



The phase transition of $MClO_4$ (where M is K, Rb, Cs) monitored by simultaneous AE–DTA measurement[☆]

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Abstract

The reversible transition of the orthorhombic to the cubic phase in powdered $MClO_4$ (where M is K, Rb, Cs) was followed by a home-made simultaneous AE–DTA apparatus. It was found that the mechanical events occurring prior to the transition as well as by the transition itself in both directions are detected by the AE method. Repeated AE runs reduced the cumulative counts for both transitions, finally giving almost constant values. The cumulative counts for the backward transition were greater than in the forward one.

Keywords: AE; Alkali metal perchlorate; Coupled technique; DTA; Perchlorate; Phase transition

1. Introduction

Acoustic emission (AE) is emitted when a mechanical event, such as the occurrence of cracks, release of stress or movement of dislocation, takes place in a solid. Because a phase transition in a solid accompanies a mechanical event, the AE technique provides a useful means of following this phase transition. The author has designed an apparatus for the simultaneous measurement of AE and differential thermal analysis (DTA) and has reported on its application to studies of the phase transition [1–4]. As a successful application, a study of the γ to α transition of KNO_3 has been reported; the AE method could follow sensitively the very slow

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process of the transition, which was not detected by DTA [4]. The present paper describes simultaneous AE–DTA measurements for the reversible change of the orthorhombic \rightleftharpoons cubic transition of powdered $MClO_4$ (where M is K, Rb, Cs) samples by repeated heating and cooling runs.

2. Experimental procedure

As-received powdered samples of $MClO_4$ (where M is K, Rb, Cs) were used as a starting material. $\alpha\text{-Al}_2\text{O}_3$ powder was used as the reference material. The sample and reference powders were placed in two fused silica holders covered with a cap. A fused silica rod, fixed at the bottom of the sample holder, acted as a wave-guide. A piezoelectric sensor resonating at a frequency of 140 kHz was attached to the end of the rod. The acoustic waves generated in the sample were transmitted through the rod to the end where they were converted by the sensor to voltage amplitude–time signals. The signals were changed to two AE parameters of the event count rate and the cumulative event count by a discriminator and dual counter. This homemade AE apparatus was reported in more detail elsewhere [1].

The sample was observed during heating and cooling by a high-temperature optical microscope, comprising an optical microscope equipped with a hot stage. The details of this apparatus were also reported elsewhere [3, 4].

3. Results and discussion

Fig. 1 shows the simultaneous AE and DTA curves obtained by eight repeated heating/cooling cycles of the $KClO_4$ sample; the 3rd to 7th runs were omitted because they gave almost the same results as the 8th run. The first heating run gives an endothermic peak at 305–330°C on the DTA curve and two bundles of AE signals around 120°C and at 170–325°C. It is clear that the endothermic peak is due to the transition from the orthorhombic to cubic phase. Referring to the previous paper [2], the early AE peak at around 120°C is associated with the formation of grooves or angulation of particles 100–300 μm in size. The later pre-transition AE peak should arise from the break-up of the surface skins of large particles and cracking on the surface of small particles emerging from large ones. The AE peak from the phase transition is hidden under the pre-transition peak. The first cooling run from 350°C gives the exothermic DTA peak due to the cubic to orthorhombic transition at 310–275°C. Judging from the good correspondence with the DTA result, the AE peak seen in the narrow temperature range of 315–300°C must be attributed to the transition.

The second heating run reproduces the endothermic peak due to the forward transition, and extinguishes the pre-transition AE signals, revealing the AE signals for the transition in the narrow temperature range of 310–320°C, which had been hidden. Thus, these pre-transition events were only manifested in the virgin samples. The 8th heating and cooling runs give almost the same AE and DTA

