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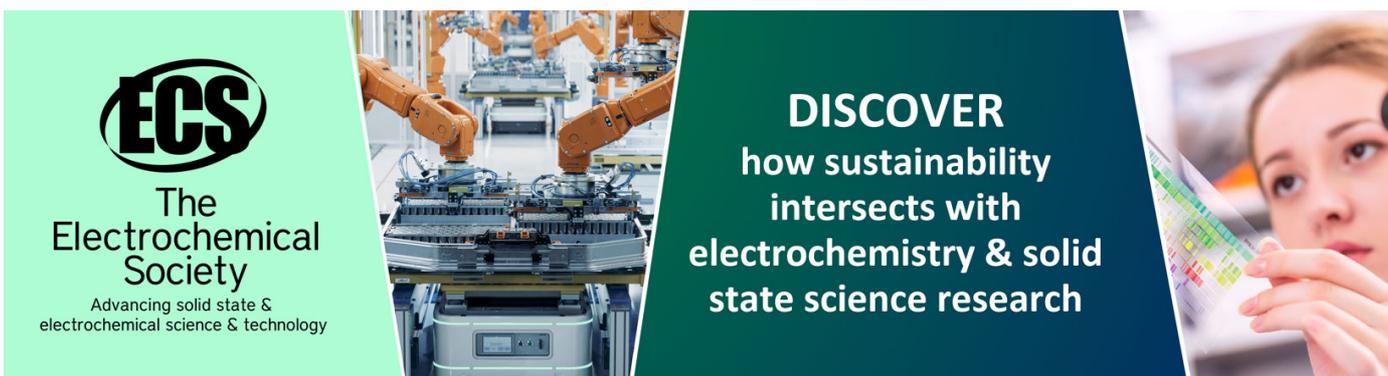
## Preparation and Characterization of Direct Write Explosive Ink Based on CL-20

To cite this article: Lei Zhang *et al* 2019 *J. Phys.: Conf. Ser.* **1209** 012016

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# Preparation and Characterization of Direct Write Explosive Ink Based on CL-20

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**Abstract.** In this paper, a new CL-20-based explosive ink formulation used for direct written was designed and prepared. The explosive ink can be smoothly written by microinjection and precisely patterned explosive film can be obtained. The CL-20 explosive ink was characterized by SEM and XRD, and DSC was used to analysis the thermal decomposition performance of the explosive ink. The critical thickness of the CL-20 explosive ink was 0.153mm and the average detonation velocity was 8088.9m/s.

**Keywords:** explosive ink, CL-20, direct write technology, detonation performance

## 1. Introduction

With the development of micro electro-mechanical system (MEMS) fusing technology, it requires that energetic materials must have micro- or nano-scale to ensure their activity [1,2]. In addition, the charging method for MEMS fusing must have features such as high precision, automation, intelligence, and safety. There are two traditional ways of explosive charging: mold pressing and cast molding [3-6]. The method of mold press molding is relatively simple, but the shape of the energetic agent is limited by the mold, and this method is mostly used for large charging. The cast molding method can produce uniform charging and the combustion stability is good. However, the solidification of the drug column is slow, and when casting a small-sized explosive column, the surface tension and the viscosity affect the molding accuracy, which cannot meet the charging demand for MEMS fusing.

Direct-write technologies provide a high-throughput processing platform capable of precision patterning. The direct write technology of energetic materials is to mix the energetic material with binder in a certain ratio and formulate the energetic ink material with fluidity [7,8]. The computerized motion control program can be used to complete the explosive writing. However, the performance of the direct write explosive inks is influenced by very complicated process parameters due to the challenging requirements of the structures. Except for satisfying the conventional requirements such as stability, viscosity, surface tension, and uniformity, the ink must also have a property that a considerable loading density can be achieved after drying.

Currently, 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW, CL-20) with high energy density (about 2.0 g/cm), excellent detonation pressure (about 44.8 GPa ) and detonation velocity (about



9762m/s), which is regarded as one of the most promising explosive to replace HMX and RDX [9-11]. In this paper, we chose CL-20 as the energetic material to prepare a direct write explosive ink, which can be smoothly written and have high energy density and micro-scale dimensions, and could be used in MEMS. Then, the explosive ink samples were characterized by scanning electron microscope (SEM), X-ray diffraction(XRD) and differential scanning calorimeter (DSC). Finally, the written critical size and the detonation velocity were also measured, which could demonstrate the performance of this explosive ink.

