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Surface state improvement of ground AT and SC quartz cuts by controlled dissolution in NaOH, KOH, LiOH

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After the studies which allowed us to perfect the chemical thinning down, or controlled dissolution, of both AT and SC quartz plates in NaOH and KOH media, respectively, we have investigated mixtures of these with another basic compound (LiOH) in order to discover a common solvent for both AT and SC cuts. The results show that crystallographic orientation and solvent nature have a great influence on controlled dissolution especially on the surface texture. It appears that the basic compound which has the smallest cation imposes its properties and consequently, the chemical polishing of both AT and SC cuts cannot be made in good conditions with the same solvent.

1. Introduction

Since the development of piezoelectric high frequency devices based on quartz resonators, several studies have been carried out on their frequency adjustment. In the past few years, the chemical polishing method which differs from the unconventional and expensive ion beam etching (IBE) method, was more extensively studied. This research generally has been carried out using fluoride media [1–3], but has not been very successful. HF and NH_4HF_2 baths are very corrosive even with surfactant additions [4–6], and the resulting final surface states are of poor quality. In our department, based on the reverse thermodynamic relations of growth and dissolution processes [7–12], we have optimized chemical polishing of both AT quartz plates in a NaOH medium and SC cuts in a KOH medium [13–15]. These studies have shown that, if the crystalline orientation is a major factor for the controlled dissolution, the nature of the solvent is also an important parameter governing the final surface state. Thus, in the course of our research, we have investigated mixtures of basic solvents and some new basic compounds in order to find a common solvent for good chemical polishing of both AT and SC quartz plates.

So, in this paper, the thinning down and especially the evolution of surface state of AT and SC quartz plates in various mixtures of basic compounds $NaOH \cdot H_2O + KOH \cdot H_2O$, $NaOH \cdot H_2O + KOH \cdot H_2O + LiOH \cdot H_2O$ will be described.

2. Experimental conditions

Experimental conditions have been detailed previously [13–15]. Therefore, only the main characteristics of the chemical lapping conditions are mentioned here. The samples used are AT and SC ground discs of 5 to 8 mm diameter and about 600 μm thick. The thinning down of a plate is followed by frequency measurements. The resonance frequency is given by:

$$F = K/e$$

where e is the plate thickness and K is a constant related to the material and orientation studied: $K = 1670$ and 1820 MHz μm for AT and SC cuts, respectively [16].

Dissolution baths were prepared from high purity basic products in a PTFE reactor, to avoid chemical corrosion. The ratio and the percentage compositions are expressed in moles. For ternary mixtures, the percentage of $LiOH \cdot H_2O$ is given as a ratio of the mixture. Surface texture was checked by light microscopy and by rugosity measurement (*Ra* parameter). The given *Ra* value is the mean value of four different scanning directions (45° different from each other).

3. Results and discussion

Since concentrated and pure $NaOH \cdot H_2O$ [14] and $KOH \cdot H_2O$ [13] media are very good polishing solvents for AT- and SC-cuts respectively, we first investigated their binary mixture in order to establish good experiment conditions for both AT- and SC-cuts. In a second step, this search for a common solvent was extended to the ternary system (NaOH–KOH–LiOH).

3.1. Dissolution of ground AT and SC plates in the binary medium

To aid understanding of our results, in all figures, characteristic comparative curves of the surface state

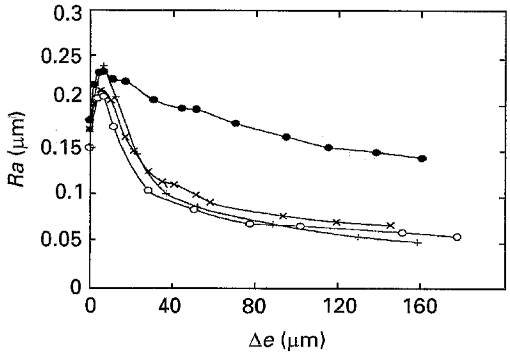

Figure 1 Ra parameter plotted against the removed depth (Δe) for AT cuts in different media at 170 °C. Key: -×- $NaOH \cdot H_2O$; —+— $NaOH \cdot H_2O + KOH \cdot H_2O$ (50/50); —○— $NaOH \cdot H_2O + KOH \cdot H_2O$ (25/75); —●— $KOH \cdot 0.48\ H_2O$.

evolution of AT and SC cuts plotted versus the removed depth $Ra = f(\Delta e)$ will be given for pure ($NaOH{\cdot}H_2O$ and (or) $KOH{\cdot}H_2O$) and binary solvents.

First, investigations of the dissolution process were carried our for two different ratios of the constituent hydroxides: $NaOH{\cdot}H_2O/KOH{\cdot}H_2O = 1/1$ and 1/3, respectively. As shown previously [14], the dissolution rate curves ($V = f(\Delta e)$) can be divided into two parts: a strong decrease due to the dissolution of the polycrystalline surface layer, damaged by cutting and polishing, followed by a stabilization corresponding to the intrinsic dissolution rate for a given orientation at a chosen temperature. For both experiments, pure [14] and binary solvents, these curves exhibit the same evolution and therefore, will not be given in this paper.

3.1.1. AT-cuts

As can be observed in Fig. 1, the Ra parameter curves, plotted in terms of the removed depth, exhibit similar polishing properties for pure and both binary solvents. As all samples used have the same initial superficial ground surface, Ra evolution exhibits its maximum value for a total removal depth close to 7 μm (for the two faces) which corresponds to the damaged surface layer as described formerly. Afterwards, the surface roughness slowly decreases to 0.06 μm for 160 μm removed material, a value which corresponds to good chemical lapping or "controlled dissolution" of AT quartz wafers.

