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Morphology of sodium bromate (NaBrO_3) under the influence of purified sodium dithionate ($\text{Na}_2\text{S}_2\text{O}_6$)

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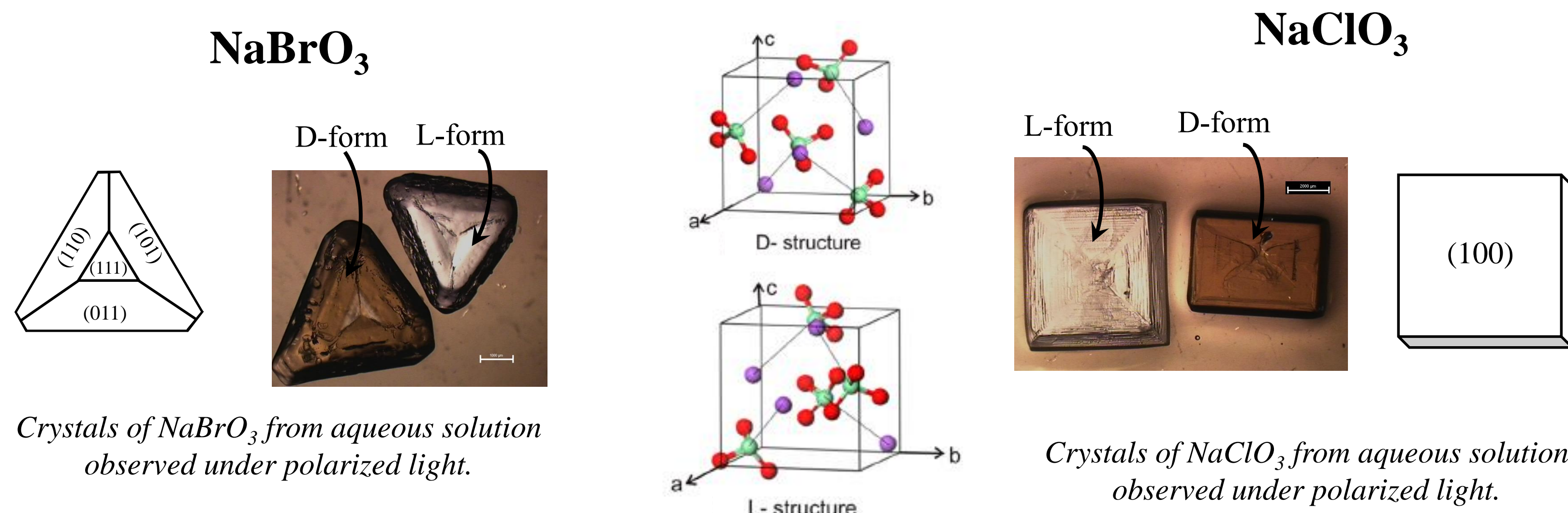
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INTRODUCTION

NaClO₃ and NaBrO₃ present **isomorphous structures** (same space group *P*₂₁₃ and same atomic positions in the unit cell).¹ Although the two substances are **achiral**, crystals of NaClO₃ and NaBrO₃ both show **supramolecular chirality**. However, the crystal habits of NaClO₃ and NaBrO₃ differ: NaClO₃ crystals exhibit large cubic {100} faces while NaBrO₃ crystals exhibit tetrahedral {111} faces.²

SUPRAMOLECULAR CHIRALITY

The use of a pair of polarizer can easily evidence the occurrence of **levo and dextro enantiomorphous crystals**.