## 2. Experiments

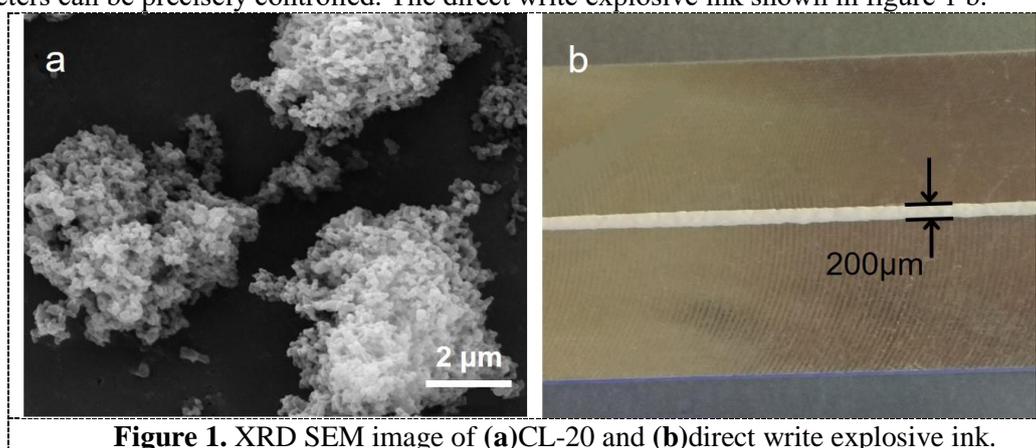
### 2.1. Instruments and Reagents

TESCAN VEGA TS5136XM Scanning Electron Microscope(Czech), OXFORD INCA 300 X-ray Energy Dispersive Spectrometer, BRUKER D8 advance X-ray Diffraction(Germany), NETZSCH DSC204F1 Differential Scanning Calorimeter(Germany), SHOTMASTER-300Ωx Three Dimensional Mobile Platform(Japan), DL32/16 velocity measuring instrument (China).

$\epsilon$ -CL-20, purity greater than 99.5%, provided by North University of China; Polyvinyl alcohol (Tianjin Ke Miou Chemical Reagent Co., Ltd.); Ethyl cellulose (Shanghai Jing Chun Biochemical Technology Co., Ltd.); Isopropyl alcohol (Tianjin Chemical Reagent Factory). All chemicals used in this investigation were of analytic grade.

### 2.2. Preparation of explosive ink

The direct write explosive ink used in this paper was composed of nano  $\epsilon$ -CL-20, binder system and other additives. The nano  $\epsilon$ -CL-20 was characterized with SEM (Fig.1a), and the results show that the crystal size of nano  $\epsilon$ -CL-20 was about 200~300nm. The binder system includes the binder and the solvent. In this paper, two different binder systems were designed with polyvinyl alcohol and ethyl cellulose, and the solvent was H<sub>2</sub>O and isopropyl alcohol. The mixture was stirred until the solids has been completely dissolved. The dry  $\epsilon$ -CL-20 was added to the solution and then the explosive ink was obtained evenly after stirring. The total solids compositions in the ink is about 60%, and the composition ratio of  $\epsilon$ -CL-20 to the binder is 19:1. A commercial inkjet printer (SHOTMASTER-300Ωx Three Dimensional Mobile Platform, Japan) was used to print and pattern explosive materials. With this device, the explosive ink can be written directly onto a surface or deposited into a cavity, and the writing parameters can be precisely controlled. The direct write explosive ink shown in figure 1 b.