In the same way, the surface texture evolution has been checked by light microscopy. Figs 2 and 3, after the disturbed surface layer removal, show characteristic dissolution features of AT cut in the binary solvents. If the surface state is similar to that obtained with ($NaOH{\cdot}H_2O$ in a 1/1 ratio mixture, the relief observed for the 1/3 ratio mixture looks like the one generated by $KOH{\cdot}H_2O$). Furthermore, according to the AT-cut orientation (two-fold axis lying in its plane), both sides display the same features and roughness evolution.

Therefore, although the surface state is modified by the concentration ratio value, 1/1 or 1/3, the Ra parameter evolution exhibits the same behaviour, close to that observed for $NaOH{\cdot}H_2O$ medium. So, it seems that the smaller cation (Na^+) strongly influences the dissolution rate and the obtained surface state.

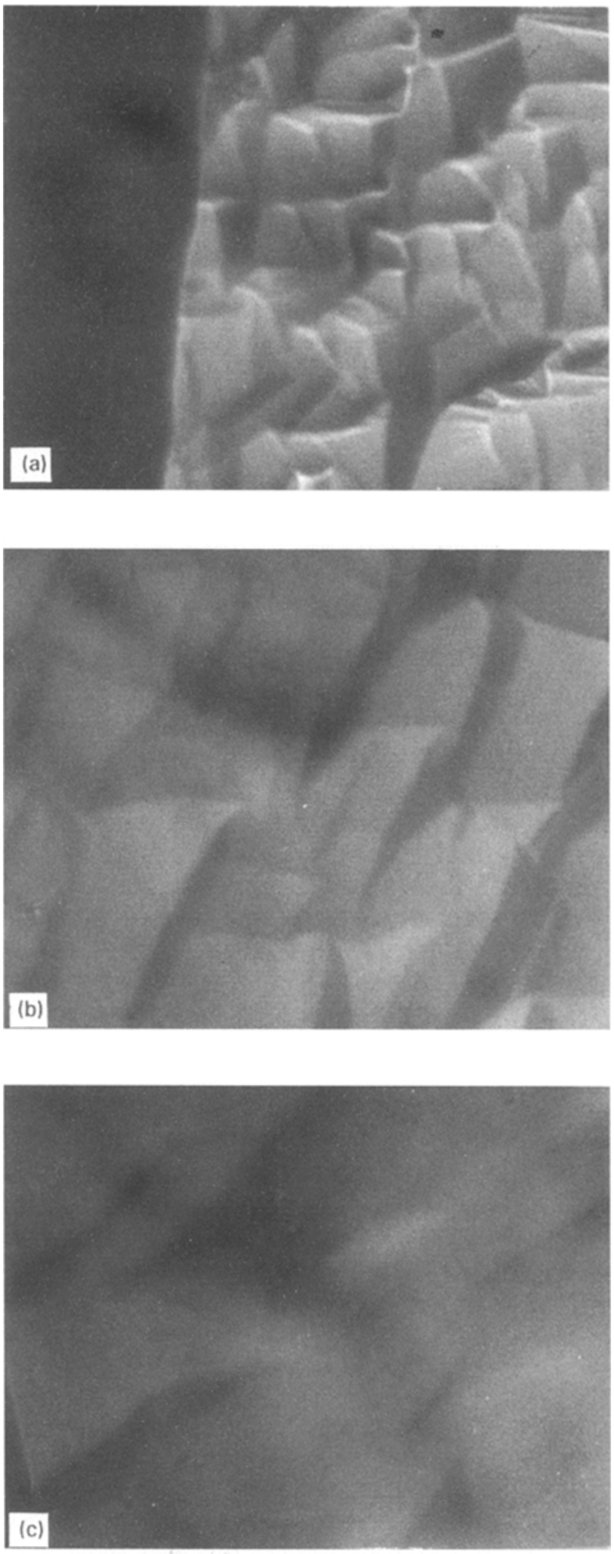

Figure 2 Dissolution feature of an AT cut thinned down in $NaOH \cdot H_2O + KOH \cdot H_2O$ (50/50). (a) $\Delta e = 23$ μm, $Ra = 0.15$ μm; (b) $\Delta e = 52$ μm, $Ra = 0.09$ μm; (c) $\Delta e = 130$ μm, $Ra = 0.055$ μm. Same scale: 1 cm = 17.0 μm has been used for all the dissolution features presented.

3.1.2. SC-cuts

On the other hand, double rotated SC-cuts have no special crystallographic symmetry and, consequently,

