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The phase transition of Rb-doped KNO_3 monitored by acoustic emission and high temperature X-ray diffraction[1]

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Abstract

The phase transitions in Rb-doped KNO_3 samples between the α, β and γ phases were followed by simultaneous acoustic emission (AE)–DTA measurement and high temperature X-ray diffraction. When the samples were cooled from 400°C (above the melting point of 340°C), the β to γ and γ to α phase transitions shifted to a lower temperature and higher temperature, respectively, with increasing amounts of Rb dopant. When 0.5 mol%-doped samples were cooled from 300°C, the ferroelectric γ phase began to transform to the α phase at about 60°C, and survived even at room temperature. The transition behaviour of the pure and 0.5 mol%-doped samples monitored by the AE technique was confirmed by high temperature X-ray diffraction.

Keywords: Acoustic emission (AE); High temperature X-ray diffraction; Phase transition; Rb-doped KNO_3

1. Introduction

Potassium nitrate, KNO_3, can exist in three different phases at atmospheric pressure. When heated from room temperature, α-KNO_3 (space group, Pmcn) transforms to the β phase (space group, R3m) at 128°C. On cooling the β phase it passes through the γ phase (space group, R3m) at around 124°C to the α phase [1]. Stabilization of the γ phase at room temperature has attracted much attention because of its useful ferroelectric property [2].

It has been reported that the γ to α transition proceeds over a wide temperature range, depending on the thermal history, sample size and/or impurities [3]. In our

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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previous papers it was demonstrated that the γ to α transition was affected by the temperature (160–450°C) from which the samples were cooled [4, 5]. It was first noted that the effect of temperature on the transition was associated with the healing of the defects formed by the α to β transition; the temperature and healing effects were confirmed by acoustic emission (AE) and high temperature microscopy [5].

It is also worthwhile investigating the effect of impurities on the γ to α transition from a viewpoint of stabilizing the γ phase at room temperature for ferroelectric applications. It was found by the authors that the γ phase in Na-doped KNO_3 samples is stabilized at room temperature (25°C) for more than one day [6] Kawabe et al. [5] reported that mixed crystals of $Rb_xK_{1-x}NO_3$ were grown using the Ramperger–Melvins method. They measured the temperature-dependence of dielectric constants along C-axis of the mixed crystals for $x = 0.23$, but did not mention the γ to α transition of the crystals. In the present paper, the three transitions of the Rb-doped KNO_3 samples were followed by simultaneous AE–DTA and high temperature X-ray diffraction techniques with particular attention being given to the γ to α transition.

2. Experimental

Starting KNO_3 powders were commercially purchased from Kanto Chemical Co. (Tokyo, Japan). Rb-doped KNO_3 samples were obtained by co-melting KNO_3 and $RbNO_3$ at 450°C with subsequent slow cooling to room temperature. The resulting solidified plate-like sample was ground and passed through a 500 μm sieve. The lattice constants of the Rb-doped KNO_3 samples were measured by X-ray powder diffraction, using Si powders as the internal standard.

The sample and reference materials (α-Al_2O_3) were placed in two fused silica sample holders. Alumel–chromel thermocouples were used for recording the sample temperature and DTA signal. The heating and cooling rates for the sample were 5°C min^{-1}, but an average natural cooling rate of 1.5°C min^{-1} resulted when the sample was cooled from 100°C. 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 at the end of the rod. The AE event rate and cumulative counts were recorded by a dual counter, after waves were discriminated at a threshold voltage of 40 mV by a discriminator.

The phase transitions of the pure and Rb-doped KNO_3 samples were also monitored by high temperature X-ray diffraction and optical microscopic methods.

3. Results and discussion

Fig. 1 shows the simultaneous AE–DTA curves of the pure samples in one heating and cooling cycle between 20 and 400°C. Referring to a previous paper [5], we consider that the low temperature DTA and AE peaks at 130 to 150°C on curves (A) and (B) are due to the α to β phase transition, the high temperature peaks being caused by the melting of KNO_3. AE signals generated between room temperature and 120°C must