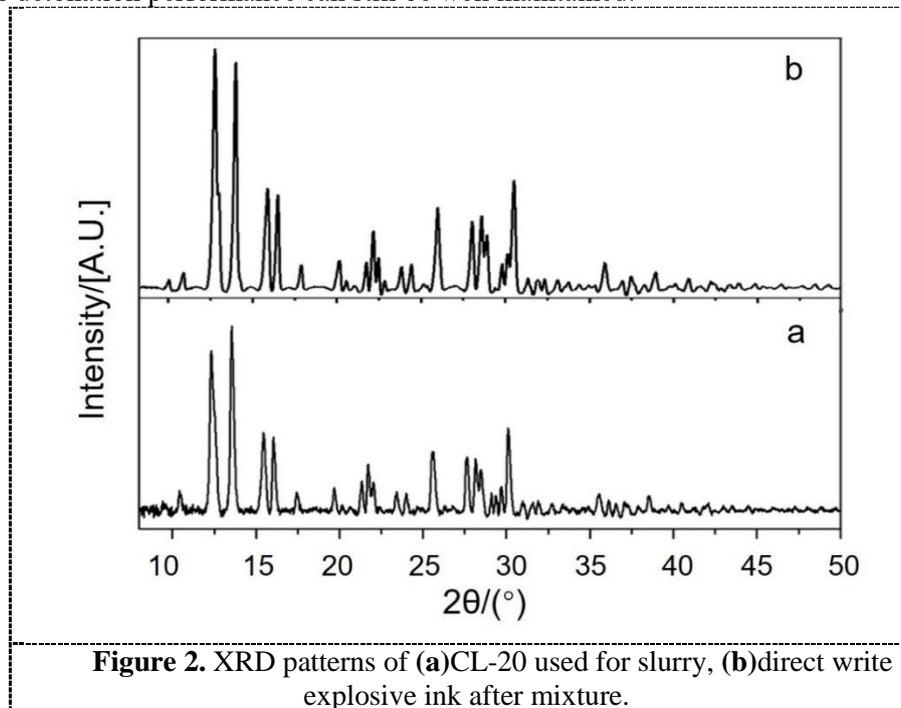
**Figure 1.** XRD SEM image of (a)CL-20 and (b)direct write explosive ink.

## 3. Characteristics and Discussions

### 3.1. X-Ray Diffraction Analysis

X-ray diffraction was used to characterize the crystal structure and the results are shown in figure 2. Comparing the X-ray diffraction curves of  $\epsilon$ -CL-20 (Figure. 2a) and CL-20 slurry (Figure. 2b) we can

see that the strong diffraction peaks of the Bragg angles of CL-20 used for explosive ink is at  $2\theta = 12.580^\circ$ ,  $13.830^\circ$  and  $30.310^\circ$ , respectively, which are same with the PDF#00-050-2045 (RDB) characteristic peaks of  $\epsilon$ -CL-20 [12]. When made into ink slurry, the crystal shape of CL-20 remains in the  $\epsilon$ -phase, which indicates that the configured ink solution does not change the crystalline form of  $\epsilon$ -CL-20, so its detonation performance can still be well maintained.



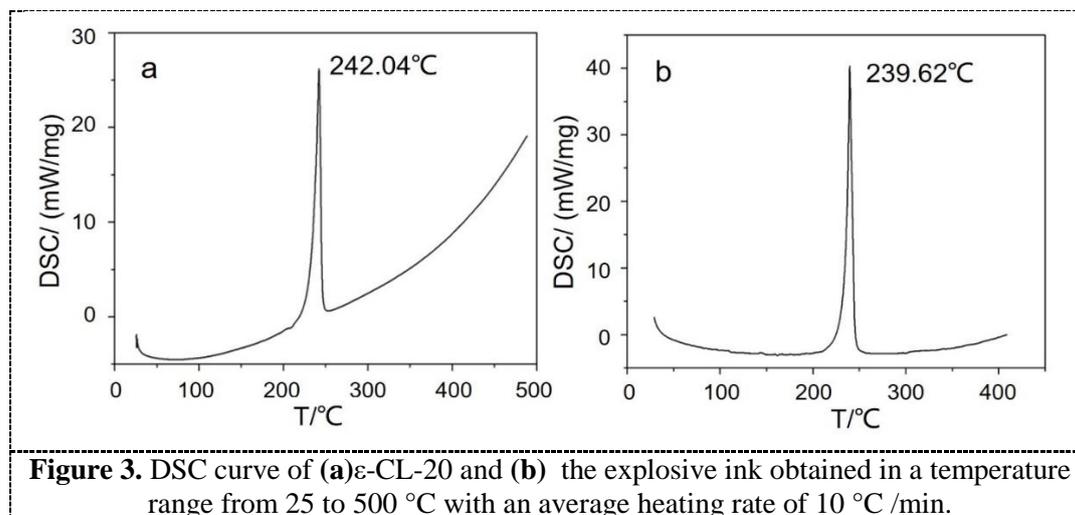
**Figure 2.** XRD patterns of (a)CL-20 used for slurry, (b)direct write explosive ink after mixture.