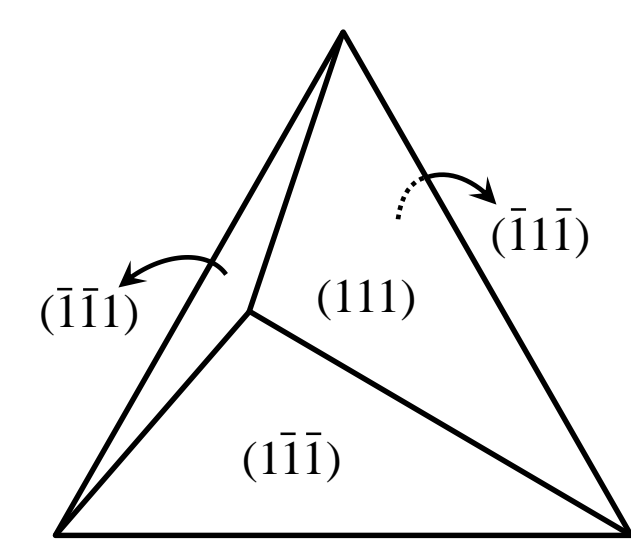
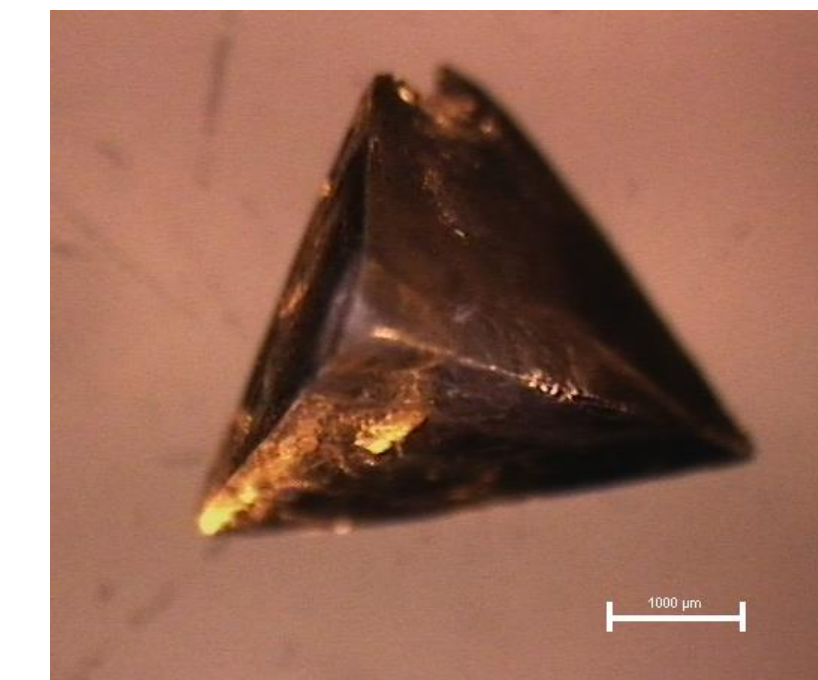


INFLUENCE OF Na₂S₂O₆ ON NaClO₃

Crystallization of NaClO₃ from aqueous solution in presence of Na₂S₂O₆ (molar ratio 1/1000)

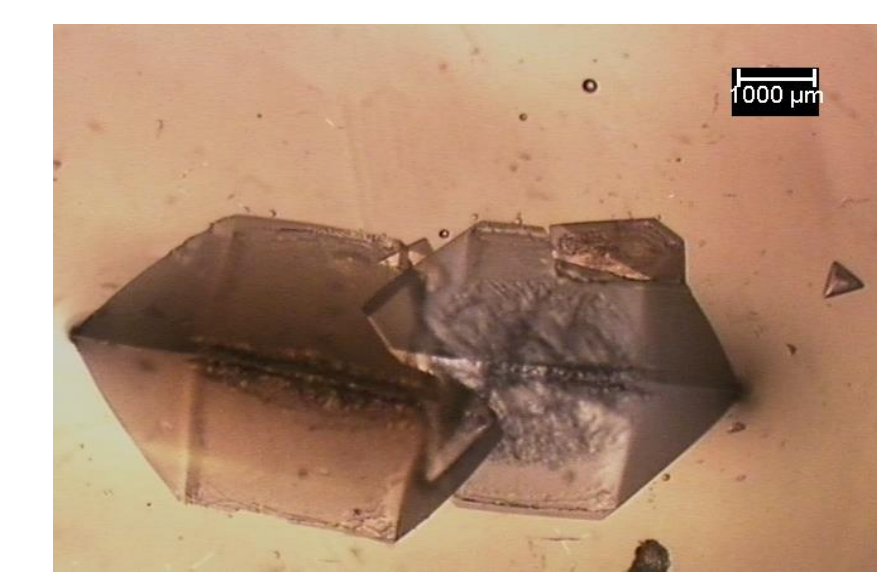
❖ **Habit modification of NaClO₃ by addition of Na₂S₂O₆**