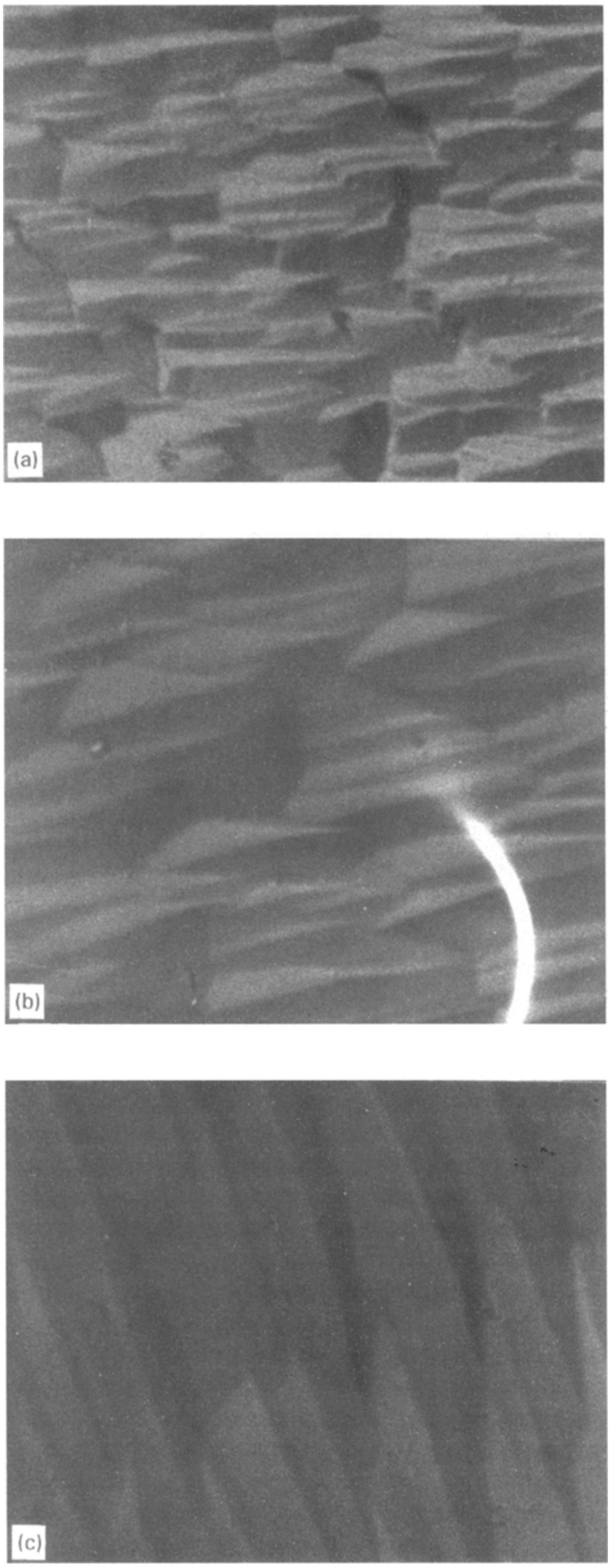

Figure 3 Dissolution feature of an AT cut thinned down in $NaOH{\cdot}H_2O$ + $KOH{\cdot}H_2O$ (25/75). (a) $\Delta e = 28$ µm, $Ra = 0.13$ µm; (b) $\Delta e = 77$ µm, $Ra = 0.07$ µm; (c) $\Delta e = 151$ µm, $Ra = 0.06$ µm.

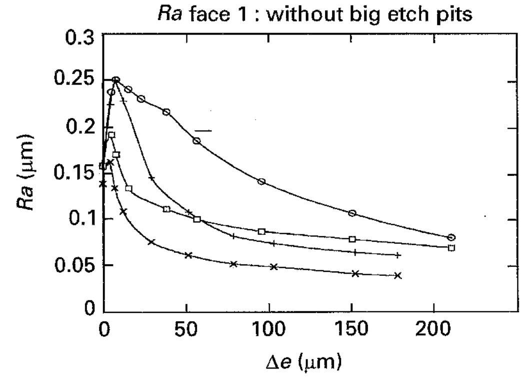

Figure 4 *Ra* parameter plotted against the removed depth of SC cuts in NaOH + KOH mixtures at 170 °C. Key: —+— face 1 Na1 + K1 (25/75); —×— face 2 Na1 + K1 (25/75); —○— face 1 Na1 + K1 (50/50); —□— face 2 Na1 + K1 (50/50); Na1 = $NaOH \cdot H_2O$; K1 = $KOH \cdot H_2O$.

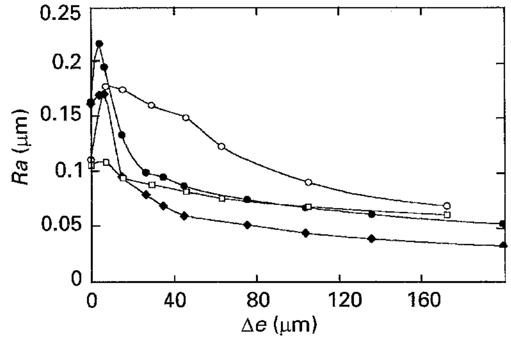

Figure 5 *Ra* parameter plotted against the removed depth of SC cuts thinned down in $NaOH \cdot H_2O$ and $KOH \cdot H_2O$ at 165 °C. Key: —●— face 1 $KOH \cdot H_2O$; —◆— face 2 $KOH \cdot H_2O$; —□— face 1 $NaOH \cdot H_2O$; —○— face 2 $NaOH \cdot H_2O$.

the two sides always show a different behaviour, Fig. 4. As for AT-cuts, *Ra* parameter evolution of SC-cuts is similar for both binary and pure $NaOH \cdot H_2O$ solvents, Figs 4 and 5. Some deep and large dissolution figures [15], etch pits, appear on one side (face 1) after about 40 µm material removed and do not give a good polishing. Nevertheless, it seems that the increase of potassium hydroxide concentration reduces the number of these defects and changes the dissolution features. Conversely, the increase of sodium hydroxide generates a change in the dissolution features, Figs 6 and 7, which looks like the relief obtained in $NaOH{\cdot}H_2O$.

So we can conclude that AT- and SC-cuts are not polished simultaneously by the binary mixtures of sodium and potassium hydroxides. It appears that the solvent with the smallest cation (Na^+) imposes its polishing and rate dissolution properties, even in small quantities (1/3 ratio). Thus the nature of the solvent, in connection with its cation size, is an important parameter for determining the final surface state of the samples.

So, in the aim to find a common solvent for AT- and SC-cuts, we have investigated another similar basic solvent with a smaller cation size: $LiOH \cdot H_2O$.

3.2. Role of $LiOH \cdot H_2O$ in the dissolution process of AT and SC quartz plates

Due to its physical properties (decomposition before melting), $LiOH{\cdot}H_2O$ has only been used as an additive to pure $NaOH{\cdot}H_2O$ (11 and 20%) and binary 1/1 solvents (10 and 20%).