### 3.2. Thermal Properties

In order to evaluate the thermal properties, we characterized the  $\epsilon$ -CL-20 and direct write explosive ink with the NETZSCH DSC204F1 Differential Scanning Calorimeter (sample quality: about 1.0 mg, reference sample:  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, atmosphere: flowing nitrogen, average heating rate: 10 °C /min, temperature range: 25 °C to 500 °C). The results is shown in Figure 3.

It can be observed that the curve of  $\epsilon$ -CL-20 rises more abruptly with a peak temperature at 242.04°C, which was approached to the peak temperature at 249.4 °C observed by Dong [13] et al. And the second curve of the direct write explosive ink based on CL-20 has its own thermal decomposition temperature at 239.62°C.

Through the comparison n of the figure 3(a)(b), it can be seen that, compared with the raw  $\epsilon$ -CL-20, the peak temperature of the explosive ink has no obvious change, which indicates that the bond system is not involved in the thermal decomposition process.

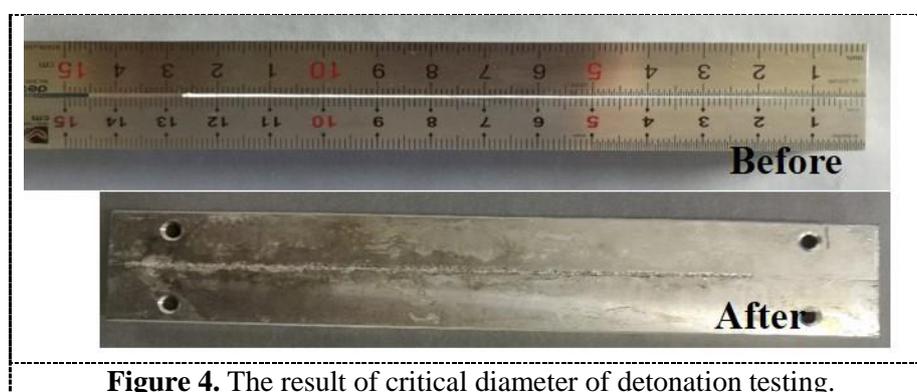


### 3.3. The Critical Diameter of detonation

Every explosive has its critical diameter of detonation which indicates that below which the detonation cannot be maintained. For this explosive inks, the critical size is related to the explosive components and the density of the explosive material within the ink. In order to get a minimum and accurate critical size, two standard steel rules (the thickness is 1mm and the length is 150mm) were fixed on a aluminum block with varying distance from 0 to 1mm, which constitute a shim stock to direct write the explosive ink, after dried and initiated with an LD-14 detonator. In order to more effectively evaluate the critical size performance of energetic inks, we prepared three specimens (1#, 2# and 3#), which were averaged to determine their critical dimensions. The results are shown in figure 4. Through the formula of  $D=(A/L) \cdot \Delta L$  we can get the critical size of this explosive ink. The parameters of explosive ink and the experiment results of the average critical size are shown in table 1.