Enhancing the {111} tetrahedral faces and suppressing the {001} cubic ones³



Crystal of NaClO₃ showing the tetrahedral morphology. Obtained by evaporation of solvent at room temperature in presence of Na₂S₂O₆.

❖ **Formation of NaClO₃ twin of opposite handedness³**



Twinned crystal of NaClO₃ showing two opposite handedness obtained by evaporation of solvent at room temperature in presence of Na₂S₂O₆.

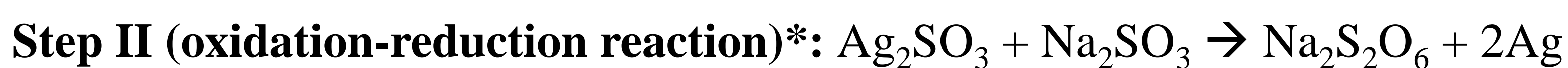
➔ **Effect of sodium dithionate on sodium bromate ?**

SYNTHESIS & CHARACTERIZATION OF Na₂S₂O₆

As the sodium dithionate is not easily available, Na₂S₂O₆ was synthesized. The synthesized product has been compared with the commercial batch.

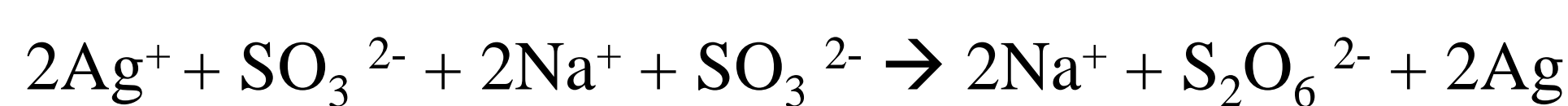
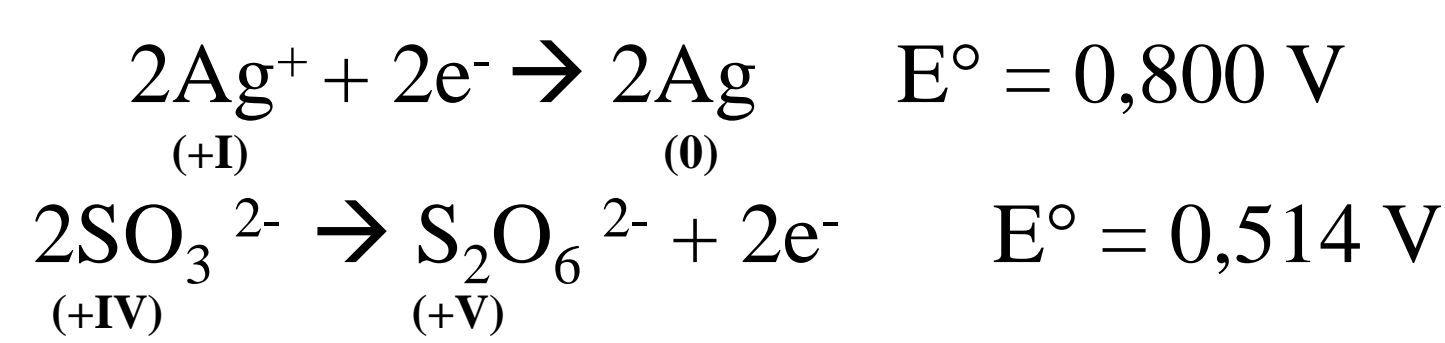
Synthesis⁴

