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A study on phase transition of CsCl ⇌ NaCl in CsCl, NH_4Cl and NH_4Br by simultaneous AE-DTA measurement[1]

S. Shimada*, Y. Katsuda[2], M. Inagaki

Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

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Abstract

The phase transition of the CsCl ⇌ NaCl type structure was followed in CsCl, NH_4Cl and NH_4Br powder samples by simultaneous AE-DTA measurement. Acoustic emission (AE) was detected during the transition, which arose from cracking and/or the transition itself. The cumulative counts of AE during the forward and backward transitions decreased with the number of repeated heating/cooling cycles, and finally became constant. The averaged power spectra of AE in three samples were found to be similar to each other and consist of low (50–400 kHz) and high frequency (above 500 kHz) components. The latter tended to decrease with a repeated number of the cycles.

Keywords: Phase transition; Acoustic emission; DTA; Power spectra; CsCl and NaCl type structure

1. Introduction

It is known that acoustic emission (AE) is generated when a mechanical event, such as occurrence of cracks, accumulation and release of stress and movement of dislocation, takes place in a solid. When the phase transition proceeds in a solid, it often emits AE waves due to mechanical events so that the AE technique can be used for its "in situ" measurement. One of the authors (S.S.) has designed an apparatus for simultaneous measurement of AE and differential thermal analysis (DTA) and has reported its application to several studies of thermal decomposition of alkali perchlorates [1–5], dehydration

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* Corresponding author.

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[2] Present address: NGK Insulators, Ltd., Mizuho, Nagoya 467, Japan.

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of $CaCrO_4 \cdot xH_2O$ [6] and phase transition of alkali perchlorates [5,7] and KNO_3 [8]. It was demonstrated in these reports that the simultaneous AE-DTA measurement enables us to follow not only the phase transition but a pre-transition event like the vibration of $CsClO_4$ particles, and to clearly detect the γ to α transition of KNO_3 which cannot be followed by DTA and DSC because it occurs very slowly over a wide temperature range.

Several alkali and ammonium halides (CsCl, NH_4Cl, NH_4Br) undergo transition between the CsCl and NaCl type structures. The transition involves a change in the primary coordination number between 6 and 8, and is considered to occur through a dilatational mechanism where the primitive cubic unit cell of CsCl is expanded along its body diagonal direction; such a transition is expected to emit AE. In this report, the simultaneous AE-DTA technique can follow mechanical and thermal changes occurring during the transition of the CsCl $\rightleftharpoons$ NaCl type structure in three samples of CsCl, NH_4Cl and NH_4Br. The averaged power spectra of AE waves were also detected during the transition.

2. Experimental procedure

The samples were commercially available powders of CsCl, NH_4Cl and NH_4Br (Kanto Chem. Co. Inc., Tokyo). As-received samples of 200 mg were used for the AE-DTA measurement. α-Al_2O_3 powder was used as the reference material. The sample and reference materials were placed in two fused silica holders. An Alumelchromel thermocouple was used for recording the heating temperature and DTA signal. The heating and

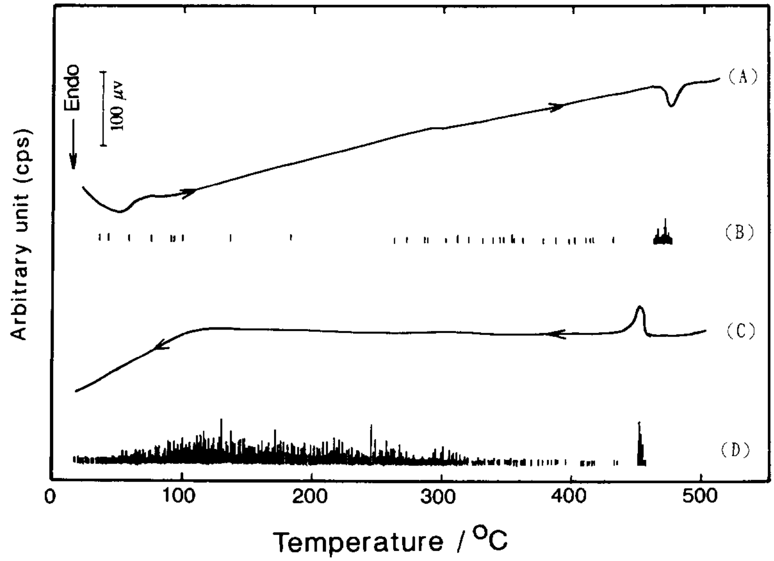

Fig. 1. Simultaneous AE-DTA curves obtained during one cycle of heating/cooling of CsCl sample: heating curves, DTA (A) and AE (B); cooling curves, DTA (C) and AE (D).