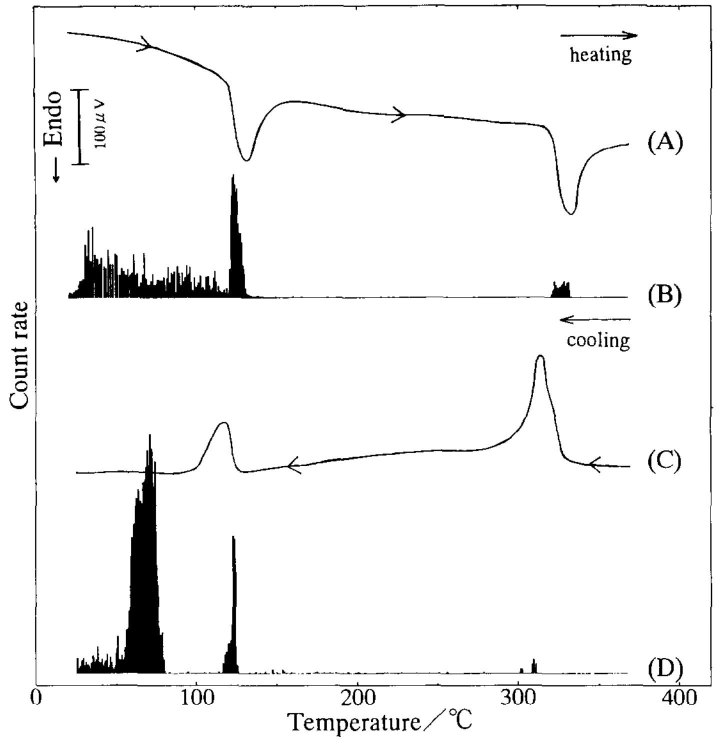

Fig. 1. Simultaneous AE–DTA curves obtained during one heating–cooling cycle of KNO_3 powders: heating curves, DTA (A) and AE (B); cooling curves, DTA (C) and AE (D); sample weight, 200 mg.

result from cracking of a part of the intact plate-like particles. When the samples were cooled from 400°C, two exothermic peaks and the corresponding AE peaks appear on DTA and AE curves ((C) and (D)), due to solidification of molten KNO_3 at 330°C and the β to γ transition at 125°C. AE signals observed below 85°C correspond to the γ to α transition. No thermal effect corresponding to the γ to α transition was observed, because the transition occurred over a wide temperature range of 85 to 50°C; AE signals below 50°C may occur as a result of microcracking of the particles.

The lattice parameters (a_0, b_0 and c_0) and cell volume of the 0.5, 5 and 15 mol% Rb-doped KNO_3 samples were plotted against Rb mol% (Fig. 2). The a_0 and c_0 values increase linearly with increasing Rb mol%, in contrast to the b_0 value which decreases with increasing Rb content. This linear relationship indicates formation of solid solution of $RbNO_3$ in KNO_3. The cell volume of the Rb-doped sample also shows a linear increase with dopant concentration, increasing by about 0.6% at 15 mol%.

A one-cycle heating–cooling AE–DTA run was performed for each of the 0.5, 5 and 15 mol%-doped samples between 25 and 400°C (Fig. 3); the heating AE–DTA curves are not shown because they were almost the same as those of Fig. 1. With 0.5 mol% doping, the β to γ transition begins at almost the same temperature (135°C) as that for

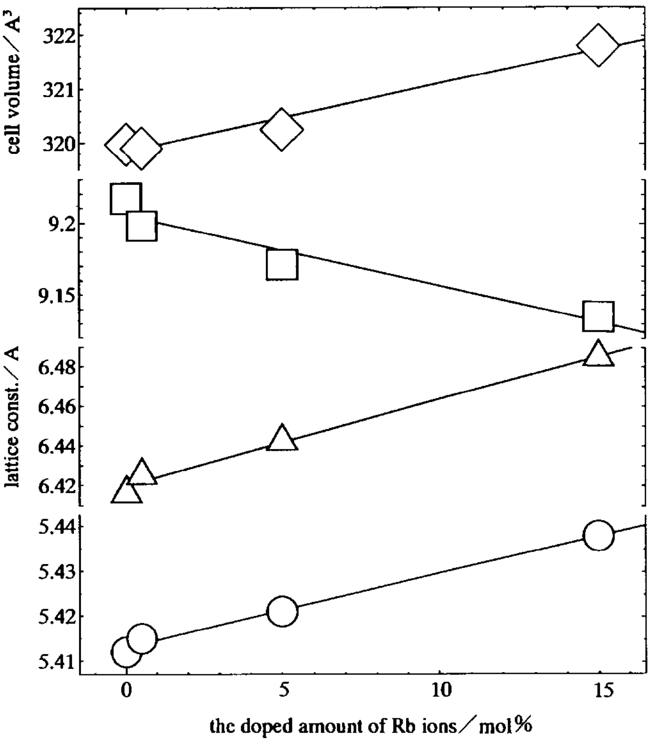

Fig. 2. Relationship between Rb dopant concentration and the lattice constants and cell volume of doped KNO_3. ○, a_0; □, b_0; △, c_0; ◇, cell volume.

