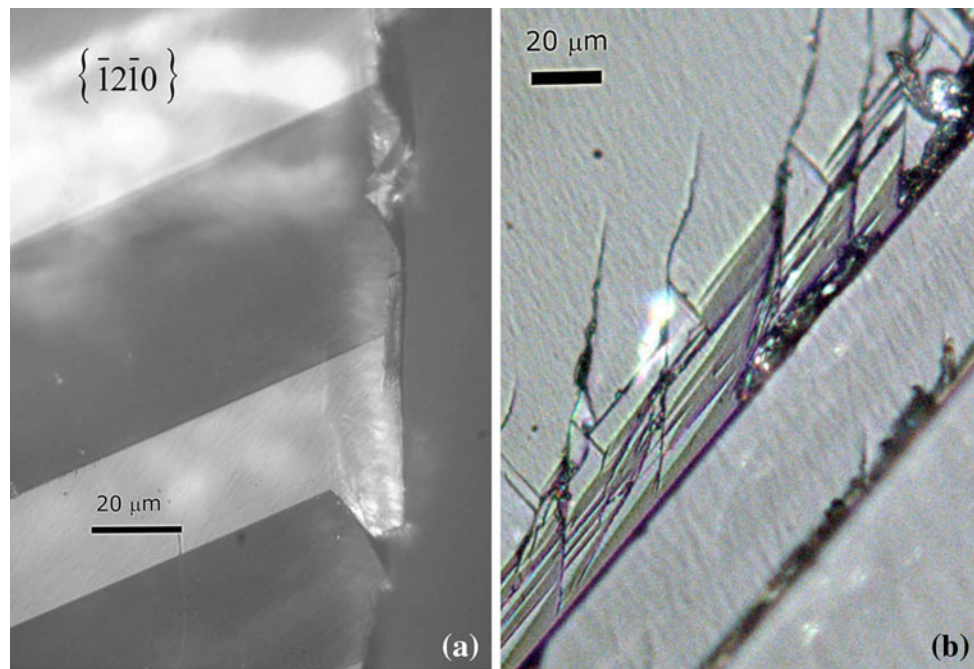
character [16]. The interaction energy between dislocations and chromium impurities is proportional to  $\mu \cdot b^2$  that appears in  $K$  of Eq. 2 [17]. The values of  $K$  found for basal slip hardening [12] are related to basal dislocations with Burgers vector  $b = 0.475$  nm giving  $\mu \cdot b^2 = 34$  nJ/m [18]. For the motion of the  $1/3\langle 01\bar{1}1 \rangle$  pyramidal dislocation (see reaction

(1)),  $\mu \cdot b^2 = 39$  nJ/m [18], a value close to that for basal slip. However, for twin boundary  $b_t = 1/21.9\langle 0\bar{1}11 \rangle$  zonal dislocations that are about 20 times less in length ( $b_t = 0.512/21.9$  nm),  $\mu \cdot b^2$  is about four hundred times less than in the case of basal and pyramidal dislocations. Therefore, the similarity of  $K$  values for basal slip [1] and for rhombohedral



**Fig. 3** Optical micrographs in the lateral faces of samples of ruby, deformed by rhombohedral twinning at  $T = 900$  °C, containing (a, b) 60 and (c, d) 3,940 mol ppm of Cr. The rhombohedral-twinning traces are clearly observed. Figures b and d, lateral faces normal to

$\{1\bar{2}10\}$  plane, show the interaction of both rhombohedral-twinning systems  $S_1$  and  $S_2$  which forms cracks (C)



**Fig. 4** Rhombohedral-twinning traces of sapphire doped with 60 mol ppm of Cr deformed at 900 °C. **a** corresponds to a  $\{1\bar{2}\bar{1}0\}$  face and **b** the orthogonal face

twinning is consistent with the Geipel model [8] where Cr atoms are obstacles to the cross-slip of  $1/3\langle 01\bar{1}1 \rangle$  dislocations.

As shown in Table 1, there is no dependence of the twinning-resolved stress with temperature. Following again Geipel's model [8] this athermal dependence can be justified. Rhombohedral twinning only needs small atom displacements because of the parameter  $s = 0.202$  and the energy of the  $b_t = 1/21.9\langle 0\bar{1}11 \rangle$  zonal dislocation, at the origin of twin boundary motion, is very low since its length is very small. Thus the Peierls barrier is so low that temperature has a small influence in the dissociation process (1), and below a certain temperature, the twinning-resolved stress does not depend on temperature any more. For undoped sapphire, below 600 °C rhombohedral twinning is thermally activated [1], but there is no information reported in the literature about the effect of impurities of chromium or titanium on this temperature range.