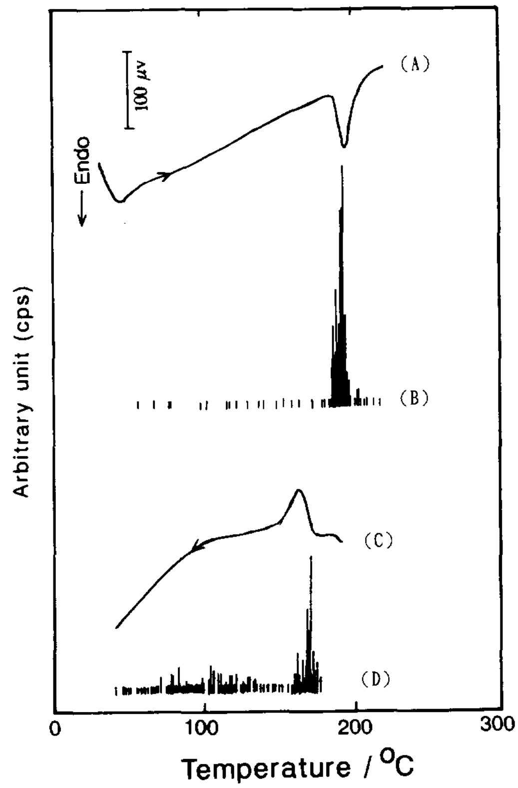

Fig. 2. Simultaneous AE-DTA curves obtained during one cycle of heating/cooling of NH_4Cl sample: heating curves, DTA (A) and AE (B); cooling curves, DTA (C) and AE (D).

cooling rates of the samples were 5°C min^{-1} in air. A fused silica rod, fixed at the bottom of the sample holder, acted as the wave guide. A piezo-electric sensor, resonating at a frequency of 140 kHz, was attached at the end of the rod. Two AE output parameters were recorded. The details of the AE-DTA apparatus have been reported elsewhere [1]. For measurements of the power spectra of AE wave generated, a wideband AE sensor was used. The monitoring procedure was also described in detail in our previous paper [3].

3. Results and discussion

3.1. Simultaneous AE-DTA measurement

Fig. 1 shows the simultaneous AE-DTA curves obtained in one heating and cooling cycle of the CsCl powder samples between 20 and 515°C. On heating, an endothermic peak is seen in the temperature range of 468–488°C on the DTA curve (A), the corre-

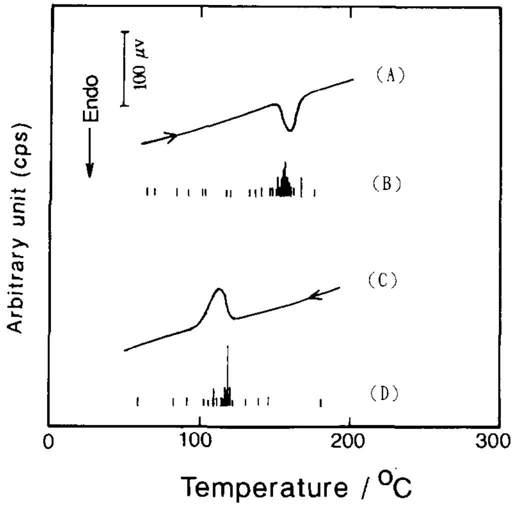

Fig. 3. Simultaneous AE-DTA curves obtained during one cycle of heating/cooling of NH_4Br sample: heating curves, DTA (A) and AE (B); cooling curves, DTA (C) and AE (D).

sponding AE peak being observed at 463 to 478°C (B). These DTA and AE peaks are due to the transition of CsCl to the NaCl structure. On cooling, the exothermic peak on the DTA curve and AE signals due to the reverse transition are seen at 457–437°C and 460–450°C, respectively. It is found that the starting temperature of both forward and backward transitions is more clearly determined on the AE curves than on the DTA curves. AE signals appearing below 360°C continued to be emitted to room temperature on cooling. These signals are not associated with the structural transition, since the sam-

