Stabilization of the Ferroelectric γ-Phase of KNO_3 by Doping with Na^+, Determined by the Acoustic Emission Method

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A stabilized region of the ferroelectric γ-phase of KNO_3 doped with Na^+ ions was detected by simultaneous acoustic emission (AE)-differential thermal analysis (DTA). The γ to α phase transition in KNO_3 was affected by doping with Na^+, which lowered the onset temperature from 60 °C in the pure samples to 38 and 42 °C for 0.5 and 1 mol% doped samples, respectively. At 5 mol% Na^+, the γ phase was stabilized at room temperature (25 °C). The AE results were confirmed by high-temperature X-ray diffraction.

Potassium nitrate, KNO_3, can exist in three modifications at atmospheric pressure.[1] At room temperature, it has an orthorhombic structure (α-phase). On heating to 128 °C, the α-phase transforms to a trigonal structure (β-phase). On cooling, the β-phase passes through another trigonal modification (γ-phase) at around 124 °C before reverting to the α-phase. The γ-phase exhibits ferroelectric properties with the spontaneous polarization along the c-axis.[2]

Recent work has suggested that it is possible to use the ferroelectric γ phase films in the construction of non-volatile random access memory devices.[3] Since then, a stability of the γ phase prompted a revival of interest in the bulk and thin film forms. Thin film has shown to be stable over a wide temperature range of 130 to below 0 °C.[4] However, the bulk samples showed considerable variability in the stability temperature range of the γ phase, depending on the preparation,[5] particle size,[6] thermal history[7] or impurities in the samples.[8] To our knowledge, no work has been performed on stabilization of the γ phase by doping of foreign ions.

In a previous paper, it was reported that the γ to α phase transition can be detected by the AE method but not by DTA, because of the very sluggish transition,[9] and is affected by heating to above 220 °C, the temperatures from which the samples were cooled. For example, when the sample was cooled from temperatures above 220 °C, the phase transition began at 50 °C. It was previously noted that the temperature effect was associated with healing of the defects formed by the α to β phase transition.[10] The present paper describes the effect of Na^+ doping on the γ to α phase transition of KNO_3 in combination of the healing effect, which was monitored by simultaneous acoustic emission-differential thermal analysis (AE-DTA) and high-temperature X-ray diffraction (HTXRD) measurements, and examined the extent to which the γ-phase doped with Na^+ can be stabilized at room temperature.

The starting materials were as-received KNO_3 and $NaNO_3$ powders (Kanto Chemical Co.). The two nitrates were mixed at a fixed ratio for 30 min in an agate mortar and dried at 100 °C for 24 h. After melting at 400 °C, they were pulverized, and passed through a 300 mesh sieve before making the AE-DTA measurements. The samples for HTXRD were ground even more finely.

The samples and α-Al_2O_3 reference (200 mg) were placed in two fused silica sample holders. Alumel-chromel thermocouples were used for monitoring the temperature and DTA signals. Sample heating and cooling rates were 5 °C min^{-1}; below 100 °C, natural cooling resulted in an average rate of 1.5 °C min^{-1}. A fused silica rod fixed at the bottom of the sample holder acts as a wave guide, to which a piezoelectric sensor, resonating at a frequency of 140 kHz is attached. The AE parameters recorded were the event count rate and cumulative count. Further details of the AE-DTA apparatus are reported elsewhere.[9]

Figure 1 shows the simultaneous AE-DTA curves obtained during one heating/cooling cycle of pure KNO_3 between room temperature and 400 °C. On heating, two endothermic DTA peaks (Figure 1(A)) and the corresponding AE peaks (Figure 1(B)) are seen around 130 °C and 340 °C, due to the α to β phase transition and melting, respectively. When the samples were cooled from 400 °C, two exothermic DTA peaks appeared (Figure 1(C)), due to solidification of the melt and the β to γ phase transition. The corresponding AE peaks (Figure 1(D)) were also observed. As

