

Synthesis of alkaline-earth metal picrates

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Picric acid is known to react with metals to form highly unstable metallic picrates, which are known to have been involved in serious explosive accidents. In this study, alkaline-earth metal picrates of magnesium, calcium, strontium and barium salts are synthesized. Then, their thermodynamic and explosive properties such as initiation sensitivity are examined.

The decomposition of alkaline-earth metal picrates begins at a higher temperature than that of picric acid. The heat of decomposition of alkaline-earth metal picrates was found to be lower than that of picric acid. Alkaline earth-metal picrates contain crystalline H₂O, which dehydrates stepwise with increasing temperature. Experimental results show that the amount of crystalline H₂O in picrate in metastable phase is 9.2–9.9 H₂O for Mg-picrate, 10.4–10.7 H₂O for Ca-picrate, 5.0–5.1 H₂O for Sr-picrate, and 5.9–6.4 H₂O for Ba-picrate. However, the respective picrates changed to the stable form which contained the following amounts of crystalline water such as 6.5 H₂O for Mg-picrate, 4.8 H₂O for Ca-picrate, 4.0 H₂O for Ba-picrate (Sr-picrate was not changed). The dehydration of crystalline water occurred between room temperature (about 298 K) and 480 K. Alkaline-earth metal picrates were dehydrated by heating in a vacuum at 473 K under 133 Pa. The activation energies at the initiation stage of exothermic decomposition are 125.6 kJ for Mg-picrate, 140.3 kJ for Ca-picrate, 171.3 kJ for Sr-picrate, and 257.7 kJ for Ba-picrate. Drop hammer test results show that Sr-picrate and Ba-picrate are more sensitive than picric acid.

1. Introduction

Picric acid was used as a military explosive from World War I until the end of World War II¹⁾. At that time, picric acid was known to react with metals to form very unstable metallic picrates. Lea and other authors^{2) 3)} attempted to synthesize these picrates. Metallic picrates were said to be sensitive. For example, one type of accident was ascribed to metallic picrate which was produced when picric acid was brought into contact with metal. Explosion of metallic picrate by striking was other examples of accidents, in which it was produced by splashing of picric acid onto a metal steam pipe after a metal fragment fell into burning picric acid¹⁾. Also,

Ca-picrate was synthesized when picric acid came into contact with concrete, leading to accidental explosion⁴⁾. In recent years, only a few studies on metallic picrates have been carried out using modern analytical techniques to examine chemical and pyrotechnic properties.

In this study, alkaline-earth metal picrates (Mg-, Ca-, Sr-, Ba-picrate) were synthesized from picric acid and alkaline-earth metal carbonate. Figure 1 shows a synthesis reaction, where two picrate anions forms bond to an alkaline-earth metal cation. Then, chemical and pyrotechnical properties, mainly thermal properties, were analyzed. The results of analysis were compared with the data on picric acid properties. Moreover, the amount of crystalline H₂O in metallic picrate is known to influence explosion sensitivity^{4) 5)}, and this is an important factor in consideration of safety. Therefore, research has been conducted on crystalline H₂O in alkaline-earth metal picrates.

2. Experiments

2. 1 Sample

Picric acid obtained from Kanto Kagaku was prepared

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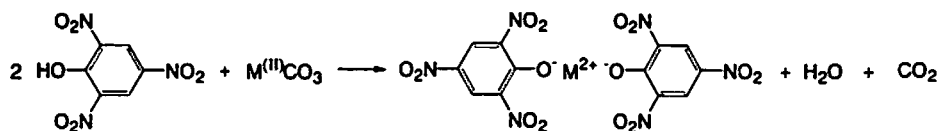


Fig.1 Alkaline-earth metal picrate synthesis equation (M means alkaline earth-metal element).

by recrystallization from a deionized H_2O solution. Metal carbonate hydroxides from Kanto Kagaku were used without modification. Deionized water was used as a synthesis solvent. The synthesized samples were dried by vacuum, subsequently; the samples were bathed in deionized H_2O at 24 hours to stabilize the crystalline H_2O condition, and wet samples were dried in a vacuum chamber at 298K.

2. 1. 1 Synthesis of magnesium picrate (Mg-picrate) from magnesium carbonate hydroxide and picric acid

Magnesium carbonate hydroxide (4 g) was added slowly to 1500 ml of picric acid solution (1%), and the mixture was stirred for two hours at room temperature. Bubbles were generated in the reacting solution, and these seemed to be by-produced carbon dioxide. After reaction, the solution was filtered, and unreacted magnesium carbonate hydroxide was separated as residue. The filtrate was poured into a plastic vessel and dried by draft ventilation, yielding a crude crystal. The crude crystal was then dissolved in 100 ml of acetone, and impurities were removed by filtration. Drying the acetone solution yielded a refined product from which insoluble impurities had been removed. The filtrate was added to CH_2Cl_2 (2000 ml) for purification to remove picric acid as a contaminant, and for recrystallization. Unreacted picric acid was extracted as a filtrate⁵⁾. The synthesis procedure produced 18.9 g of final product.