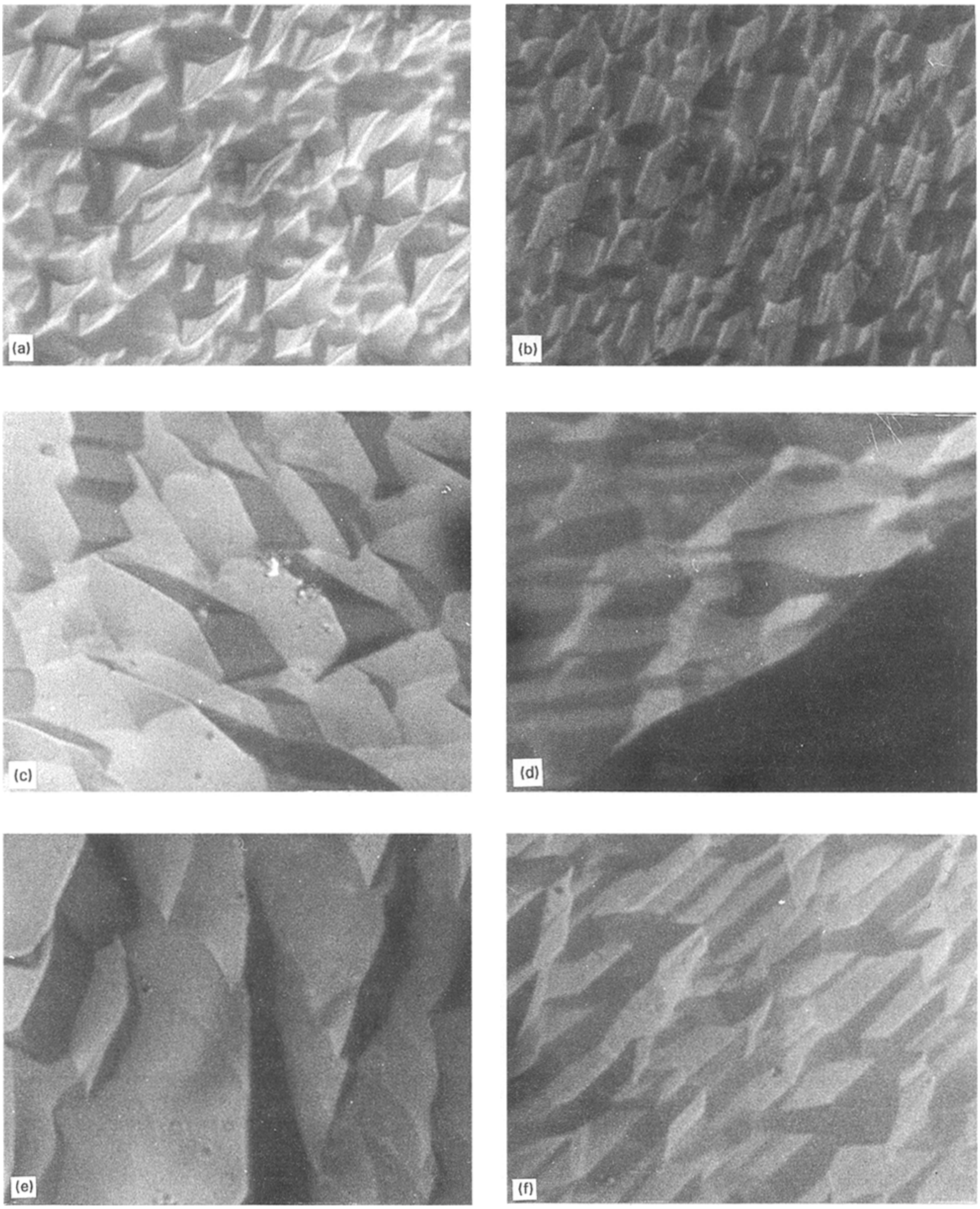

Figure 6 Dissolution feature of an SC cut thinned down in $NaOH \cdot H_2O$ + $KOH \cdot H_2O$ (50/50). Face 1: (a) $\Delta e = 15$ µm, $Ra = 0.24$ µm; (c) $\Delta e = 57$ µm, $Ra = 0.19$ µm; and (e) $\Delta e = 95$ µm, $Ra = 0.14$ µm. Face 2: (b) $\Delta e = 15$ µm, $Ra = 0.13$ µm; (d) $\Delta e = 57$ µm, $Ra = 0.10$ µm; and (e) $\Delta e = 95$ µm, $Ra = 0.09$ µm.

3.2.1. AT and SC quartz plates dissolution in $NaOH \cdot H_2O + x\%$ $LiOH \cdot H_2O$ ($x = 11, 20$) medium

3.2.1.1. AT-cuts. In Fig. 8 *Ra* parameter evolutions of AT plates versus the removed depth in pure $NaOH \cdot H_2O$ and its mixture with lithium hydroxide are compared. As for the binary systems, the three curves show a similar behaviour. They converge to $Ra \approx 0.05$ µm after 180 µm removed, which corresponds to good chemical lapping. So, the addition of lithium hydroxide neither improves nor destroys the polishing properties of $NaOH \cdot H_2O$, although, as shown in Fig. 8, the maximum *Ra* value seems to be reduced when the per cent of $LiOH \cdot H_2O$ increases. On the other hand, the surface structure of AT-cuts is similar to the dissolution features generated by the pure solvent, Figs 9 and 10.