Reaction involved:

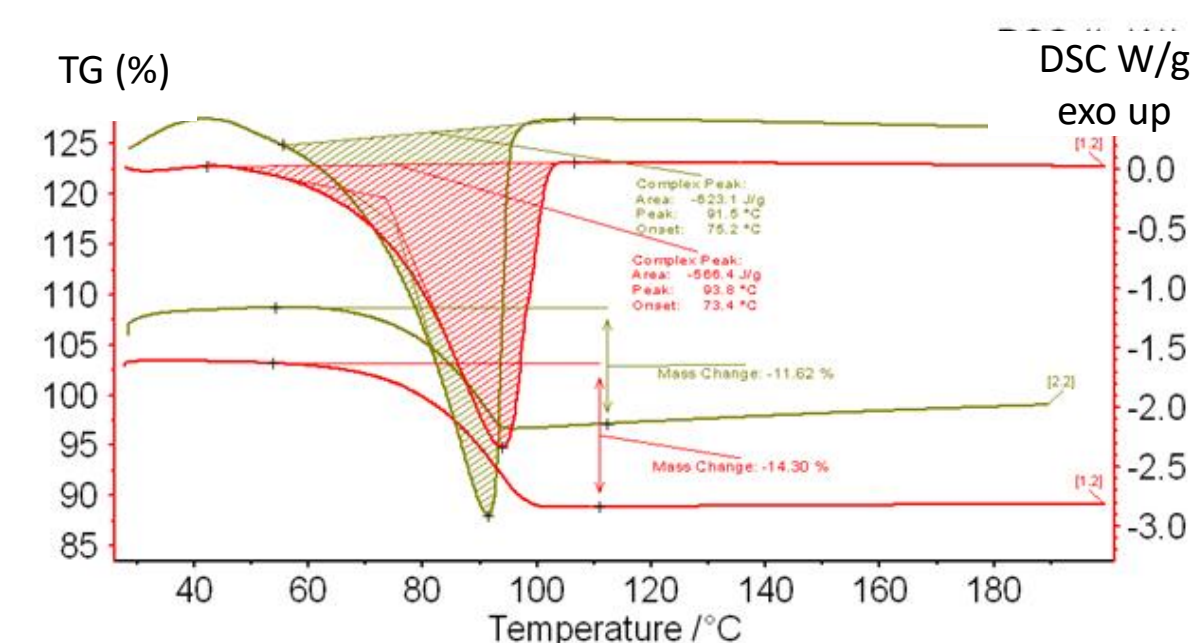


Experiment: Reagents mixture is kept 30 min under stirring and boiling. White precipitate of Ag₂SO₃ disappears and Ag crystallizes. After filtration of silver, solution of dithionate is concentrated by evaporation of solvent. Crystallization of dihydrated dithionate is induced by addition of antisolvent (ethanol and acetone). **Yield:** 75%