2. 1. 2 Synthesis of calcium picrate (Ca-picrate) from calcium carbonate and picric acid

Calcium carbonate (2 g) was added slowly to 500 ml picric acid solution (1%), and the mixture was stirred for two hours at room temperature. Bubbles were generated in the reacting solution caused by by-produced carbon dioxide. After reaction, the solution was filtered, and unreacted calcium carbonate was separated as residue. The filtrate was poured into a plastic vessel and dried by draft ventilation, yielding a crude crystal. The crude

crystal was then dissolved in 500 ml of acetone, and impurities were removed by filtration. Drying the acetone solution yielded a refined product from which insoluble impurities had been removed. The filtrate was concentrated to 100 ml, and the concentrated solution was added to CH_2Cl_2 (2000 ml) for purification to remove picric acid as a contaminant, and for recrystallization. Unreacted picric acid was extracted by a method similar to that described in section 2.1. The synthesis procedure produced 8.3 g of final product.

2. 1. 3 Synthesis of strontium picrate (Sr-picrate) from strontium carbonate and picric acid

Strontium carbonate (5 g) was added slowly to 1500 ml picric acid solution (1%), and the mixture was stirred for two hours at room temperature. Bubbles were generated in reacting solution caused by by-produced carbon dioxide. After reaction, the solution was filtered, and unreacted strontium carbonate was separated as residue. The filtrate was poured into a plastic vessel and dried by draft ventilation, yielding a crude crystal. The crude crystal was then dissolved in 500 ml of acetone, and impurities were removed by filtration. Drying the acetone solution yielded a refined product from which insoluble impurities had been removed. The filtrate was concentrated to 100 ml, and the concentrated solution was added to CH_2Cl_2 (2000 ml) for purification to remove picric acid as a contaminant, and for recrystallization. Unreacted picric acid was extracted by a method similar to that described in section 2.1, yielding a yellowish refined crystal. The synthesis procedure produced 19.45 g of final product.

2. 1. 4 Synthesis of barium picrate (Ba-picrate) from barium carbonate and picric acid

Barium carbonate (12 g) was added slowly to 1000 ml picric acid hot solution (2.3%) and the mixture was stirred for two hours. Bubbles were violently generated in the reacting solution caused by by-produced carbon dioxide. After reaction, the solution was filtered, and

unreacted barium carbonate was separated as residue.

The filtrate was poured into a plastic vessel and dried by draft ventilation, yielding a crude crystal. The crude crystal was then dissolved in 500 ml of acetone, and impurities were removed by filtration. Drying the acetone solution yielded a refined product from which insoluble impurities had been removed. The filtrate was concentrated to 100 ml. For purification the concentrated solution was added to CH_2Cl_2 (2000 ml) to remove picric acid as a contaminant before recrystallization. Unreacted picric acid was extracted by a method similar to that described in section 2.1, yielding a yellowish refined crystal. The synthesis procedure produced 32.75 g of final product.

2. 2 Analysis of sample

2. 2. 1 Thermal analysis

Differential scanning calorimetry analysis (DSC) was used to characterize the thermodynamic properties of the product. DSC measurements were conducted on a TA Instruments differential scanning calorimeter, model DSC2920. Device parameters, heat property and temperature property, were calibrated with respect to fusion temperature and endothermic heat of melt of indium. The sample was sealed in an Au evaporated aluminum crimp cell and loaded into the apparatus, which maintains a 3 MPa nitrogen gas environment. Analysis was performed on samples weighing approximately 0.5 mg at a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. The measurement range was from room temperature (about 298 K) to 823 K. Measurements were also conducted at heating rates of 1, 2, 5, 10, and $20 \text{ K}\cdot\text{min}^{-1}$ in order to obtain activation energy.

Thermogravimetry (TG) was performed in order to determine the crystalline water content of the products. Measurements were conducted using a TA Instruments simultaneous thermogravimetry and differential thermal analysis (TG-DTA) instrument, model SDT2960. Temperature property of device parameter was calibrated with respect to fusion temperature of melt of indium. During measurement, the apparatus was flushed by Ar gas flowing at atmospheric pressure. Sample weight was approximately 10 mg, and heating rate was $10 \text{ K}\cdot\text{min}^{-1}$.