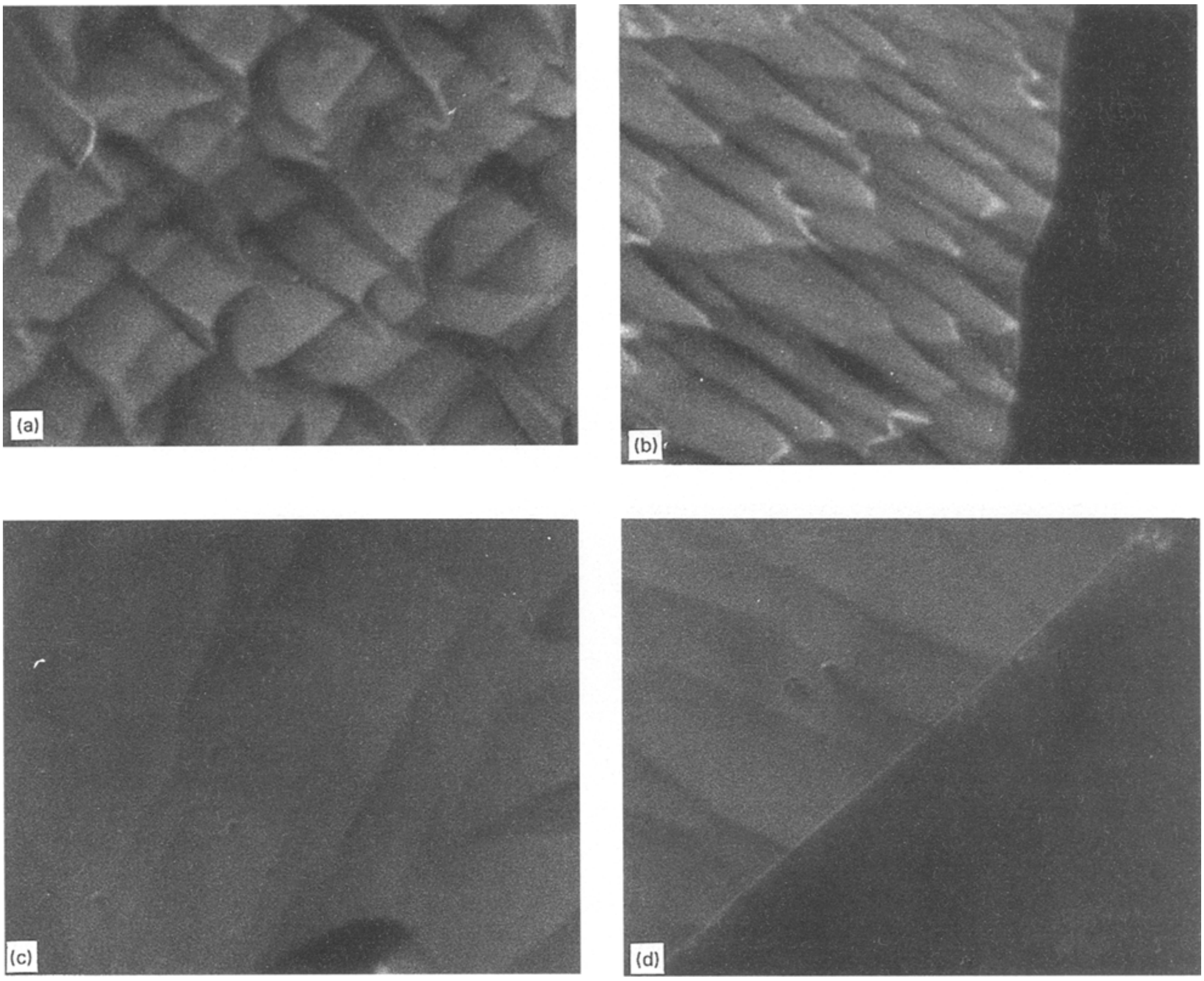

Figure 7 Dissolution feature of an SC cut thinned down in $NaOH \cdot H_2O + KOH \cdot H_2O$ (25/75). Face 1: (a) $\Delta e = 29$ µm, $Ra = 0.075$ µm; and (c) $\Delta e = 152$ µm, $Ra = 0.040$ µm. Face 2: (b) $\Delta e = 29$ µm, $Ra = 0.145$ µm; and (d) $\Delta e = 152$ µm, $Ra = 0.065$ µm.

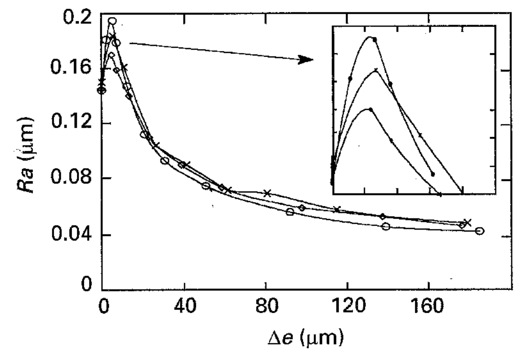

Figure 8 *Ra* parameter plotted against the removed depth of AT cuts in $NaOH \cdot H_2O + x\%$ $LiOH \cdot H_2O$ ($x = 0, 11, 20$) at 170 °C.

3.2.1.2. *SC-cuts.* Roughness evolutions of SC-cuts are plotted in Fig. 11. As for pure $NaOH \cdot H_2O$, only one side is well polished ($Ra = 0.05$ µm after 150 µm removed) while the other side, face 1, is drastically damaged ($Ra = 0.20$ µm after 150 µm removed). After about 40 µm material removed, as in pure $NaOH \cdot H_2O$ solvent [14], some big etch pits appear. In this case, these etch pits are distributed among large and deep dissolution features, Fig. 12, which explain the high final value of *Ra*.

Therefore, the use of lithium hydroxide as an additive in sodium hydroxide solution does not improve the superficial surface state of AT and SC quartz plates. On the other hand, as described elsewhere [17], the increase of lithium hydroxide concentration in the system LiOH/NaOH strongly increases the dissolution rate of both cuts. So, as already observed for the binary system NaOH/KOH, the presence of a smaller cation (Li^+) modifies the polishing properties. In fact, it seems that the smallest cation prescribes its properties. Consequently, the ternary system LiOH–NaOH–KOH system has been investigated.