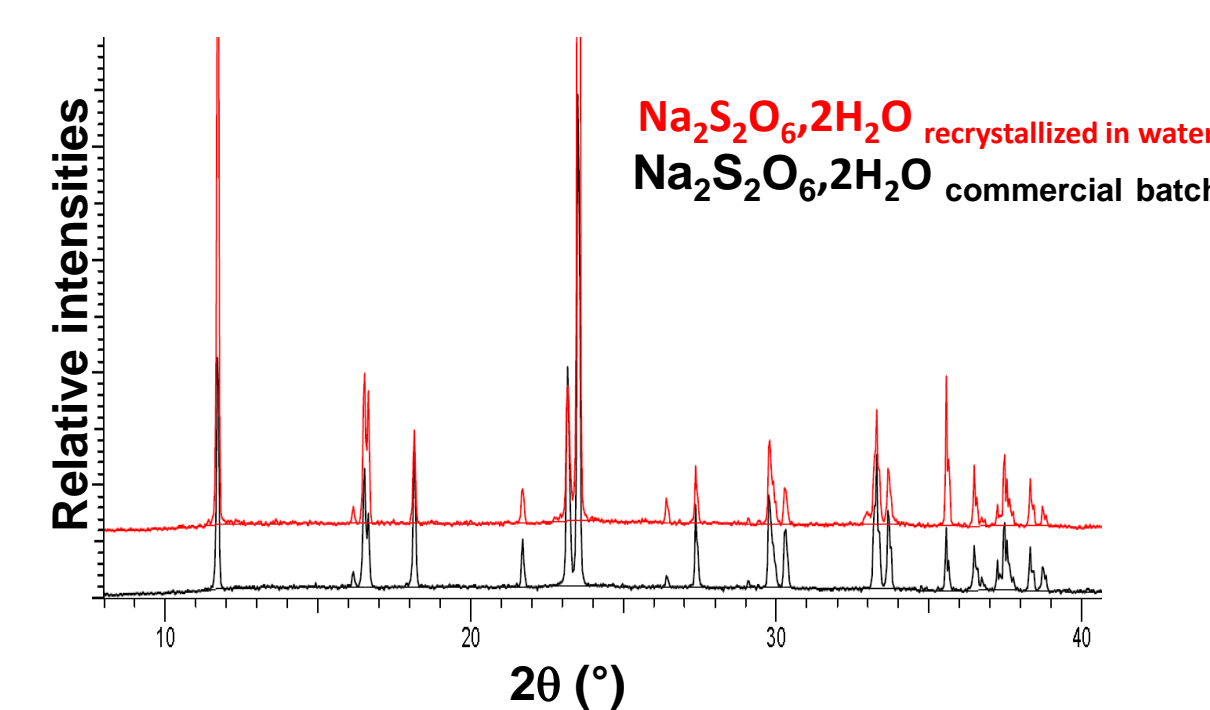
***Involved oxidation-reduction reaction:** Strongest oxidizing agent (Ag⁺) reacts with the weakest reducing agent (SO₃²⁻).



Characterization of synthesized product



TG-DSC of the commercial batch (red) and the synthesized product (green).