2. 2. 2 Crystalline water amounts analysis

Crystalline water content was also investigated by the Karl Fischer method, by use of a Metrohm 758 KFD

Titrimo apparatus. Riedel-deHaen Hydranal Composite 5 was used as Karl Fischer reagent, and the machine was calibrated by use of approximately $30 \mu\text{L}$ of deionized water.

2. 2. 3 Metallic element detection

X-ray fluorescence analysis was employed to determine the metallic elements contained in the products. Measurements were conducted by use of a Shimadzu wavelength dispersive x-ray fluorescence spectrometer, model XRF 1500. Analysis of Ca, Sr, and Ba employed an LiF crystal having a lattice constant ($2d$) of 4.0267 angstroms, and analysis of Mg employed a TAP (Thallium Acid Phthate) crystal.

2. 2. 4 Molecular form analysis

Molecular forms of the products were analyzed by Fourier transform infrared (FT-IR) spectroscopy by the KBr method using a Shimadzu spectroscope, model FTIR-8200PC. The measurement range was chosen as 400 to 2000 cm^{-1} in order to avoid influence from moisture in the air.

2. 3 Sensitivity test

A drop hammer test and a friction sensitivity test were performed in accordance with JIS K 4810⁶⁾.

3. Results and Discussion

3. 1 Thermal properties (DSC and TG-DTA results)

Figure 2 and Table 1 show the results of DSC analysis. The results of analysis show that all alkaline-earth picrates have exothermic peaks caused by thermal decomposition which are split into two peaks, and these appear at nearly equal or slightly higher temperature than that of picric acid. Under a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$, exothermic decomposition started at the following temperatures: Mg-picrate: 538.5 K; Ca-picrate: 550.6 K; Sr-picrate: 579.0 K; Ba-picrate: 579.4 K. These temperatures are nearly equal to or higher than the temperature at which exothermic decomposition of picric acid starts (542 K). Observation of peak form revealed that the exothermic curve of decomposition of alkaline-earth picrate has a steeper slope than does the exothermic curve of decomposition of picric acid. Consequently, production of alkaline-earth picrates was assumed, in which the reaction of thermal decomposition progressed rapidly. The heat of decomposition of

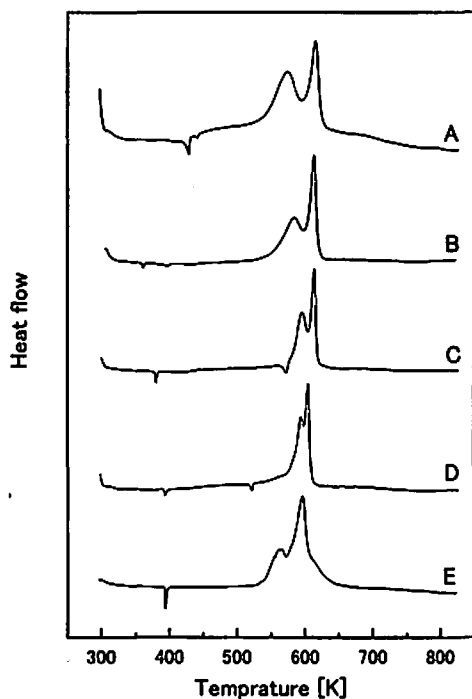


Fig.2 DSC results for alkaline-earth metal picrates and picric acid.
A; Mg-picrate, B; Ca-picrate, C; Sr-picrate, D; Ba-picrate, E; Picric Acid

alkaline-earth picrate falls within $3600 - 4400 \text{ J} \cdot \text{g}^{-1}$, which is lower than the heat of decomposition of picric acid, $5590 \text{ J} \cdot \text{g}^{-1}$.

Figure 3 shows TG-DTA analysis results. Immediately after synthesis of the crystals, crystalline water properties can be changed by refinement. Thus, the synthesized sample, which dissolved in deionized H_2O , was recrystallized and dried in vacuum at 298 K for 24 hours. Results of TG-DTA of alkaline earth metal picrates revealed that every endothermic phenomenon accompanied weight reduction, and the weight reductions of Mg-picrate, Ca-picrate, Ba-picrate started at room temperature and ended at about 480 K. The weight reduction of Sr-picrate started at about 340 K, and ended at about 480 K. The weight reductions obtained from TG curves occurred in a few steps, and dehydration of crystalline water was