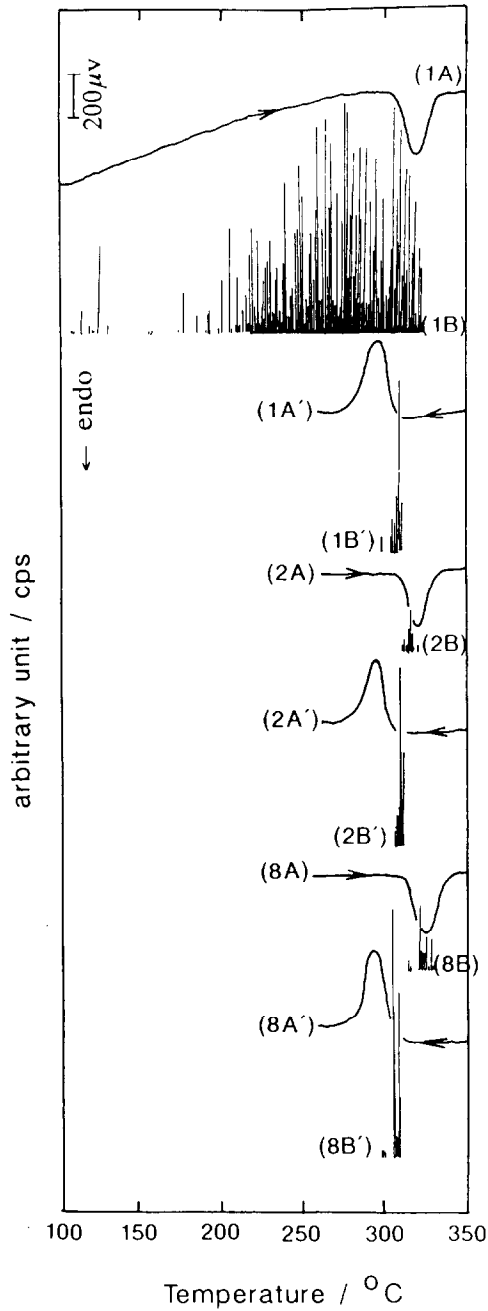


Fig. 1. Repeated runs for simultaneous AE-DTA measurement in the orthorhombic \rightleftharpoons cubic transition of KClO_4 . A, DTA curve; B, AE curve. A heating run is labelled A and B, a cooling run A' and B'; sample mass, 200 mg.

results as the second runs. It is understood that the transition in both directions can be clearly detected by the AE technique, as compared with DTA; the initiation temperature becomes more distinct on the AE curves.

The AE and DTA curves in the reversible transition of the orthorhombic \rightleftharpoons cubic phase of RbClO_4 are shown in Fig. 2. In the first heating run, AE signals appear at 200–310°C, which may be caused by mechanical events similar to those in the KClO_4 , and hide the AE signals due to the transition, which are revealed on the second heating. On cooling, the very sharp AE peak at a narrow temperature interval of 10°C is recognized, as compared with the DTA curve. The DTA and AE peaks obtained from 2nd to 10th runs give almost the same results.

Fig. 3 shows the AE–DTA curves obtained by the 10 repeated heating and cooling runs on the reversible transition of the orthorhombic \rightleftharpoons cubic phase of CsClO_4 . It is seen that AE signals begin at 110°C, continuing to be emitted to 200°C. After that, the intense peaks a and b appear, which are correlated with the phase transition, as understood from correspondence with the DTA curve. An SEM photograph of the samples heated to 185°C showed that the surface of the particles becomes uneven and pitted, with small particles emerging from the mother particles. These changes must be caused by loss of the surface skin of the mother samples, which give rise to AE signals at 110–200°C, as for KClO_4 .

It is interesting that peak a is strong 200–210°C, just before the transition. Peak b roughly corresponds to the endothermic DTA peak due to the transition. It was observed by high temperature microscopy, as seen from Fig. 4B which is out of focus, that on heating to 200°C the aggregate particles began to shake vigorously, some seeming to almost detach themselves from the mother particles, as compared with those at 185°C (Fig. 4A). It is likely that peak a is attributed to the shaking of the particles prior to the transition. Immediately after the particles cease to shake (216°C), distinct bright lines (see the arrow in Fig. 4C), which are indicative of a phase boundary, were observed to move on the surface of the particles. After the particles have gone through the transition, they become deformed or rearranged and cracked. Thus, peak b is associated with the deformation/rearrangement and cracking of the particles, caused by the phase boundary movement.

