Letter

Sol-gel preparation of PZT powders and its catalytic effect on burning rate of RDX-CMDB propellant

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Abstract

Perovskite-type Lead zirconate titanate (PZT) powders were synthesized by a modified sol-gel method. In this route, citric acid (C A) was used a chelating agent to keep the metal ions in homogeneous solution without undergoing precipitation. The obtained powders were characterized by XRD, FT-IR, SEM-EDS techniques. Phase-pure perovskite structure was formed at 500°C. Combustion tests were carried out to investigate the effect of PZT powders on the burning rate of NC/RDX/NG propellant. It is found that PZT powders increase the burning rate of the propellant to the extent 50% as well as bring down the pressure exponent n to 0.25 (5-20 MPa).

Keywords : PZT, sol-gel, burning rate, pressure exponent

1. Introduction

Lead zirconate titanate ($PbZr_xTi_{1-x}O_3$ or PZT) material continues to be well-studied system because of its technologically important applications[1]. The composite with Zr : Ti molar ratio of 0.52 : 0.48 Pb ($Zr_{0.52}Ti_{0.48}$) O_3 (PZT 52/48) exhibit high dielectric constant. In 1994, Taylor et al found that "Bi-plateau Burn Rate was formulated by adding TiO_2 or ZrO_2 to solid rocket motor propellant[2]. Apart from lead, PZT also contains zirconium and titanium. Therefore, PZT is expected to become a potential combustion catalyst which may produce dual-platform in solid propellant. However, to our knowledge, the use of perovskite-type oxides like PZT has not been reported so far.

Conventionally, PZT powders are prepared by solid state reaction using the constituent oxides PbO, ZrO_2 and TiO_2. However, this method encounters difficulties such as composition inhomogeneity, low chemical purity, broad particle size distribution and high sintering temperature[3)-5)]. Recently, various chemical methods for the preparation of PZT had been developed such as sol-gel method, co-precipitation and hydrothermal synthesis[6)-10)]. Among the chemical methods, sol-gel method has the potential for good homogeneity, ease of chemical composition control, high purity and low sintering temperature.

In the present work, we report a modified technique for PZT powders synthesis using citric acid (C A) as the chelating agent. For the first time, the combustion catalytic of PZT was investigated by adding PZT to RDX-CMDB propellant. The reason of we using RDX-CMBD propellant not DB propellant is that RDX-CMBD propellant is superior to DB propellant in energetic and mechanical properties.

Table 1 Propellant main compositions

Sample	Compositions [%]			
No1	NC 24	NG 32	RDX 33	ϕPb3
No2	NC 24	NG 32	RDX 33	PZT3

*NC : nitrocellulose NG : nitroglycerine RDX : cyclotrimethylenetrinitramine ϕPb : lead phthalate

2. Experimental

2.1 Preparation

Lead nitrate ($Pb(NO_3)_2$), zirconate nitrate ($Zr(NO_3)_4 \cdot 5H_2O$) and tetrabutyl titanate ($Ti(OC_4H_9)_4$) were used as metallic ion sources. The citric acid (C A) was used as chelating agent. All the chemicals used are of analytical grade.

The preparation route of the Pb ($Zr_{0.52}Ti_{0.48}$) O_3 powders is as follows : The molar ratio of Pb : Zr : Ti is 1 : 0.52 :

0.48. C A solution was prepared by mixing citric acid in deionized water at room temperature. The molar ratio of Pb : Zr : Ti is 1 : 0.52 : 0.48. Lead nitrate solution and zirconate nitrate solution were added to the above C A solution. This mixture was heated to 80°C under stirring. After 30 min, the tetrabutyl titanate was added to the previous solution under the same conditions. The metallic solution was stirred for 1h and $NH_3 \cdot H_2O$ was gradually added until the system became transparent. Te clear solution was kept at this temperature for additional 2h to get light yellow transparent gel. The gels were heated to 120°C at 10°C min^{-1} in static air and kept this temperature for 2h. The obtained drying gel were then calcined at 300, 400, 500 and 600°C for 2h, respectively.

2.2 Characterization

A Fourier transform infrared spectroscopy spectrometer (FT-IR, Nicolet-60SXR-FT-IR) was used for studying the coordinated structure of the precursor and the thermal-treated powders, in the frequency range 400-4000 cm^{-1}, with 4 cm^{-1} spectral resolution, using KBr pellets. The powders were characterized by powder X-ray diffractometry using Cu Kα radiation (λ=1.5418Å). The X-ray diffraction (XRD) patterns were recorded at a scan rate of 1°/min for phase and structure analysis. SEM-EDS were obtained on a JSM5800 scanning electronic microscope.