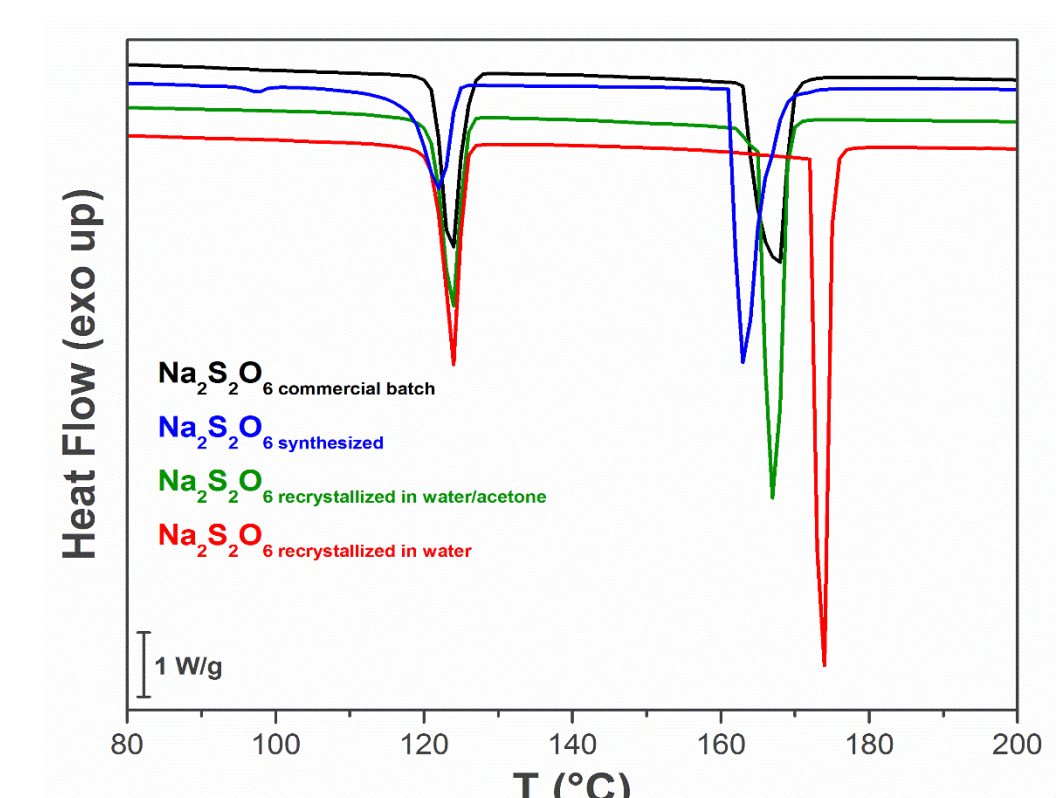


XRPD patterns of commercial batch (in black) and synthesized product (in red)

➔ **Recrystallization in water is more efficient to purify Na₂S₂O₆ ; the drawback is the low yield (47%).**

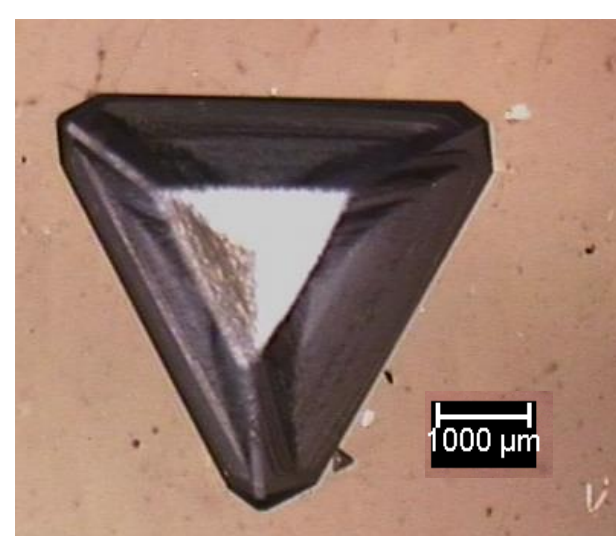
➔ **Commercial batch and synthesized product are sodium dithionate dihydrate.**

➔ **Dehydration occurs at 90°C as described in literature.⁵**



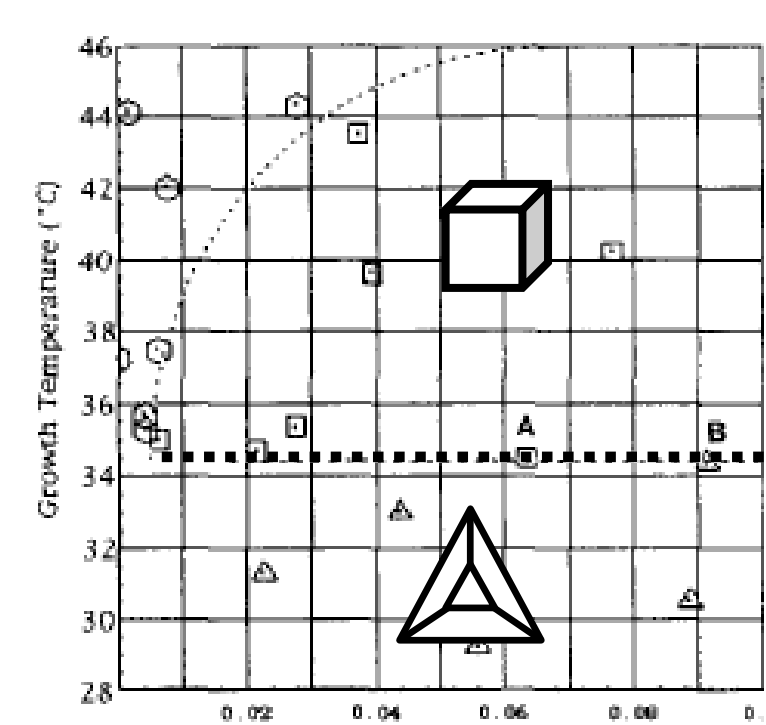
DSC analyses of different samples of Na₂S₂O₆. Comparison of different purification of synthesized product. (heating rate: 5K/min, closed crucibles)