In the first cooling run, weak AE signals are seen prior to the backward transition, followed by a relatively intense AE peak corresponding to the exothermic DTA peak. In this cooling run, the particles did not shake as much as during the first heating run. The second heating run does not produce any pre-transition events such as vigorous shaking and moving particles, whereas a reduced AE peak due to the transition is observed. In the second cooling run, AE signals are similar to those observed in the first cooling run. The 10th heating and cooling runs still show the AE peak due to the transition in both directions.

Fig. 5 shows the effect of the number of repeated cycles on the cumulative counts emitted during the forward and backward transitions for the samples of KClO_4 , RbClO_4 and CsClO_4 . It is found that in each sample, the cumulative counts for both transitions decrease abruptly during the 2nd–5th cycles, after which they tend to become constant. A large decrease in the count during the 2nd–5th cycles is correlated with a decrease in the degree of cracking of the particles with the

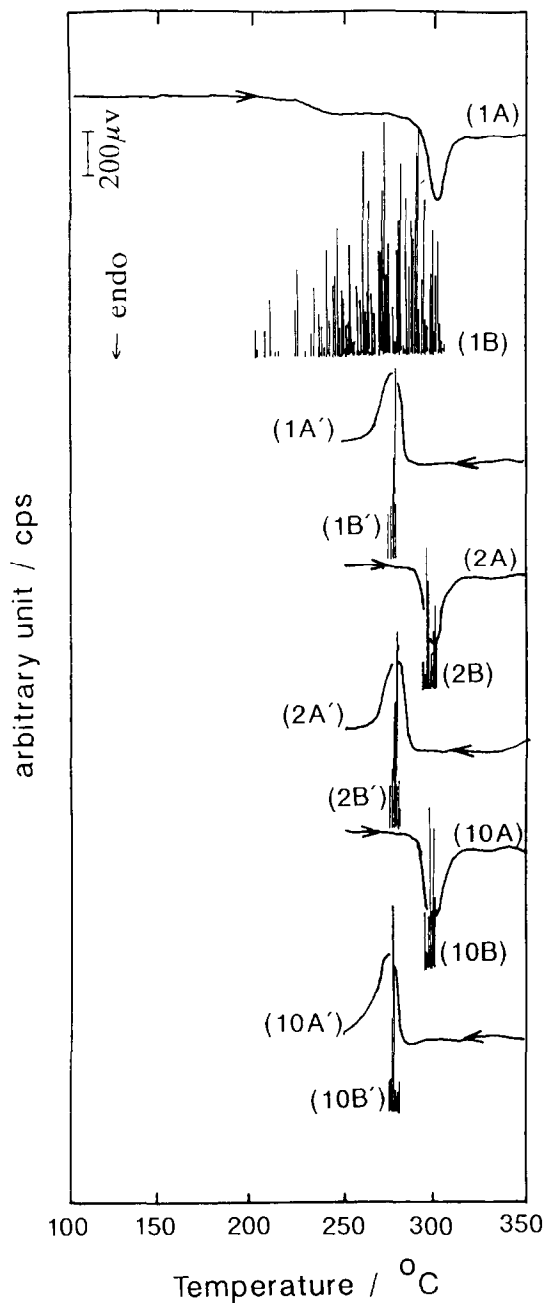


Fig. 2. Repeated runs for simultaneous AE-DTA measurement in the orthorhombic \rightleftharpoons cubic transition of RbClO_4 . The labels A, A', B and B' are the same as in Fig. 1; sample mass, 200 mg.