2.3 Burning rate test method

For the sake of the possible application of PZT in propellants as the combustion catalyst, the burning rates [u/(mms^{-1})] of the control propellant (No.1) and the propellant containing PZT (No. 2) were measured under different pressures (P/MPa). All the samples involved in this investigation, which were prepared by mould process at the temperature of 35°C and then solidified for 96h (70°C), were machined to fixed dimension (shape : cylinder ; length : 100~150 mm ; diameter : 5~8 mm)

The resistance wire with alternating voltage of 30 V was introduced to ignite the propellant sample (diameter= 5~6 mm, length = 120 mm) at the initial temperature of 20°C. The samples were placed vertically on the combustion rack and sealed in a chamber which was filled with nitrogen atmosphere. After the testing parameters were located, the samples were ignited and the real time data was collected by a computer which can process the data and calculate the burning rate. The experiment will be repeated for 5 times at each test pressure and the average experimental results were obtained. The inherent measurement error of the burning rate test and the standard deviation of the burning rates is less than 2% (parallel error) and the repeatability is well. The diagram of the apparatus was presented in the appendix of the published literature [11]. Measurements were made at 7 pressures (3, 5, 8, 12, 15, 18, 20MPa).

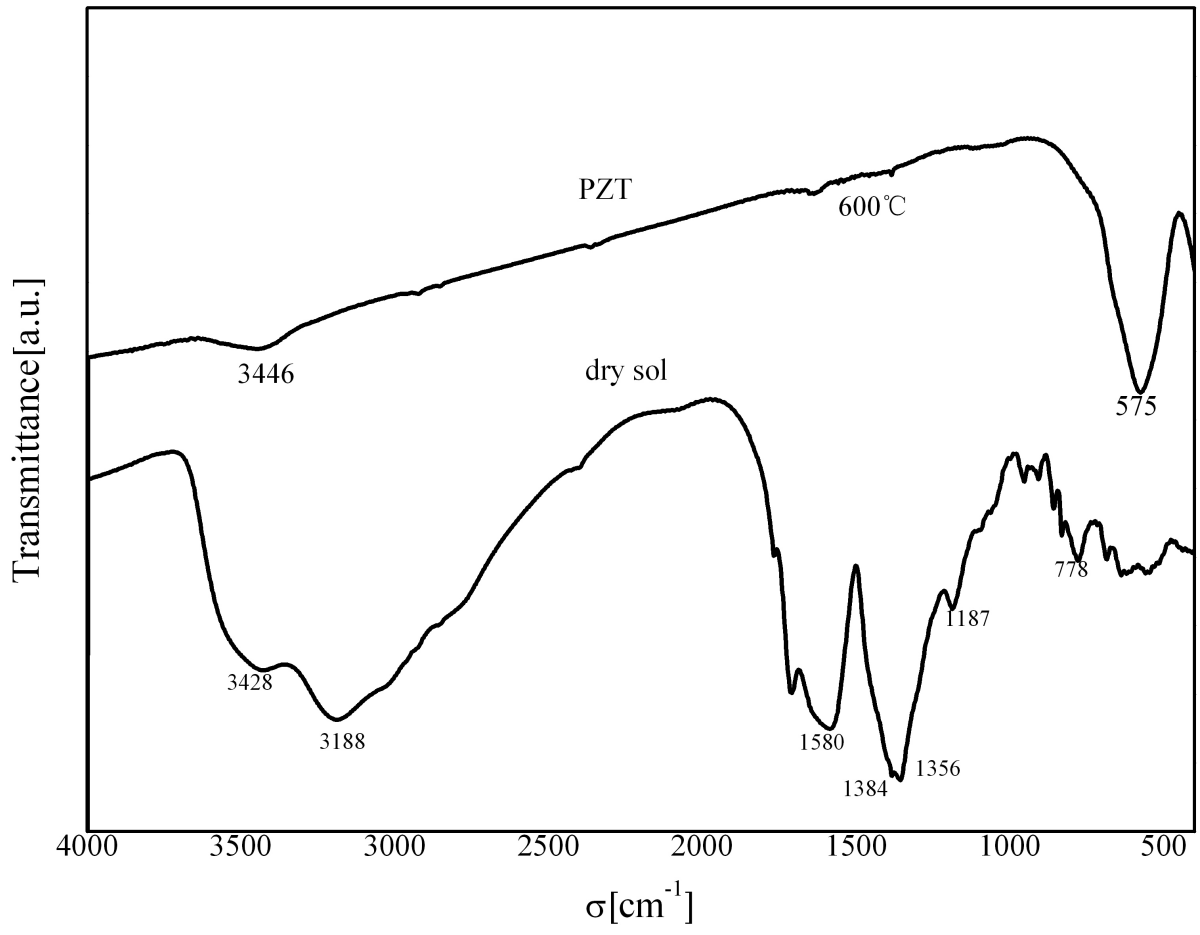