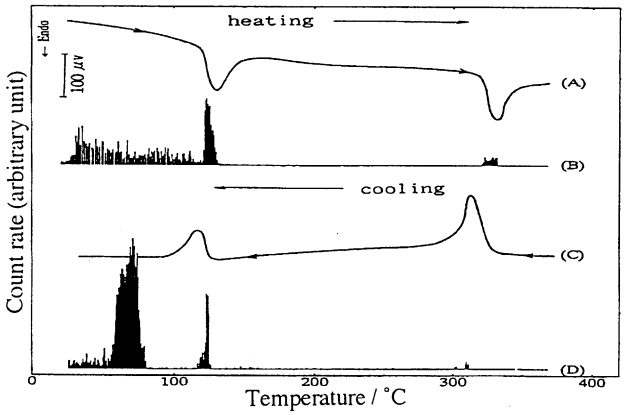

Figure 1. Simultaneous AE-DTA curves of pure KNO_3 during heating and cooling between 25 and 400 °C. (A): heating DTA, (B): heating AE, (C): cooling DTA, (D): cooling AE.

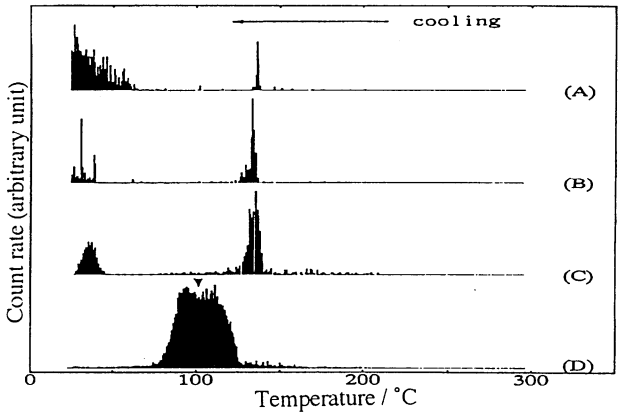

Figure 2. AE curves of the Na^+-doped samples during cooling from 300 to 25 °C. (A): undoped, (B): 0.5 mol%, (C): 1 mol% and (D): 5 mol% Na^+.

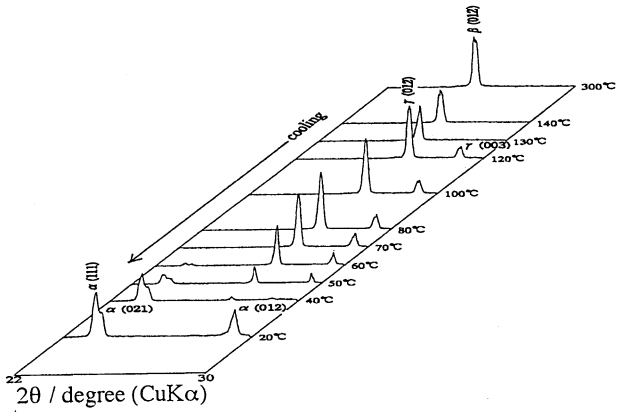

Figure 3. High temperature X-ray diffraction patterns of pure KNO_3 cooled from 300 to 20 °C.

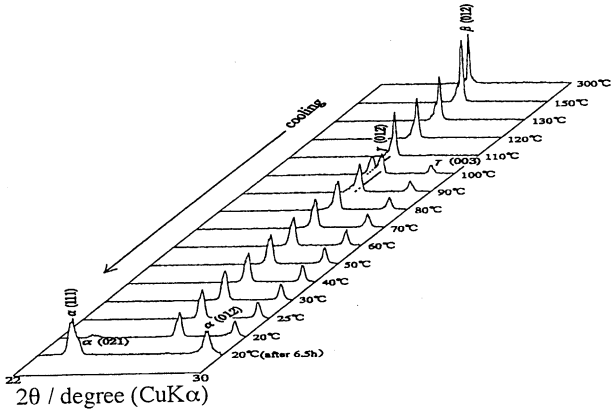

Figure 4. High temperature X-ray diffraction patterns of KNO_3 doped with 5 mol% Na^+ cooled from 300 to 20 °C.

described previously, the γ to α phase transition was not detected by DTA, but gives rise to AE signals which continue to occur from 87 °C. AE signals detected below 120 and 50 °C on heating and cooling, respectively, may result from cracking of the samples. The α to β phase transition of the doped samples is omitted below, because they showed similar behaviour to the pure samples. Since it was previously observed that the maximum temperature above 220 °C lowered the onset temperature of the γ to α phase transition,[10] the behaviour of the Na^+ doped samples was examined on cooling from 300 °C.