3.2.2. AT and SC quartz plate dissolution in $[NaOH \cdot H_2O + KOH \cdot H_2O] + x\%\ LiOH \cdot H_2O$ ($x = 10, 20$) medium

3.2.2.1. *AT-cuts.* In Fig. 13 *Ra* parameter evolutions of AT plates versus the removed depth in the binary system NaOH/KOH and its mixture with lithium hydroxide are compared. Taking into account the slight initial surface state difference and the experimental

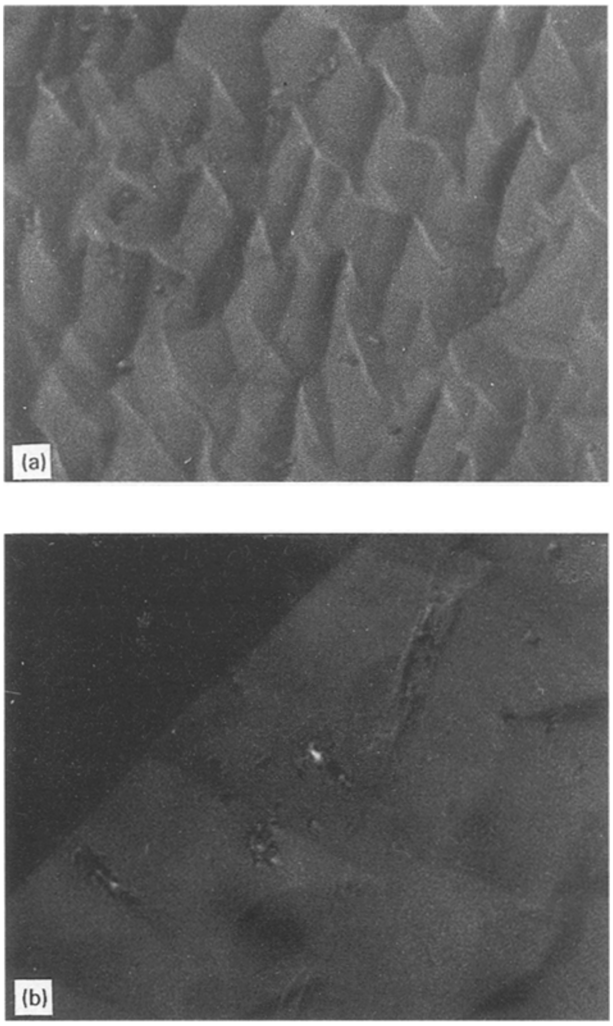

Figure 9 Dissolution feature of an AT cut thinned down in $NaOH \cdot H_2O + 11\% \ LiOH \cdot H_2O$. (a) $\Delta e = 27$ µm, $Ra = 0.105$ µm; and (b) $\Delta e = 115$ µm, $Ra = 0.06$ µm.

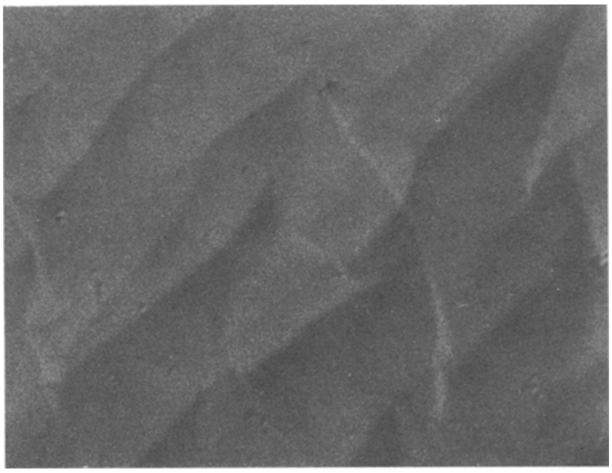

Figure 10 Dissolution feature of an AT cut thinned down in $NaOH \cdot H_2O + 20\% \ LiOH \cdot H_2O$. $\Delta e = 108$ µm, and $Ra = 0.06$ µm.

error range, all the curves exhibit the same behaviour. On the other hand, whatever the additive concentration, the dissolution features are quite similar to those obtained in pure $NaOH \cdot H_2O$, Fig. 14.

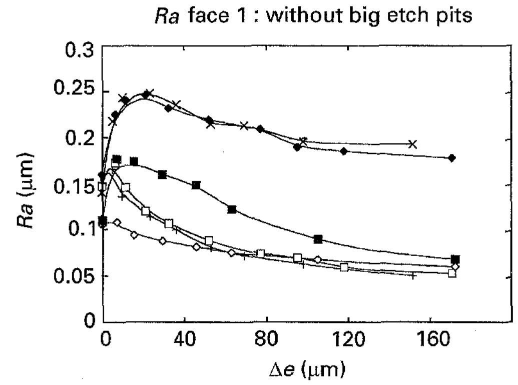

Figure 11 *Ra* parameter plotted against the removed depth of SC cuts in $NaOH \cdot H_2O + x\% \ LiOH \cdot H_2O$ ($x = 0, 11, 20$) at 168 °C. Key: —■— 0% face 1; —×— 11% face 1; —◆— 20% face 1; —◇— 0% face 2; —+— 11% face 2; —□— 20% face 2.

3.2.2.2. SC-cuts. In this case, we observe the same roughness evolution as in sodium hydroxide and NaOH/LiOH media, i.e. only a good dissolution process for one side of the plates, face 2 of Fig. 15. On the other side, face 1, etch pits and large dissolution features are observed as in the NaOH/LiOH mixture, Fig. 16. Furthermore, this face seems to be more damaged when the value of x increases.

So, the use of $LiOH \cdot H_2O$ as an additive in the binary system NaOH/KOH does not improve simultaneously the surface state of AT and SC quartz plates. Furthermore, the changes of dissolution features induced by the introduction of lithium hydroxide in the mixtures confirms the strong influence of the cation size. The smallest one, Li^+, controls the dissolution process:

- good controlled dissolution of the AT quartz plates;
- worse dissolution process of SC quartz plates even for small concentration;
- strong increase of the dissolution rates for both orientations.