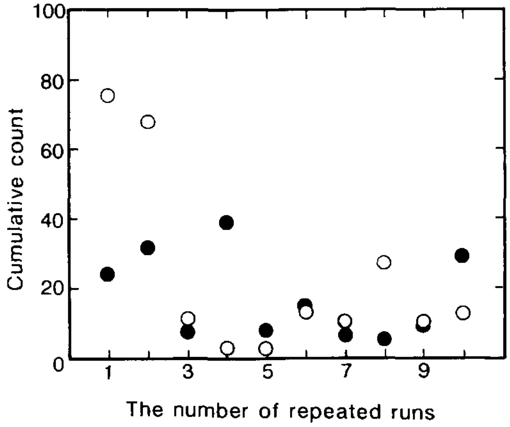

Fig. 4. Influence of the number of repeated heating/cooling cycles of CsCl sample on the cumulative counts: ○, forward transition; ●, backward transition.

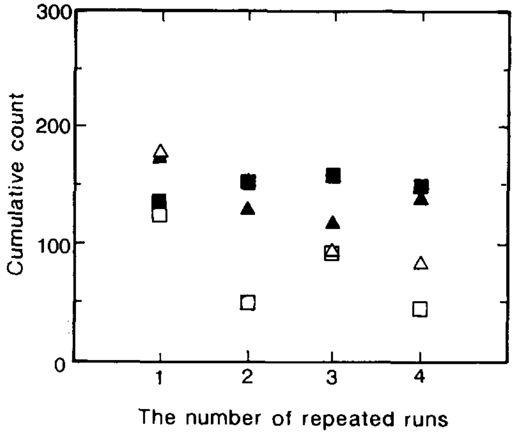

Fig. 5. Influence of the number of repeated heating/cooling cycles of the NH_4Cl and NH_4Br samples on the cumulative counts: boxes, NH_4Cl; triangles, NH_4Br; open symbol, forward transition; closed symbol, backward transition.

ples heated up to 450°C which had not experienced the transition also produced similar signals at 330–20°C. It is probable that these signals resulted from deformation or cracking due to shrinkage of the particles which had sintered on cooling. This is supported by SEM observations which showed the particles to be deformed, cracked and angular.

The simultaneous AE-DTA curves in one heating/cooling cycle of the NH_4Cl powder samples between 20 and 230°C are shown in Fig. 2. The forward and backward transitions between the CsCl and NaCl structures produce AE peaks with endothermic and exothermic DTA peaks at 182–198°C and 180–160°C, respectively, and the AE generation finishes five degrees earlier than the thermal change. It is likely that AE signals occurring below 140°C on cooling are due to deformation or cracking of NH_4Cl particles, in a similar way to that of CsCl.

The forward and backward transitions of the NH_4Br samples between the CsCl and NaCl structures are shown in Fig. 3, in which the AE peaks corresponding to the DTA endothermic and exothermic peaks are produced. In the NH_4Br samples, no AE signals are seen on cooling at temperatures below the transition, unlike in the CsCl and NH_4Cl samples. It is understood that the AE signals are detected during the transitions of the CsCl $\rightleftharpoons$ NaCl structure in the powder samples of CsCl, NH_4Cl and NH_4Br, and terminated several degrees earlier than the thermal change. The structural transition from CsCl to NaCl causes volume expansion of 27.3, 20.0 and 20.9 vol.% in CsCl, NH_4Cl and NH_4Br, respectively. Therefore, acoustic emissions observed must result from stress relaxation or cracking due to such a large volume change.

Fig. 4 shows the influence of the number of repeated heating/cooling cycles between 20 and 515°C on the cumulative counts emitted during the forward and backward transitions in CsCl. In the forward transition, the first and second heatings give about 70–80 counts in contrast to 20–30 counts in the backward transition. After the 4th cycle, the count number hardly changes, becoming constant at 10–30 counts, in both directions of