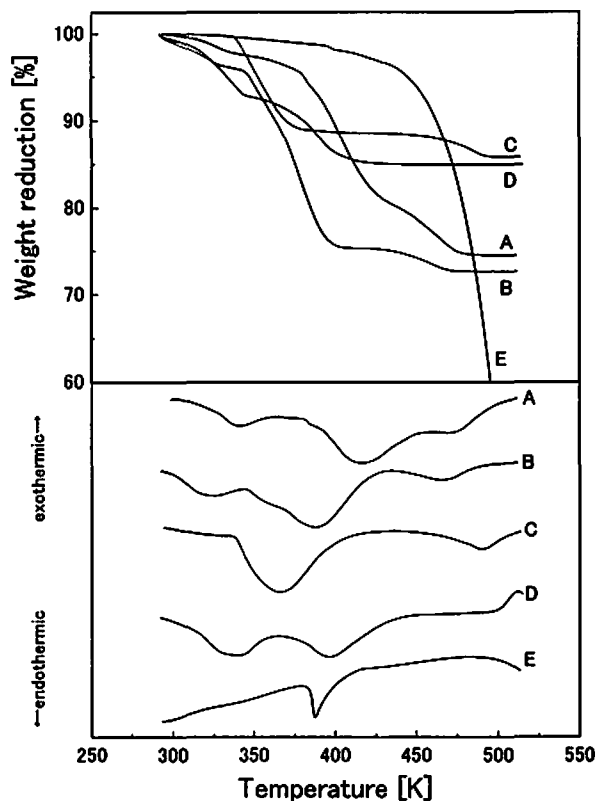


Fig.3 TG-DTA results for alkaline-earth metal picrates and picric acid, (upper column: TG, lower column: DTA)

A; Mg-picrate, B; Ca-picrate, C; Sr-picrate, D; Ba-picrate, E; Picric Acid.

thought to occur stepwise on heating.

The endothermic phenomenon was observed in DTA trace of alkaline-earth metal picrates. Largest endothermic peak of each picrate were appeared at about 420 K in Mg-picrate, at about 380 K in Ca-picrate, at about 370 K in Sr-picrate, and at about 400 K in Ba-picrate. TG-DTA analysis clarified that the endothermic peak of the DTA curve accompanied weight reduction in the TG curve.

DSC and TG-DTA traces of alkaline earth metal picrates have endothermic peaks, which appeared at different temperatures in each analysis method. That reason for this is ascribed to different sample conditions; in DSC measurement the sample was kept in a crimped

Table 1 DSC data for alkaline-earth metal picrates.

		Mg-picrate	Ca-picrate	Sr-picrate	Ba-picrate	Picric Acid (reference)
Exothermic peak	1 st peak	575 K	584 K	596 K	594 K	555 K
	2 nd peak	616 K	614 K	614 K	605 K	596 K
Heat of exothermic reaction		$4141 \text{ J} \cdot \text{g}^{-1}$	$4397 \text{ J} \cdot \text{g}^{-1}$	$4094 \text{ J} \cdot \text{g}^{-1}$	$3662 \text{ J} \cdot \text{g}^{-1}$	$5590 \text{ J} \cdot \text{g}^{-1}$

cell under 3 MPa pressure, whereas in TG-DTA measurement the sample was kept in an open cell at atmospheric pressure. The endothermic phenomenon observed in TG-DTA measurement of picric acid indicated melting of picric acid crystal, whereas the weight reduction at approximately 430 K is thought to be due to decomposition or evaporation of the picric acid, or both⁷⁾.

3. 2 Structure of picrates

The result of X-ray fluorescence analysis, obtained by TAP spectrum crystal, revealed that Mg-picrate has reflection patterns at 45.1 degrees. This pattern is characteristic to X-rays of magnesium. The result obtained by LiF spectrum crystal revealed that Ca-picrate has reflection patterns at 100.2 degrees and 113.1 degrees. These patterns are characteristic to calcium. Sr-picrate has reflection patterns at 25.1 degrees and 22.4 degrees. These patterns are characteristic to strontium. Moreover, Ba-picrate has reflection patterns at 87.1 degrees, 79.2 degrees, 77.3 degrees, 73.2 degrees, 67.6 degrees, and 64.0 degrees. These patterns are characteristic to barium.

Figure 4 shows the results of FT-IR analysis of all alkaline-earth metal picrates. FT-IR results are similar for all alkaline-earth metal picrates, which are similar to the results for iron picrate, copper picrate, and zinc picrate^{7) 8) 9)}. Adsorption of 1270 cm^{-1} in the FT-IR results indicates bond stretching between a phenyl group and an oxygen atom. Furthermore, absorptions at approximately 1330 cm^{-1} and 1560 cm^{-1} suggest N-O bond stretching. The peak at 1315 cm^{-1} , which appears in picric acid and disappeared in alkaline-earth metal picrates, indicating O-H bond stretching of the phenol group. The results of FT-IR of alkaline-earth metal picrates and picric acid are very

similar, and therefore alkaline-earth metal picrates are thought to have a molecular form similar to that of picric acid. Similar results have been obtained in previous studies^{7) 8) 9)} of iron picrate, copper picrate, and zinc picrate.