4. Conclusion

The combination of previous studies [13, 14] with this one, has allowed the identification of parameters controlling the polishing properties. As has been reported in previous works [15, 17], the controlled dissolution depends on the crystallographic orientation. For the same solvent or media, the thinning down of AT and SC cuts differs with the variation of the dissolution features and the dissolution rate. It is why we must use different solvents to polish different plates.

It appears that the only specie which changes from one solvent to another is the alkali cation and especially its size. In this work, the studies of mixtures of two or three basic compounds allowed us to show that the cation size is the most important parameter which controls the roughness parameter evolution and the dissolution rate. To explain these evolutions, we have studied the dissolution mechanism of quartz plates in concentrated basic media. These results, associated with the kinetic curves of all the studied media, can explain the influence of the cation size on the dissolution [17].

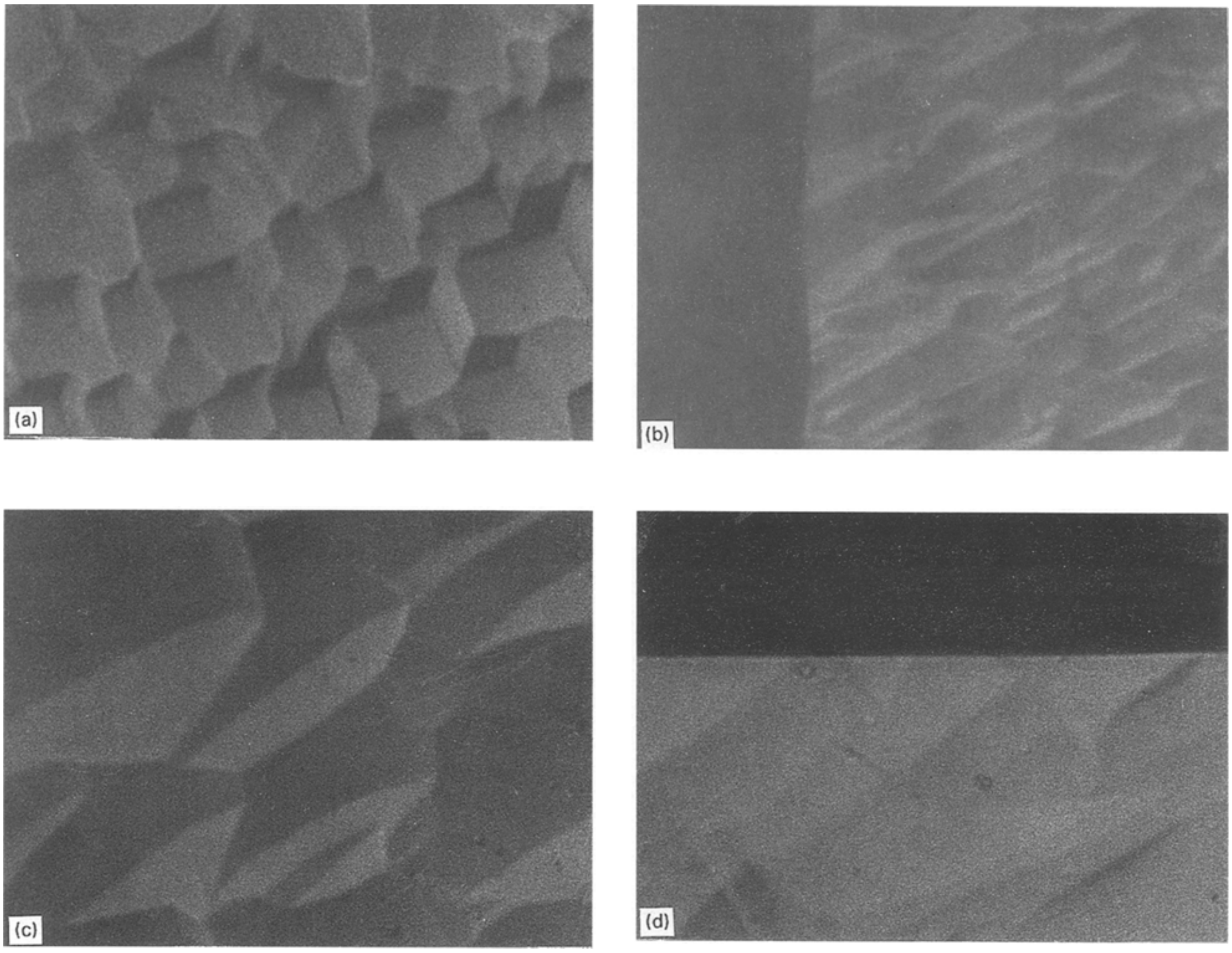

Figure 12 Dissolution feature of an SC cut thinned down in $NaOH \cdot H_2O$ + 20% $LiOH \cdot H_2O$. Face 1: (a) $\Delta e = 32$ µm, $Ra = 0.230$ µm; and (c) $\Delta e = 171$ µm, $Ra = 0.18$ µm. Face 2: (b) $\Delta e = 32$ µm, $Ra = 0.110$ µm; and (d) $\Delta e = 171$ µm, $Ra = 0.055$ µm.

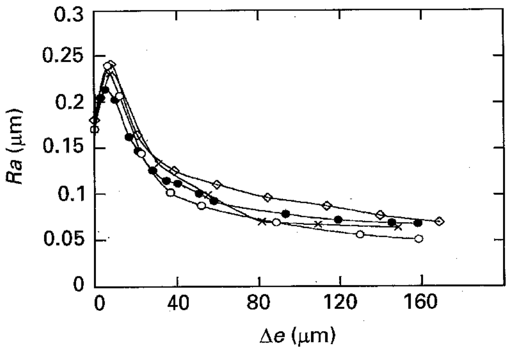

Figure 13 Ra parameter plotted against the removed depth of AT cuts in $NaOH \cdot H_2O + KOH \cdot H_2O$ (50/50) + x% $LiOH \cdot H_2O$ ($x = 10, 20$) at 170 °C. Comparison with $NaOH \cdot H_2O$. Key: -×- Na1 + K1 (50/50) + 10% Li1; —◇— Na1 + K1 (50/50) + 20% Li1; —●— Na1; —○— Na1 + K1 (50/50). Na1 = $NaOH \cdot H_2O$; K1 = $KOH \cdot H_2O$; Li1 = $LiOH \cdot H_2O$.