Figure 1 FT-IR spectra of the precursor and PZT powders calcined at 600°C for 2h

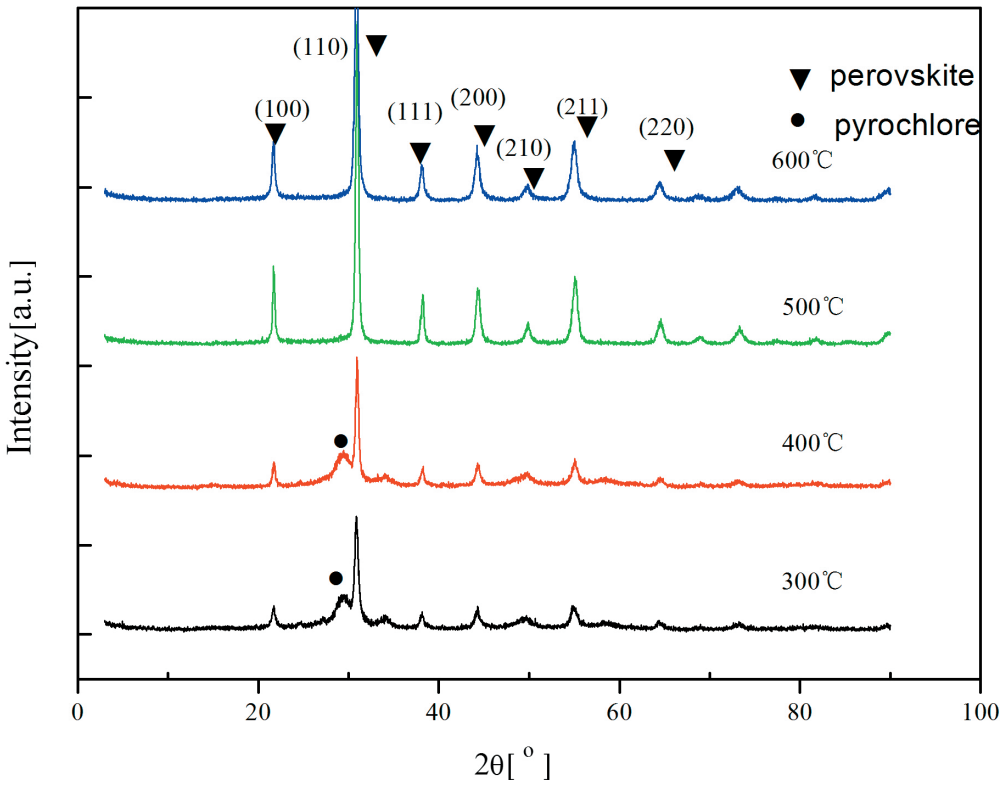

Figure 2 XRD patterns of the powders calcined at different temperature for 2h

3. Results and discussion

3.1 FT-IR of gels and powders

Figure 1 shows FT-IR spectra of the precursor and powders of PZT. Four bands relate to carboxylate stretching modes at 1720, 1580, 1384 and 1356 cm^{-1} of the precursor can be observed in the precursor. The band at 1720 cm^{-1} could be assigned to the C=O stretching mode of the ester which was formed by polymerization of CA. The 1580 cm^{-1} band could be assigned to asymmetric COO^{-1} stretching mode for a unidentate complex and a bridging complex, respectively, formed from the chelation of C A and lead zirconium ions. The 1384 cm^{-1} and 1356 cm^{-1} band could be assigned to symmetric COO^{-1} stretching mode from the chelation of C A and lead or zirconium ion. The other bands at 1500-700 cm^{-1} and 3500-2000 cm^{-1} were attributed to the polymeric network of OH, CH_2 and CH groups, respectively. The polymeric network is formed by the hydrolysis and condensation reaction of metal ions. The bands below 600 cm^{-1} are assigned to metal oxygen stretching mode from the chelation of C A and metallic ions. However, when the precursor are calcined at 600°C, the FT-IR of PZT powders shows the bands at 3500-700 cm^{-1} disappear. A band at the range of 400-750 cm^{-1} is attributed to the absorption of PZT (52/48) structure.