3. 3 Stability of crystalline water

Alkaline-earth metal picrate mono crystal, obtained by

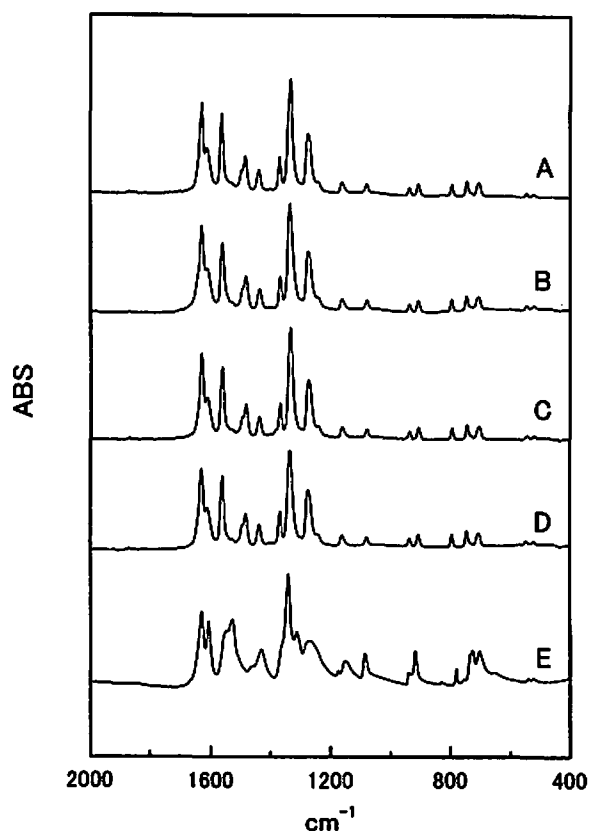


Fig.4 FT-IR spectra of alkaline-earth metal picrates and picric acid.

A; Mg-picrate, B; Ca-picrate, C; Sr-picrate, D; Ba-picrate, E; Picric Acid.

Table 2 Water contents in metastable phase of alkaline-earth metal picrates obtained from TG analysis.

	Mg-picrate	Ca-picrate	Sr-picrate	Ba-picrate
Weight reduction	25.5%	27.4%	14.2%	15.1%
H ₂ O molecules*	9.2	10.4	5.0	5.9

*Numbers of H₂O molecules per 1 metal-picrate molecule

Table 3 Water contents in metastable phase of alkaline-earth metal picrates obtained from Karl Fischer method analysis.

	Mg-picrate	Ca-picrate	Sr-picrate	Ba-picrate	Picric Acid
H ₂ O quantity	27.0%	27.9%	14.5%	16.2%	0.22%
H ₂ O molecules*	9.9	10.7	5.1	6.4	—

* Numbers of H₂O molecules per 1 metal-picrate molecule

synthesized alkaline-earth metal picrate, was dissolved in H₂O solution and pulled from solution. After exposure to atmospheric conditions the alkaline-earth metal picrates were devitrified after a few minutes. The suspected reason is the breakdown of crystallinity. Specifically, crystalline H₂O molecules in picrate crystal were dehydrated to dissipate in the atmosphere. This suggests that a few molecules of crystalline H₂O of alkaline-earth metal were in metastable phase under atmospheric conditions, and that these were dehydrated. Two types of alkaline-earth metal picrate were analyzed in order to compare the amounts of crystalline H₂O; one with crystalline H₂O fully included (metastable phase), and another, which had been dried by vacuum chamber, was a few molecules less amount of crystalline H₂O included than fully included sample (stable phase).

3. 3. 1 Metastable phase samples

Samples for the crystalline H₂O analysis, which fully included H₂O molecules, were used after the moisture adhering to the crystal surface was wiped off. The liquid of solution, which adhered to the surface of picrate crystal just having been pulled up from solution, was washed by dichloromethane, and the sample was quickly set in the analysis apparatus.

Table 2 shows the results of TG analysis, and Table 3 shows the results of water content obtained from the Karl Fischer method. The two results do not confirm a large difference in crystalline H₂O quantity. TG analysis confirmed that Mg-picrate contained 9.2 H₂O molecules, Ca-picrate contained 10.4 H₂O molecules, Sr-picrate contained 5.0 H₂O molecules, and Ba-picrate contained 5.9 H₂O molecules, respectively. Karl Fischer method confirmed that Mg-picrate contained 9.9 H₂O molecules, Ca-picrate contained 10.7 H₂O molecules, Sr-picrate contained 5.1 H₂O molecules, and Ba-picrate contained 6.4 H₂O molecules, respectively. The results obtained from Karl Fischer method show slightly more crystalline H₂O than from TG analysis.