pure KNO_3, as shown by the DTA and AE peaks (curves (A) and (B)). On increasing the dopant content, the thermal and AE effects of this transition shift to a lower temperature. The AE signals which occur on the rising part of the DTA curve are greatly increased as the dopant content is increased. A packet of AE signals which appears prior to the β to γ transition extends to higher temperatures and becomes more intense with increasing Rb content. High temperature optical microscopic observation of the 15 mol%-doped samples showed severe surface cracking of solidified plate-like particles, indicating that the AE signals generated before the β to γ transition arise as a result of cracking of the bulk sample during cooling.

From the AE curve, the γ to α transition of the 0.5 mol%-doped samples begins at approximately 60°C, 25° lower than in the pure samples (Fig. 3(B)). AE signals continue to occur for 3 h even at room temperature. At 5 mol%, AE signals resulting from the transition begin around 90°C, reaching a maximum, then decaying at about 60°C (Fig. 3(D)). With 15 mol% dopant, weak AE signals which occur at approximately 100°C persist down to room temperature (Fig. 3(F)). Compared with the β to γ transition, the γ to α transition occurs over a wide temperature range from 60°C (or 90°C) to room temperature.

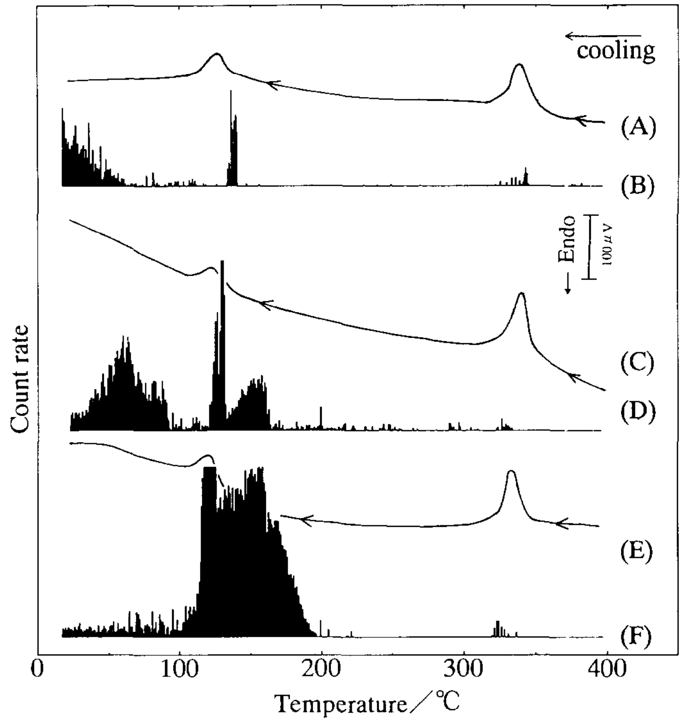

Fig. 3. Simultaneous AE–DTA curves obtained on cooling from 400°C of KNO_3 samples doped with 0.5, 5 and 15 mol% Rb ions: DTA (A) and AE (B) at 0.5 mol%, DTA (C) and AE (D) at 5 mol%, DTA (E) and AE (F) at 15 mol%; sample weight, 200 mg; full scale count rate = 10^5 counts.

In our previous paper [5], the γ to α transition is affected by the maximum heating temperature immediately preceding sample cooling. The transition range became narrower (55 to 20°C) on cooling samples from 220°C or above. In a similar way, the β to γ and γ to α phase transitions were monitored by the AE–DTA method in samples cooled from 300°C (Fig. 4). The doped samples used here were those which had been melted, cooled to room temperature, and crushed. The DTA and AE results from the α to β transition are also omitted from this paper because of their similarity to that of Fig. 1. AE signals which appeared prior to the β to γ transition in the samples solidified from 400°C were not observed, probably because the samples had already been crushed. The AE peak from the β to γ transition is also greatly increased and shifted to a lower temperature with increasing Rb content. The cumulative counts occurring in this transition are 2.6×10^2, 25×10^2 and 109×10^2 for the pure, 0.5 and 15 mol%-doped samples, respectively, showing a linear correlation with the dopant concentration. This could be because the increased Rb concentration increased stress in the cell which was then released during the transition.