3.2 XRD of powders

In general, for a given composition, the structure of PZT powders depends on the annealing temperature. To investigate the phase distribution and crystallization, the obtained drying gel were calcined at 300, 400, 500 and 600°C for 2h, respectively. Figure 2 shows X-ray diffraction patterns of PZT (52/48) drying gel calcined for 2h in static at 300, 400, 500 and 600°C. When the calcinations temperature is 300°C, the development of the peaks of crystalline PZT (52/48) can be detected at 2θ values of about 30.5°, a weak and sharp peak at 2θ=30° could be assigned to the pyrochlore phase of PZT compared to the standard XRD pattern of the pervoskite PZT phase. The development of the pyrochlore phase of PZT can be detected at 2θ=30°. When calcined at 500°C, while the peak of the pyrochlore phase disappear, the diffraction peaks of the perovskite PZT phase become stronger and sharper and no peaks of else phase appear, with the treatment temperature increasing. This indicates that the crystal particle of perovskite PZT phase grows bigger and perfect and the powders obtained is of a single phase. The mean crystalline sizes of powders calcined at 300, 400, 500 and 600°C calculated from XRD date using Scherrer equation are 19, 20, 23 and 30 nm, respectively. The results suggest that the calcined temperature plays an important role for the crystal and the mean size of the synthesized powders. The reason of crystalline size of PZT increased with the temperature increasing is that as the temperature increase, the driving force for sintering reaction was improved which will increase the move rate of grain boundary resulting in a growth of the grain.

3.3 SEM-EDS of powders

The morphology of the PZT powders shown in SEM micrograph (Figure 3) indicates that most residues of the PZT powders present as flake and appear some holes interiorly. The SEM observation clearly gives direct evidence to the existence of internal particle. The EDS pattern of pure PZT powder recorded using the spectrometer attached to SEM instrument indicate the stoichiometry of the elements. The elemental composition