Figure 2 shows the AE curves obtained for pure and Na^+ doped samples on cooling from 300 °C. X-ray diffraction showed the lattice constants of the doped samples to be almost the same as for the pure KNO_3 samples, but $NaNO_3$ peaks were not observed even at 5 mol% concentration, suggesting that Na^+ ions are substituted for K^+ ions in the KNO_3 structure. At low Na^+ doping concentrations (0.5 and 1 mol%), the onset temperature of the β to γ phase transition was almost the same as for the pure samples (Figures 2(A)(B)(C)). The cumulative AE counts emitted during the phase transition increased with Na^+ concentration (2×10^2, 3.6×10^2, 4.8×10^3 and 9.3×10^4 for 0, 0.5, 1 and 5 mol% Na^+, respectively). The γ to α phase transition temperature of the doped samples was lowered to about 40 °C from 60 °C in undoped KNO_3; the doping therefore slightly increased the region of the γ-phase. At room temperature (25 °C), AE signals continued to be emitted from the doped samples for 2 to 3 h. In the 5 mol% samples, a broad AE peak which appeared at 75 to 125 °C is seen to consist of two overlapping peaks which can be distinguished in the cumulative count curve as a two-step event around 100 °C (Figure 2D, arrow). The higher temperature AE event (> 100 °C) may be caused by cracking of the samples, whereas the peak < 100 °C is due to the β to γ phase transition, a conclusion which is confirmed by HTXRD (see below). In this samples, AE signals arising from the γ to α phase transition were not detected even after one day at room temperature (25 °C), indicating stabilization of the γ-phase down to room temperature. Figures 3 and 4 show the HTXRD patterns corresponding to one cycle of heating/cooling (20 to 300 °C) of pure and 5mol% Na^+ samples, respectively. During cooling of pure KNO_3 (Figure 3), the β to γ and γ to α phase transitions occur at 120 and 60 °C, respectively, in agreement with the AE results (Figure 2). In the samples containing 5 mol% Na^+, the β to γ phase transition begins at 100 °C, about 20 °C lower than for pure KNO_3 (Figure 4). The HTXRD results also confirm that the lower temperature event of the overlapping AE signals (Figure 2(D)) results from the β to γ phase transition. The HTXRD pattern at 25 °C shows only the γ-phase; further cooling to 20 °C initiates the γ to α phase transition.

Table 1. The initial temperature of the γ to α phase transition of Na^+-doped and undoped-KNO_3 determined by AE and HTXRD

Sample	AE(°C)	HTXRD(°C)
KNO_3	62	60
Na^+ 0.5 mol%	38	30
Na^+ 1 mol%	42	30
Na^+ 5 mol%	(25)[a]	20

a; The signals were not detected, because the AE apparatus can not cool below room temperature(25 °C)

The onset temperatures of the γ to α phase transition determined by AE and HTXRD measurements are summarized in Table 1, which shows reasonable agreement between the AE and HTXRD results. These results support the conclusion that doping by Na^+ lowers the onset temperature of the γ to α phase transition and in samples doped with 5 mol% Na^+, the γ-phase is stabilized down to room temperature (25 °C). Since the ionic radius of Na^+ (9.9 nm)[11] is smaller than that of K^+ (13.8 nm)[11], the structure of the Na^+ doped KNO_3 experiences constrained internal stress[12], which may be the reason for the stabilization of the γ phase at room temperature (25 °C) in this sample.

References and Notes

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