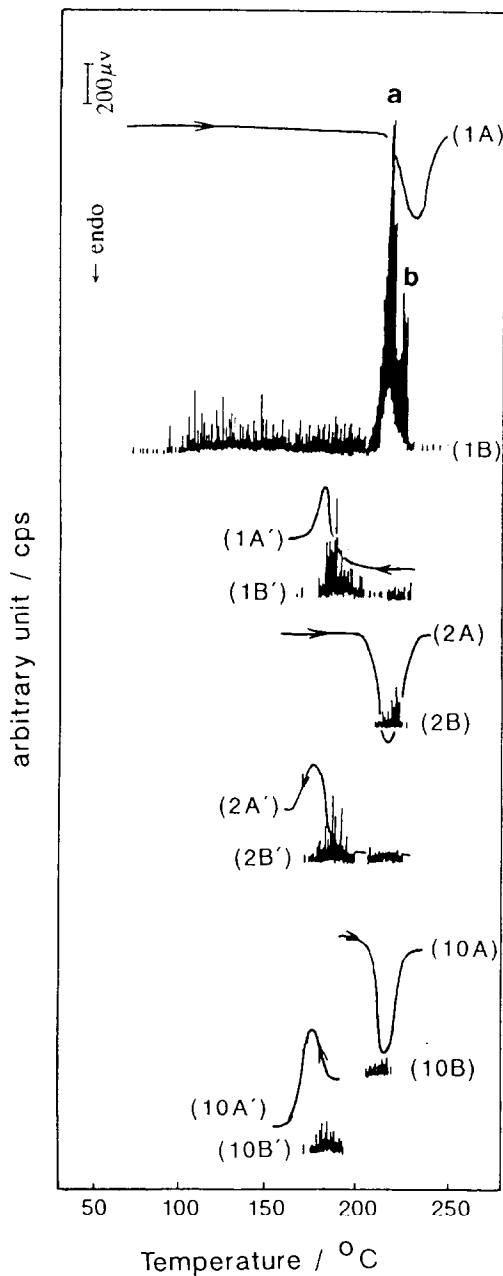


Fig. 3. Repeated runs for simultaneous AE-DTA measurement in the orthorhombic \rightleftharpoons cubic transition of CsClO_4 . The labels A, A', B and B' are the same as in Fig. 1; sample mass, 200 mg.

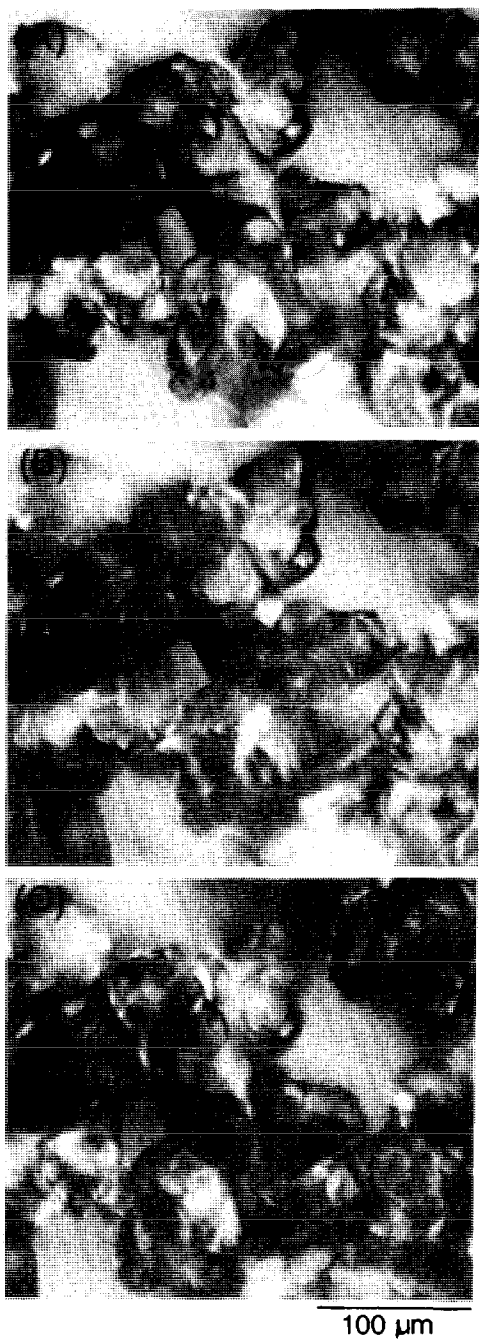


Fig. 4. High temperature optical micrographs of the orthorhombic \rightarrow cubic transition of CsClO_4 : A, 185°C; B, 200°C; C, 216°C.