3. 3. 2 Stable phase samples

Metal-picrate under a stable condition was employed to determine the amount of crystalline H₂O; the sample crystal was used just after synthesized (drying method was written in section 2.1). Table 4 shows the results of the Karl Fischer method, which confirmed the amount of crystalline H₂O as 6.5 H₂O molecules for Mg-picrate, 4.8 H₂O molecules for Ca-picrate, 5.1 H₂O molecules for Sr-picrate, and 4.0 molecules for Ba-picrate. Therefore, except for the case of Sr-picrate, vacuum drying at room temperature reduced the a few molecules of crystalline H₂O in alkaline-earth metal picrates, and it was become in stable phase. The Karl Fischer method gave a greater amount of crystalline H₂O than TG analysis. The supposed reason is that TG analysis involved a longer sample loading time than the Karl Fischer method, and during that time crystalline H₂O was dehydrated slightly.

Meanwhile, in the case where the alkaline-earth metal picrate was recrystallized from solution, only Ca-picrate was not recrystallized at room temperature (290–300 K), but lamellar crystal was recrystallized when the solution was cooled. This suggests that when Ca-picrate is recrystallized, the crystalline H₂O did not take a stable position in the crystal near room temperature, but when the solution is cooled the crystalline H₂O takes a stable position in the crystal, whereby recrystallization occurs. The above analysis suggests that near room temperature crystalline H₂O in alkaline-earth metal picrates is easily dehydrated and therefore very unstable. As indicated by the results of TG analysis, shown in Fig. 3, the weight reduction of Sr-picrate started at approximately 340 K. Consequently, Sr-picrate was estimated to be too hard to undergo dehydration at room temperature.

3. 3. 3 Hygroscopicity of picric acid

The results of the Karl Fischer method for picric acid show that picric acid has a slight amount of H₂O. Consequently, Fig. 3 shows that picric acid was reduced in weight at approximately 400 K on heating, not because

Table 4 Water contents in alkaline-earth metal picrates, which pretreated by vacuum at 298 K, obtained from Karl Fischer method analysis.

	Mg-picrate	Ca-picrate	Sr-picrate	Ba-picrate
H ₂ O quantity	19.6%	14.9%	14.3%	10.8%
H ₂ O molecules*	6.5	4.8	5.1	4.0

* Numbers of H₂O molecules per 1 metal-picrate molecule

of dehydration of crystalline H₂O, but supposedly because of vaporization of picric acid. Vaporization from the sample cell of TG is considered to occur because that the cell did not have a cover and that analysis was performed by use of an open cell.

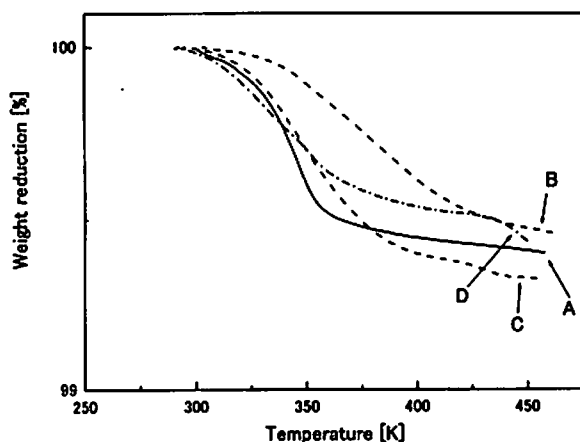


Fig.5 TG results for alkaline-earth metal picrates dehydrated under vacuum (133 Pa) at 473 K, 1 h.

A; Mg-picrate, B; Ca-picrate, C; Sr-picrate, D; Ba-picrate.

3. 4 Dehydration of crystalline water

Alkaline-earth metal picrates were dehydrated under the conditions of 473 K in a vacuum chamber (under 133 Pa), thereby confirming the occurrence of dehydration. Figure 5 and Table 5 show the dehydration behavior of picrates obtained from the TG results, and Table 6 from the Karl Fischer method for the vacuum-heated sample. The results of analysis indicate the presence of a slight quantity of H₂O in the vacuum-heated sample. Consequently, alkaline-earth metal picrate was confirmed to have been almost completely dehydrated at 473 K under vacuum (of 133 Pa). The results of prior dehydration tests for iron picrate, copper picrate, and zinc picrate confirm occurrence of dehydration under identical conditions^{7) 8) 9)}.