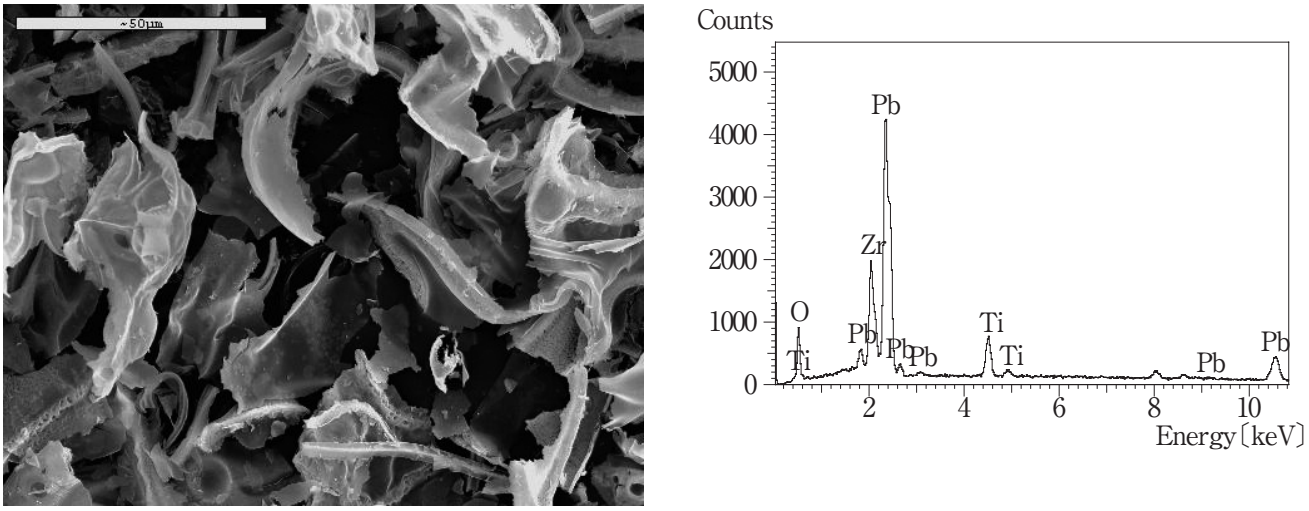

Figure 3 SEM images and EDS of PZT powders calcined at 600°C

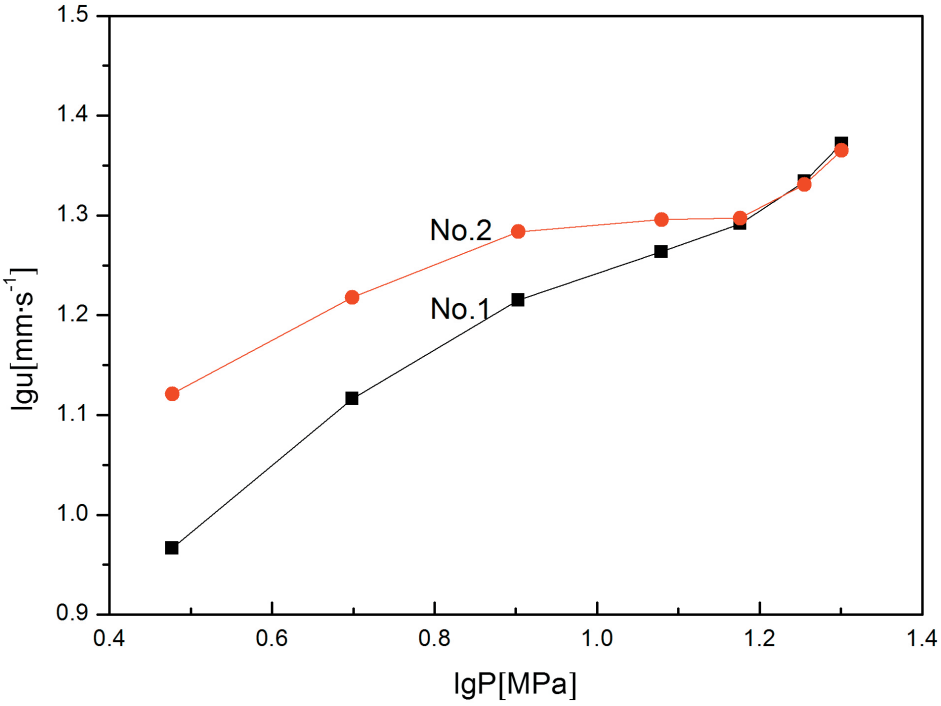

Figure 4 Effects of PZT powders on the burning rates (mms^{-1}) of NG/RDX/NC propellant

determined from the EDS pattern of PZT powder are Pb: 67.10%, Zr: 16.60%, Ti: 7.34% and O: 9.68% (wt.), respectively. EDS analysis only describes surfaces might be modified by scattering effect. Therefore, the given element ratios of the composition should be considered to be tentative.

3.4 Burning rate characteristics

The relationship between the burning rate of propellant samples and pressure obtained from the combustion tests is shown in Figure 4. For comparison, results for propellant samples prepared in a similar manner with different catalysts, PZT powders calcined at 600°C enable the burning rate of the propellant to increase higher than that of conventional propellant at no more than 18 MPa. A plateau effect is observed between 8 and 15 MPa. There is no significant change in burning rate between 15 and 20 MPa. As one can seen, the addition of with the help of the catalysis PZT, the burning rate of the propellant is improved markedly. Generally, the burning rate of solid propellants and pressure exhibit linear characteristic called Vieille law[11]:

$$u = a P^n$$

Where u is the burning rate of propellants samples, a is a constant, P is pressure, and n is pressure exponent. The pressure exponent is the parameters that represent the effect of the change of pressure on the burning rate. From Figure 4, the calculated pressure exponent decreases from 0.45 for the propellant sample with ϕ Pb catalyst to 0.25 with the addition of PZT catalysts in the pressure range of 5~20MPa.

4. Conclusions

The preparation and characterization of PZT powders were investigated, perovskite-type PZT powders were

successfully synthesized by a modified sol-gel method and it was used as a combustion catalyst for the NC/RDX/NC propellant. The results show PZT powders can be effective to increase the burning rate, reduce the pressure exponent of the NC/RDX/NC propellant and induces a plateau burning of the double base propellant formulation in the range 8-15 MPa.

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