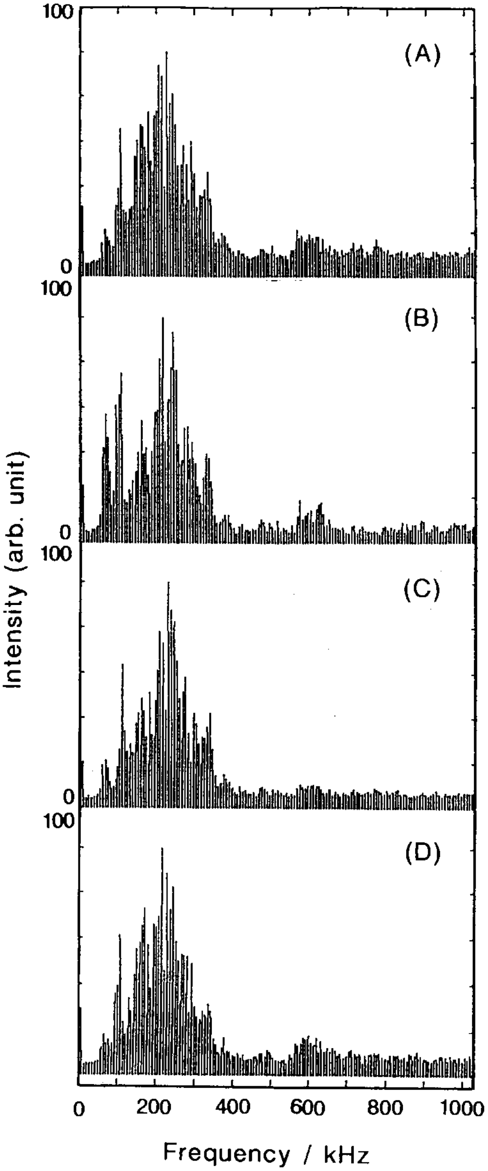

Fig. 6. Averaged power spectra obtained by the forward and backward transitions of the CsCl sample: the first heating/cooling (A/B); the second heating/cooling, (C/D).

transition. The counts in the 1st to 4th cycles should involve both the external and internal events like cracking and stress relaxation, respectively. After the 4th cycle, the counts must arise from only the internal events. In the NH_4Cl and NH_4Br samples, the repeated runs gradually decrease the cumulative counts (Fig. 5), then becoming almost constant.

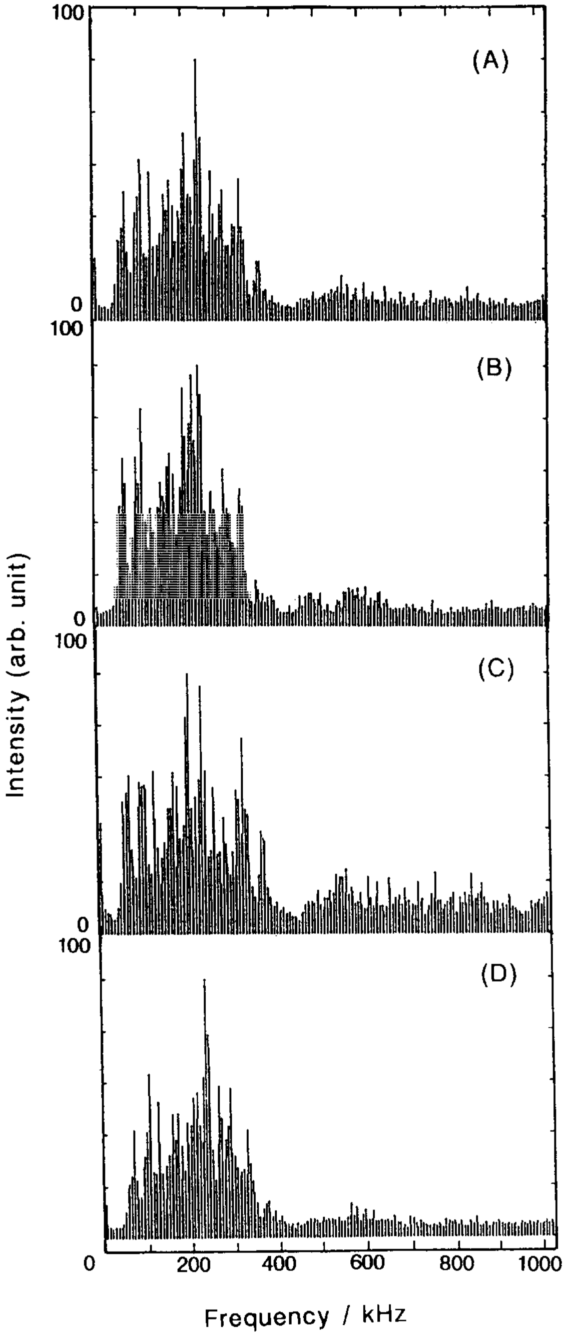

Fig. 7. Averaged power spectra obtained by the forward and backward transitions of the NH_4Cl sample: the first heating/cooling (A) and (B); early and later periods of the first heating (C) and (D).