The AE curve (Fig. 4(B)) shows that the γ to α transition of the pure samples begins at approximately 60°C, lower than for the pure solidified samples directly cooled from

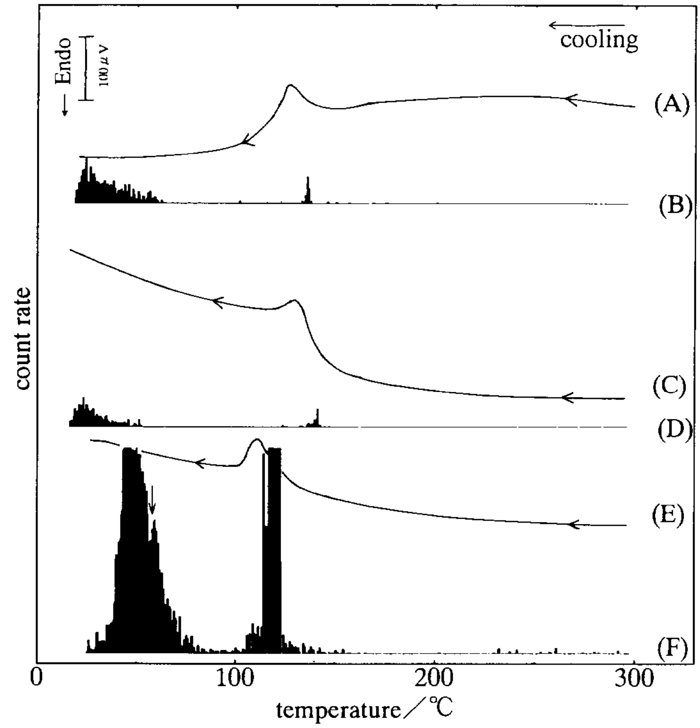

Fig. 4. Simultaneous AE–DTA curves obtained on cooling of pure, 0.5 and 15 mol% Rb-doped KNO_3 samples from 300°C: DTA (A) and AE (B) for pure samples, DTA (C) and AE (D) for 0.5 mol%-doped samples, DTA (E) and AE (F) for 15 mol%-doped samples; sample weight, 200 mg; full scale count rate = 10^3 counts in (B) and 10^4 counts in (D) and (F).

400°C, for which the transition is at 85°C (Fig. 1(D)), and the AE signals also continue to be emitted to room temperature. At 0.5 mol%, the AE signals began at approximately 50°C, and continued to be emitted at room temperature for 5 h. At 15 mol%, they began to arise at approximately 60°C, as shown by an arrow, and finished at approximately 25°C; the overlaping signals above 60°C arise as a result of cracking; this may be observed by high-temperature optical microscopy.

High temperature X-ray diffraction of the pure and 0.5 mol%-doped ground samples was carried out, as shown in Figs. 5 and 6, respectively. The heating–cooling cycle was the same as for Fig. 4. In both samples, the α to β and β to γ phase transitions began at approximately 130°C and 120°C, respectively, in reasonable agreement with the AE results (Fig. 4). On cooling, the α phase in the pure samples appeared at 60°C (arrow in Fig. 5), but the γ phase still remained; the amount decreased abruptly and disappeared at 20°C. At 0.5 mol%, the α to β and β to γ transition behaviour was similar to that of the pure samples. On cooling, the α phase began to appear at approximately 60°C, but the γ phase survived at 20°C and disappeared after 1.5 h at this temperature. At 15 mol%, the β to γ and γ to α phase trnasition behaviour was very similar to that of the 0.5