3. 5 Yield

Table 7 shows the synthesis yields of alkaline-earth metal picrates. The description in section 3.3.2 is showing that alkaline-earth metal picrates crystals included crystalline H₂O. Therefore, amount of crystalline H₂O was calculated using the results of Table 4. Yield of Ca-picrate was lower than that of the other picrates, but

Table 5 Water contents obtained from Karl Fischer method analysis for alkaline-earth metal picrates which dehydrated at 473 K, under 133 Pa, 1 hour.

	Mg-picrate	Ca-picrate	Sr-picrate	Ba-picrate
Weight reduction	0.60%	0.54%	0.67%	0.56%
H ₂ O molecules*	0.2	0.2	0.2	0.2

* Numbers of H₂O molecules per 1 metal-picrate molecule

Table 6 Water contents obtained from TG analysis for alkaline-earth metal picrates which dehydrated at 473 K, under 133 Pa, 1 hour.

	Mg-picrate	Ca-picrate	Sr-picrate	Ba-picrate
H ₂ O quantity	0.41%	0.57%	0.71%	0.45%
H ₂ O molecules*	0.1	0.2	0.2	0.1

* Numbers of H₂O molecules per 1 metal-picrate molecule

Table 7 Yield of alkaline-earth metal picrate based on crystalline H₂O amount.

	Molecule weight as anhydrate	Crystalline water molecules*	Yield [%]
Mg-picrate	481.60	6.5	96.4
Ca-picrate	497.38	4.8	86.8
Sr-picrate	544.92	5.1	93.3
Ba-picrate	594.64	4.0	97.9

* Crystalline H₂O value was obtained from Table 4, Karl Fischer method.

the other picrates had a yield higher than 90%.

3. 6 Activation energy of exothermal decomposition

The DSC traces were measured at the heating rate of $1 \text{ K}\cdot\text{min}^{-1}$, $2 \text{ K}\cdot\text{min}^{-1}$, $5 \text{ K}\cdot\text{min}^{-1}$, $10 \text{ K}\cdot\text{min}^{-1}$, and $20 \text{ K}\cdot\text{min}^{-1}$, and the temperatures at which the decomposition starts (T_0) were obtained from the exothermic curve of decomposition. The activation energies of alkaline-earth metal picrates were obtained by the Ozawa method¹⁰⁾.

The temperature at which decomposition of Mg-picrate and Ca-picrate start are lower than those of Sr-picrate and Ba-picrate, and the activation energies of Mg-picrate and Ca-picrate are lower than the others.

3. 7 Sensitivity test

Table 9 shows drop hammer and friction sensitivity test results for the sample that had been pretreated by vacuum at 298 K. The results of the drop hammer test revealed that Sr-picrate and Ba-picrate are more sensitive than picric acid. The results of the friction sensitivity test revealed that all alkaline-earth metal picrates are less sensitive than picric acid or equally sensitive.

4. Conclusions

X-ray fluorescence analysis results prove that the synthesized products had the respective elements of the synthesis subjects of alkaline-earth metal picrates, and

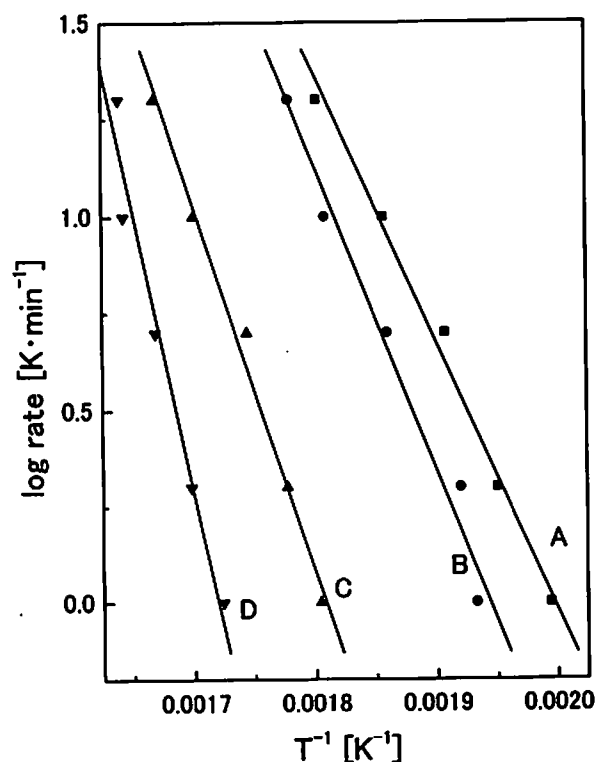


Fig.6 Ozawa's plots for the decomposition of alkaline earth metal picrates.

A; Mg-picrate, B; Ca-picrate, C; Sr-picrate, D; Ba-picrate.