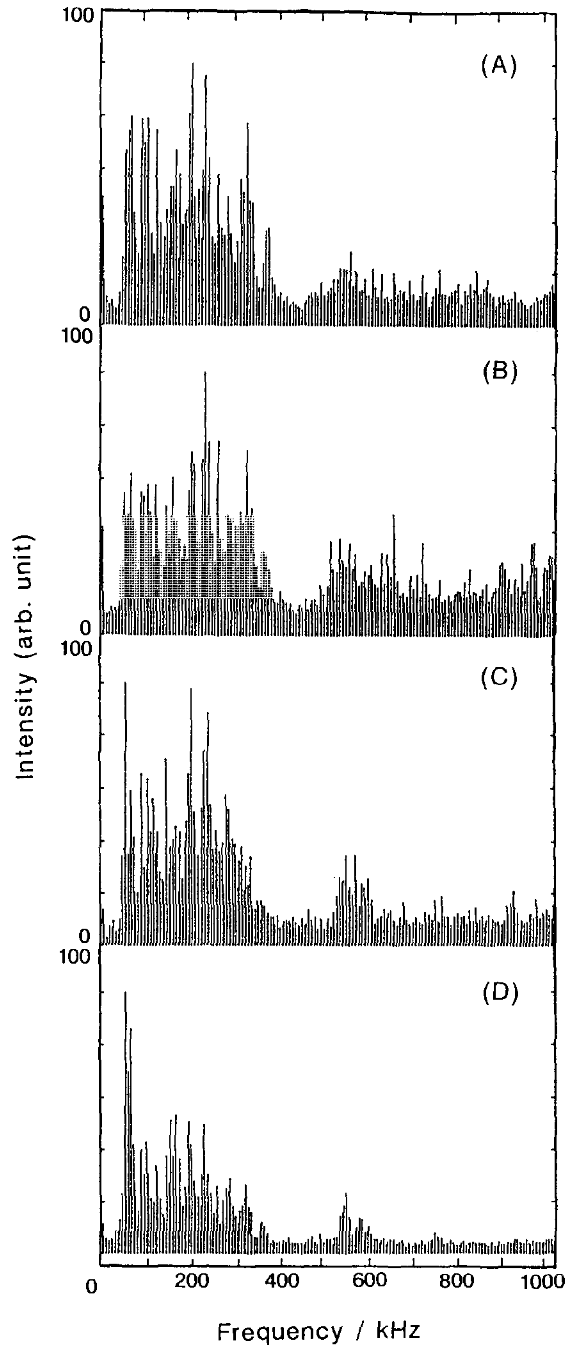

Fig. 8. Averaged power spectra obtained by the forward and backward transitions of NH_4Br sample: the first heating/cooling (A/B); the second heating/cooling (C/D).

The backward transition finally gives rise to about 150 counts in spite of 40–80 counts in the forward transition. The backward transition may contain a part of the stress remaining unreleased even after the forward transition, which was freed by heating before the backward transition began. Both transitions gave similar counts in CsCl, which can be explained by the high temperature heating which had already released stress during the forward transition.

3.2. Power spectra

Fig. 6 shows the averaged power spectra of AE during the CsCl $\rightleftharpoons$ NaCl transition of the CsCl samples, which are obtained from 35 AE signals by the first heating/cooling cycle (A/B) and the second heating/cooling cycle (C/D) of the CsCl samples. It is found that all the power spectra are similar and consist of low frequency components in a range of 50–400 kHz and high frequency components around 550 kHz.

As shown in Fig. 7A,B, there is no great change in the averaged spectra of the two transitions in the first heating/cooling runs of NH_4Cl. The averaged spectra obtained in the early (<180°C) and later period (>180°C) in the first forward transition (Fig. 7C,D) show that the high frequency components above 450 kHz are reduced with increase in either time or temperature. This suggests that the early forward transition involves events associated with the high frequency components, like cracking, after which events in the low frequency region predominate.

The power spectra of the two transitions obtained by the first and second heating/cooling cycles in NH_4Br are shown in Fig. 8A–D. The spectra also consist of low and high frequency components below and above 450 kHz. The high frequency components above 600 kHz in the first backward transition are remarkable (Fig. 8B). Compared with the first cycle, the second heating/cooling cycle reduces the high frequency components above 600 kHz, particularly in the backward transition. This is probably because cracking comprising of the high frequency components has occurred in the first transitions. It is summarized that the spectra obtained in the three samples are similar, consisting of low (50–400 kHz) and high frequency (above 400 kHz) components. The latter is reduced by the repeated heating/cooling cycles, since the first cycle cracks the particles.

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