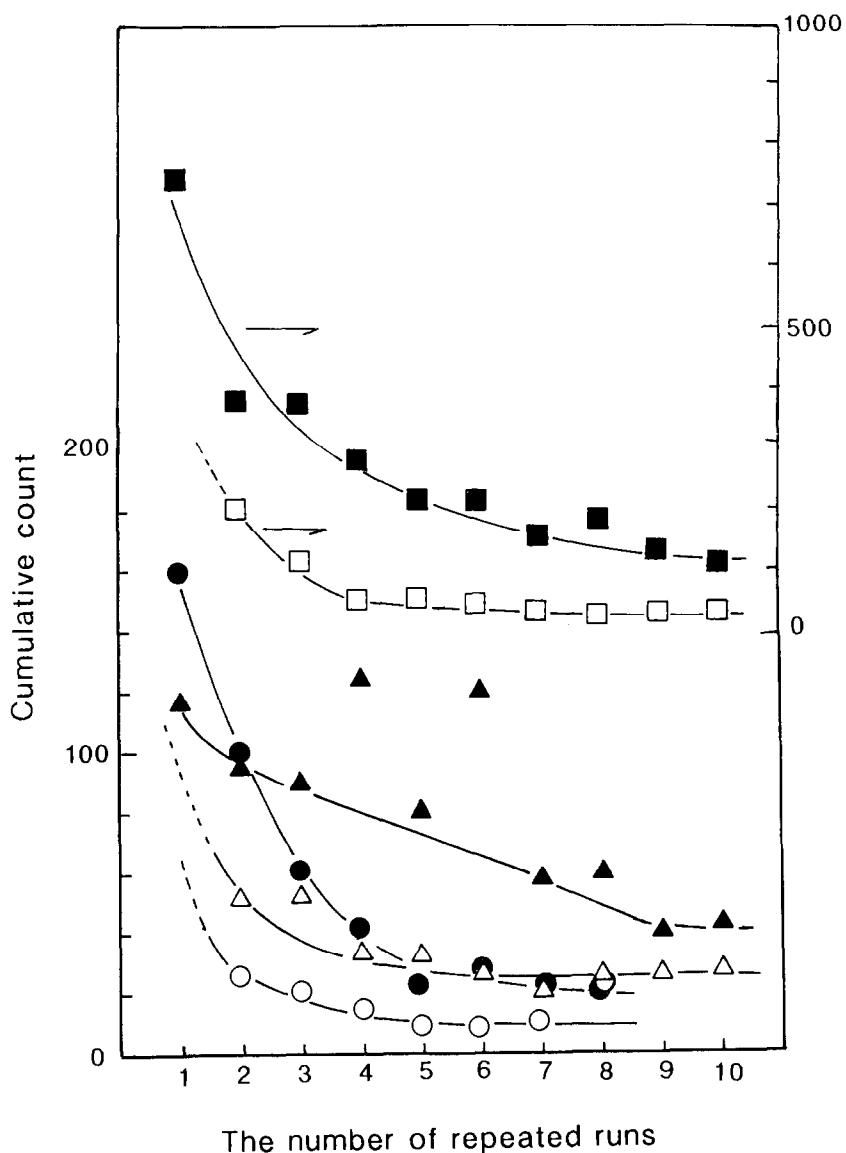


Fig. 5. The effect of the number of repeated heating/cooling cycles on the cumulative counts during the transition in both directions: \circ , \bullet , KClO_4 ; \triangle , \blacktriangle , RbClO_4 ; \square , \blacksquare , CsClO_4 . Open symbols indicate orthorhombic to cubic transition; solid symbols represent cubic to orthorhombic transition.

repeated cycles. After much cracking of the particles up to above the 6th cycle, only AE signals due to the transition are thought to be emitted from the sample, giving the constant counts. The counts in the backward transition are greater than in the forward. This may be explained in terms of a healing effect of the cracked particles

by heating to 50°C higher than the phase transition. These healed particles could crack again during the backward transition.

4. Conclusions

It is assumed that in the powdered $MClO_4$ (where M is K, Rb, Cs) samples, the AE signals emitted over a wide temperature range prior to the phase transition resulted from mechanical changes caused by loss of surface skin of the particles. The reversible transition of the orthorhombic to the cubic phase of $MClO_4$ could be followed by the AE technique. In the case of $CsClO_4$, it was observed that the aggregate particles shook or moved vigorously just before the transition, which gave an intense AE peak, peak a. The repeated AE runs reduced the cumulative counts for the transition, finally giving almost constant values. The cumulative counts for the backward transition were greater than for the forward transition.

References

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