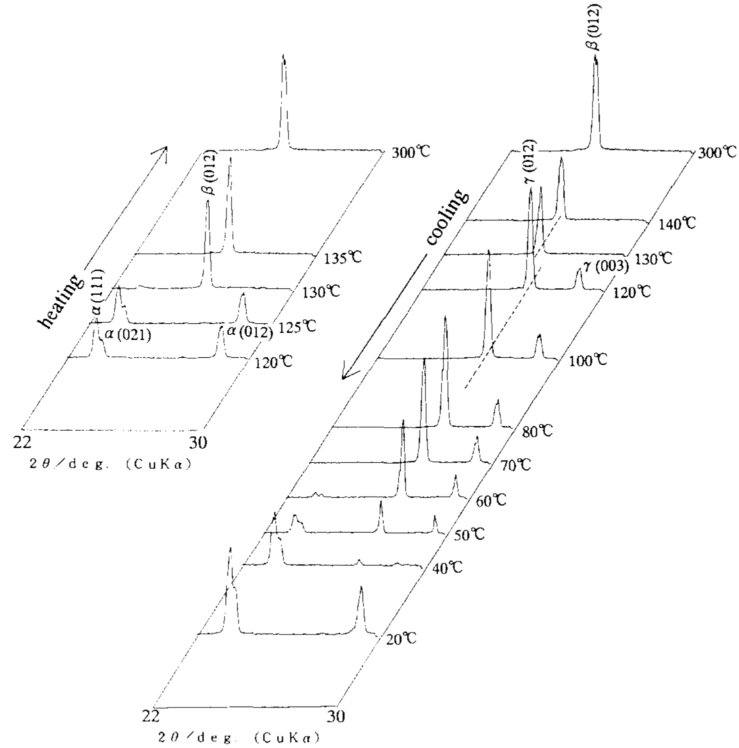

Fig. 5. High temperature X-ray diffraction patterns obtained during one heating–cooling cycle for pure KNO_3 between 20 and 300°C.

mol%-doped samples except that the α phase disappeared at approximately 30°C. Thus, the transition behaviour observed by X-ray diffraction results is very similar to that revealed by AE. Compared with the Na-doped samples, for which the γ phase is stable at room temperature, doping with Rb does not provide sufficient stabilization of the γ phase.

4. Conclusion

The three transitions of Rb-doped KNO_3 samples, involving the α, β and γ phases, were followed by AE and high-temperature X-ray diffraction techniques. It was concluded that,

(1) The α to β transition is not greatly affected by the concentration of Rb dopant.

(2) The AE peak due to the β to γ transition shifts to a lower temperature with increasing dopant concentration. The cumulative AE counts also increased linearly with dopant concentration.

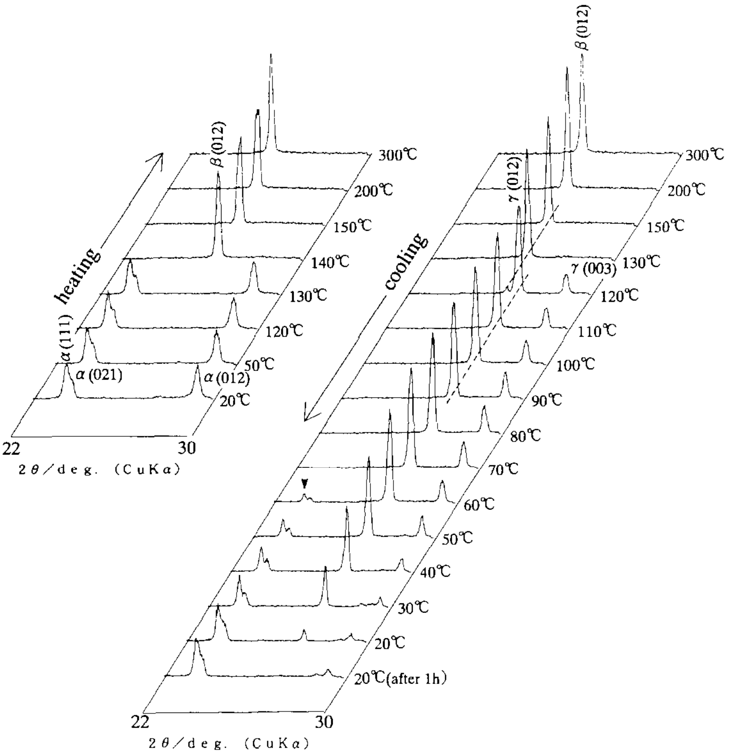

Fig. 6. High temperature X-ray diffraction patterns obtained during one heating–cooling cycle for 0.5 mol% Rb-doped KNO_3 between 20 and 300°C.

(3) At 0.5 mol% Rb, the γ phase survived for a prolonged time at room temperature, irrespective of whether the samples were cooled from the melt or not.

(4) High-temperature X-ray diffraction confirmed the β to γ and γ to α transition behaviour determined by the AE measurements.

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