**Table 1.** The parameters of average detonation velocity.

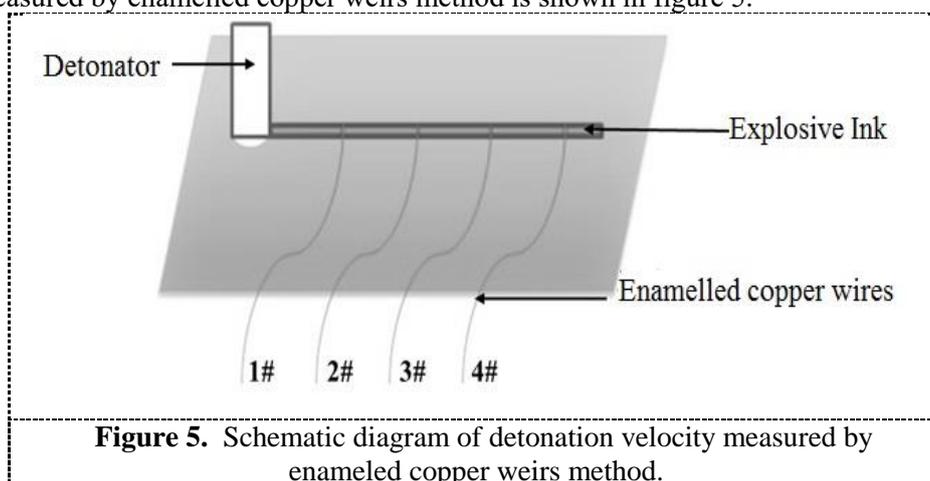
No.	Density L/(mm)	Diameter A/mm	Distance $\Delta L$ /mm	Critical size D/mm	Average velocity $\bar{D}$ /(mm)
1#	10	2300	3499	4738	8074.6
2#	10	1947	3208	4450	8024.1
3#	20	2780	5252	7766	8019.6



### 3.4. Average detonation velocity

Detonation velocity is the main parameter for characterizing the detonation performance of explosives. In this paper, the average detonation velocity of  $\epsilon$ -CL-20 explosive ink is obtained using a DL32/16

time interval measuring instrument, which is an 8-channel, Chinese-manufactured. The range of time interval between each channel is from 50ns~820ms, the time resolution is 1ns, which can improve the accuracy and reliability of the test results effectively. We place the enamelled copper wires at the bottom of the explosive ink as shorting pins. Making and breaking of shorting pins produces a pulse signal to measuring instrument, and then the interval time between each channel would be recorded. Using those time values, the average detonation velocity can be calculated. The schematic diagram of detonation velocity measured by enamelled copper weirs method is shown in figure 5.



To ensure the accuracy of the data obtained, we set the enamelled wires with an average of 10mm and 20mm, those distances are measured accurately with the vernier caliper to reduce errors. The experiment results of the average detonation velocity are shown in table 2. The four target lines used in this experiment were disconnected at the beginning, and when the detonation wave passed, they turned on due to ionization. The time interval  $\Delta t$  for detonation waves passing through the two target lines is calculated by  $\Delta t = t_{i+1} - t_i$ . The interval between each two targets is  $d$ . Calculated by the formula  $v = d / \Delta t$ , the average velocity  $v$  between detonation waves passing through two target lines can be obtained. It can be seen that under the same distance condition of four enamelled wires, the maximum velocity measured was 8237.1 m/s, and the average detonation velocity of those four test specimens were 8088.9 m/s. This value is close to the detonation velocity of CL-20's press charging (9061m/s, 1.932g/cm) [14], which means that this ink formulation improves CL-20's charging process without affecting its detonation performance.

**Table 2.** The parameters of average detonation velocity.

No.	Distances mm	Channel 1 T/ns	Channel 2 T/ns	Channel 3 T/ns	Channel 4 T/ns	Average velocity V/( m/s)
1#	10	2300	3499	4738	6018	8074.6
2#	10	1947	3208	4450	5686	8024.1
3#	20	2284	4676	7086	9570	8237.1
4#	20	2780	5252	7766	10262	8019.6

#### 4. Conclusions

This study demonstrates the preparation of direct write explosive ink based on  $\epsilon$ -CL-20, the results of XRD and DSC show that the crystal type of  $\epsilon$ -CL-20 is not changed in the explosive ink slurry and its thermal decomposition temperature is at 239.62°C, which is approached to the peak temperature of pure  $\epsilon$ -CL-20. Moreover, through the critical size test at different diameters when the CL-20 solid content of

direct write explosive ink is 60%, it can propagate the detonation waves successfully in the groove at 0.134 mm, and the largest detonation velocity of this explosive ink can reach 8237.1m/s. The above performances make the explosive ink a promising additive to be used in MEMs explosive train.

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