Lateral surfaces of twinned samples have been observed using polarized light in an optical microscope. In Fig. 3, we show optical micrographs of samples doped with 60 and 3,940 ppm of  $\text{Cr}^{3+}$ , both tested at 900 °C. After checking all samples, we find that  $\text{Cr}^{3+}$  impurity has no influence on the twin width since for the four different chromium concentrations, its value is between 15 and 125  $\mu\text{m}$ . This width range is of the same order as the value that Castaing et al. [3] measured in undoped sapphire (25 and 75  $\mu\text{m}$ ). This absence of chromium influence on the twin width is consistent with what has been observed in the strain–stress

plots, since the amplitude of the stress drops were similar for the four different rubies. Conversely, in the case of  $\text{Ti}^{4+}$  impurities, Savrum et al. [19] reported that for sapphire doped with 0.25 wt% of  $\text{Ti}^{4+}$  there was a decrease in the average twin width compared to undoped sapphire, which was ascribed to a slowing down of twin boundary movement effect because of  $\text{Ti}^{4+}$ . Savrum et al. [19] reported that  $\text{Ti}^{4+}$  impurities produce an increase on the rhombohedral-twinning-resolved stress compared to undoped sapphire for mechanically polished samples. But, this increase vanishes if undoped sapphire is annealed at 1,650 °C for 24 h and compared to borax etch-doped samples; these treatments remove defects of the crystal and then possible nuclei for rhombohedral twinning. However, Savrum et al. [19] showed that  $\text{Ti}^{4+}$  impurities cause a decrease in the average twin width. The difference in the influence of Cr and Ti because of the fact that  $\text{Ti}^{4+}$  impurities are aliovalent in sapphire and then generate charge compensation defects, producing a high distortion in the crystal, and then they exert a noteworthy effect in retarding dislocations motion [13] and twin propagation. Because of the scarcity of mechanical data for  $\text{Ti}^{4+}$  twinning hardening, no quantitative interpretation has been performed.

Optical micrographs of lateral surfaces of a sample of sapphire doped with 60 ppm of  $\text{Cr}^{3+}$  deformed at 900 °C are showed in Fig. 4. Angles between twins and the compression axis are coherent to the activation of both rhombohedral twinning  $S_1 \equiv \{K_1 = (01\bar{1}2); \eta_1 = [0\bar{1}11];$

$K_2 = (0\bar{1}14); \eta_2 = [02\bar{2}1]$ ;  $S_2 \equiv \{K_1 = (01\bar{1}2); \eta_1 = [\bar{1}101]; K_2 = (\bar{1}104); \eta_2 = [2\bar{2}01]\}$ . However, the intersection of these twins with each lateral face is quite different.  $\{\bar{1}2\bar{1}0\}$  faces are not so much damaged (Fig. 4a), but in the perpendicular ones (Fig. 4b) we observe small areas free of twins and a lot of micro-cracks through them. This different aspect could be because of the angle between the shear direction  $\eta_1$  and the lateral surfaces. For  $\{\bar{1}2\bar{1}0\}$  surfaces, the angle is close to  $27^\circ$ , but for the perpendicular ones the angle is about  $60^\circ$ . Then, the atom displacements are larger for the latter and then it favors the generation of damages. This phenomenon increases the brittleness of sapphire after rhombohedral twinning. Finally, it is worth emphasizing that in most of the tested samples, we observe that the twinning stress increases with deformation (Fig. 1). This hardening is because of the interaction of both rhombohedral-twinning systems  $S_1$  and  $S_2$  (Fig. 3) also at the origin of cracking. This interaction hinders the twin propagation and finally leads to material failure.

## Conclusions

Using “ab” orientation, rhombohedral twinning has been activated in sapphire doped with four different concentrations of Cr. In spite of the high dispersion in the twinning-resolved stress, an increase in this magnitude is clearly observed, which does not depend on the temperature. For 9,540 ppm Cr, the twinning-resolved stress is about three times higher than for undoped sapphire, which improves potentiality for technological applications of this material. Optical microscopy observations show that rhombohedral-twinning width is independent of chromium concentration. Following Geipel’s model, the hardening is justified considering the fact that chromium impurities hinder the cross slip process of  $1/3\langle 01\bar{1}1 \rangle$  pyramidal dislocations. Moreover, chromium impurities do not impede the twin propagation because of the small interaction energy between

them and the  $b_t = 1/21.9\langle 0\bar{1}11 \rangle$  zonal dislocations, and thus have no influence on the final twin width.

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