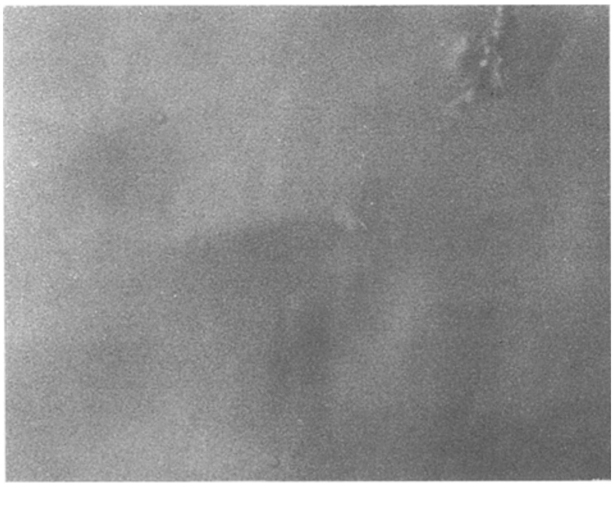

Figure 14 Dissolution feature of an AT cut thinned down in $NaOH \cdot H_2O + KOH \cdot H_2O$ (50/50) + 10% $LiOH \cdot H_2O$. $\Delta e = 148$ µm, and $Ra = 0.065$ µm.

However, to explain the differences in the polishing properties and in the dissolution features, we must take into account the crystalline surface structure of plates associated with the size of the cations. Further studies are in progress to explain these phenomena.

In conclusion, the influence of the cation size shows that the studied mixtures ($NaOH \cdot H_2O$, $KOH \cdot H_2O$, $LiOH \cdot H_2O$) allow polishing of AT and SC quartz plates but none of them is a common one for these two orientations. Work is in progress to determine the single solvent.

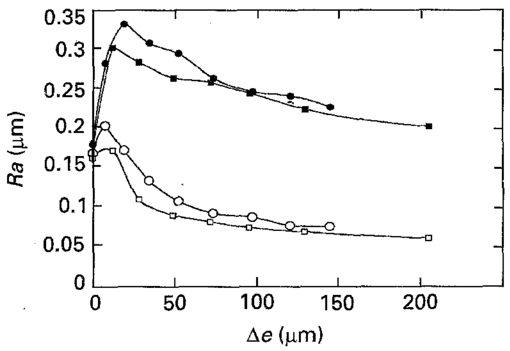

Figure 15 *Ra* parameter plotted against the removed depth of SC cuts in $NaOH \cdot H_2O + KOH \cdot H_2O$ (50/50) + x% $LiOH \cdot H_2O$ ($x = 10, 20$) at 170 °C. Key: —●— face 1 M + 20% Lil; —○— face 2 M + 20% Lil; —■— face 1 M + 10% Lil; —□— face 2 M + 10% Lil. M = $NaOH \cdot H_2O + KOH \cdot H_2O$ (50/50) and Lil = $LiOH \cdot H_2O$.

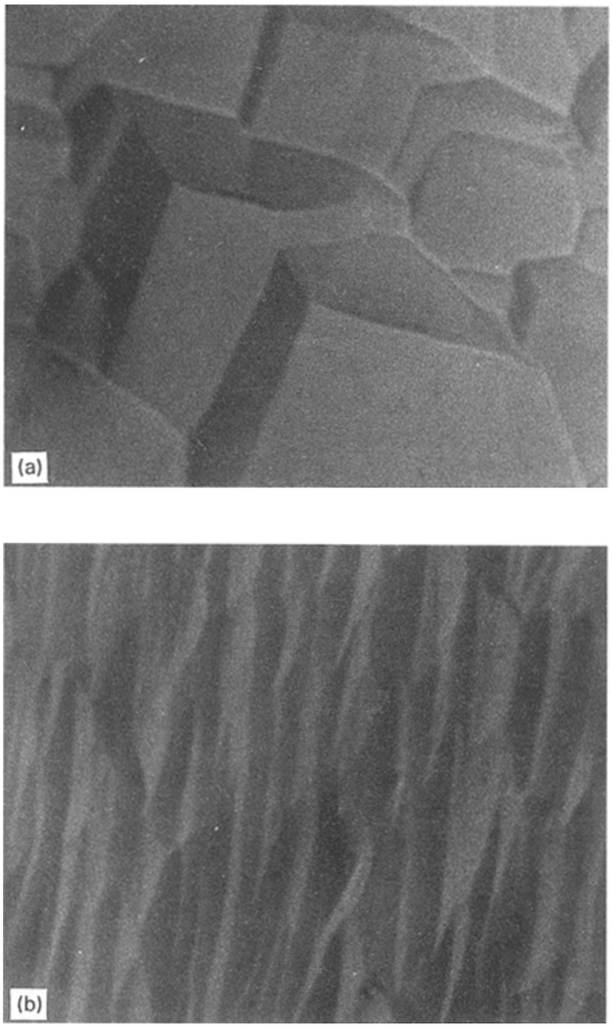

Figure 16 Dissolution feature of an SC cut thinned down in $NaOH \cdot H_2O + KOH \cdot H_2O$ (50/50) + 10% $LiOH \cdot H_2O$. $\Delta e = 49$ μm, (a) face 1, $Ra = 0.265$ μm, and (b) face 2, $Ra = 0.090$ μm.

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