FT-IR results indicate that the products have a molecular structure similar to that of picric acid. These results were obtained for all the synthesized alkaline-earth metal picrates. The results show that alkaline-earth metal

Table 8 The temperature at which decomposition starts (T_0) and activation energy of exothermic decomposition.

Heating rate	Mg-picrate	Ca-picrate	Sr-picrate	Ba-picrate	
T_0	$1 \text{ K}\cdot\text{min}^{-1}$	501.3 K	517.3 K	554.2 K	580.1 K
	$2 \text{ K}\cdot\text{min}^{-1}$	512.7 K	520.8 K	562.6 K	588.8 K
	$5 \text{ K}\cdot\text{min}^{-1}$	524.1 K	537.6 K	573.2 K	599.2 K
	$10 \text{ K}\cdot\text{min}^{-1}$	538.4 K	552.8 K	587.9 K	608.7 K
	$20 \text{ K}\cdot\text{min}^{-1}$	554.6 K	561.9 K	599.3 K	610.0 K
Activation energy	$125.6 \text{ kJ}\cdot\text{mol}^{-1}$	$140.3 \text{ kJ}\cdot\text{mol}^{-1}$	$171.3 \text{ kJ}\cdot\text{mol}^{-1}$	$257.7 \text{ kJ}\cdot\text{mol}^{-1}$	

Table 9 Drop hammer test and friction sensitivity test data for alkaline-earth metal picrates.

	Mg-picrate	Ca-picrate	Sr-picrate	Ba-picrate	Picric Acid
Drop hammer test (1/6 Explosion point)	15–20cm	15–20cm	5–10cm	5–10cm	15–20cm
	Class 4	Class 8	Class 2	Class 2	Class 4
Friction sensitivity test (1/6 Explosion point)	over 36kgf	over 36kgf	16–36kgf	over 36kgf	16–36kgf
	Class 7	Class 7	Class 6	Class 7	Class 6

picrates were synthesized.

DSC analysis results of alkaline-earth metal picrates show that the decomposition reactions of alkaline-earth metal picrates occur at a higher temperature than that of picric acid decomposition, and that the heat of decomposition reactions are lower than that of picric acid.

TG analysis results show that crystalline H₂O was dehydrated between room temperature and 480 K in a few steps. The results of TG analysis and the Karl Fischer method show that the amounts of crystalline water in samples in fully included condition (metastable phase) are 9.2–9.9 H₂O for Mg-picrate molecules, 10.4–10.7 H₂O molecules for Ca-picrate, 5.0–5.1 H₂O molecules for Sr-picrate, and 5.9–6.4 H₂O molecules for Ba-picrate. Upon vacuum dehydration at 298K (stable phase), alkaline-earth metal picrates, except Sr-picrate, show dehydration of a few H₂O molecules. Then, Mg-picrate contains 6.5 H₂O molecules, Ca-picrate contains 4.8 H₂O molecules, and Ba-picrate contains 4.0 H₂O molecules, respectively. Crystalline water of alkaline-earth metal picrates was dehydrated at 473 K under vacuum (of 133 Pa).

The activation energies of the decomposition reaction of alkaline-earth metal picrates are 125.6 kJ·mol⁻¹ for Mg-picrate, 140.3 kJ·mol⁻¹ for Ca-picrate, 171.3 kJ·mol⁻¹ for Sr-picrate, and 257.7 kJ·mol⁻¹ for Ba-picrate. Drop hammer tests show that Sr-picrate and Ba-picrate are more sensitive than that of picric acid. Moreover,

alkaline-earth metal picrates were confirmed to have low friction sensitivity.

5. Acknowledgments

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References

- 1) U.S.ARMY ARRADCOM, *ENCYCLOPEDIA OF EXPLOSIVES AND RELATED ITEMS*, 8, 285 (1978).
- 2) O. Silberrad and H. A. Phillips, *JCS*, 93, 478 (1908).
- 3) Beilstein 6,274 (1944).
- 4) T. Urbanski, *Chemistry and technology of explosives*, vol. 1, 530 (1964).
- 5) J. D. Hopper, *Journal of the Franklin Institute*, 225, 219 (1938)
- 6) Japanese Standards Association, "Testing methods of explosives". JIS K 4810 (2001).
- 7) M. Matsukawa, et al., *J. Japan Explos. Soc.*, 326, 151 (2002).
- 8) M. Matsukawa, et al., *Sci. And Tech. Energetic Materials*, 64, 145 (2003).
- 9) M. Matsukawa, et al., *Sci. And Tech. Energetic Materials*, 64, 175 (2003).
- 10) T. Ozawa, *Bull. Chem. Soc. Jpn.*, 38, 1881 (1965).