THE MORPHOLOGIES OF SODIUM BROMATE³



➔ **No significant effect** of sodium dithionate on the typical trigonal form of sodium bromate

Crystal of NaBrO₃ obtained from aqueous solution in presence of Na₂S₂O₆ (molar ratio 1/1000) by evaporation of solvent, at room temperature



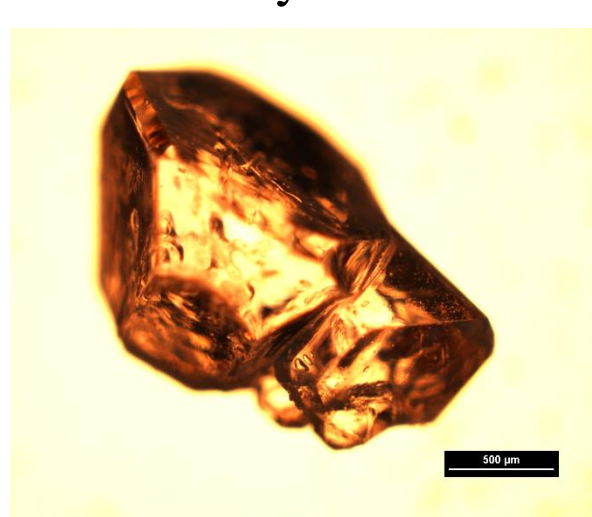
Morphodrome of NaBrO₃ as a function of the crystallization temperature and supersaturation⁶

➔ At high temperature and high supersaturation, NaBrO₃ crystals can present a cubic habit.⁶

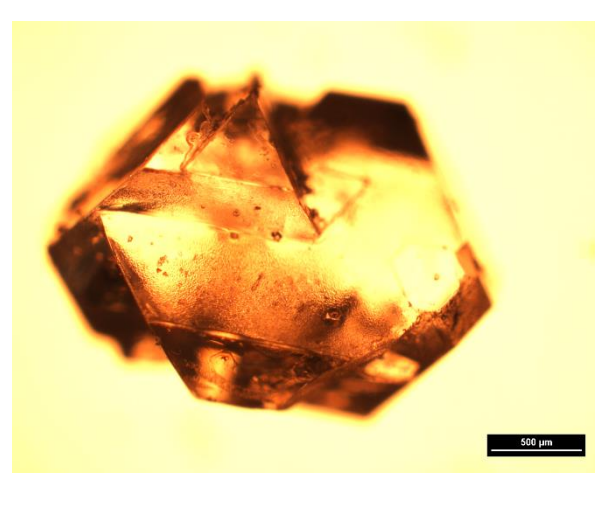
➔ **Effect of Na₂S₂O₆ on cubic morphology of NaBrO₃ ?**

In sealed vial, required amount of NaBrO₃ to achieve desired supersaturation is dissolved in water and then cooled to crystallization temperature. Without seeding, crystallization occurs in few hours.

T_{cryst}: 45°C / supersaturation: 1.05



Crystals of pure NaBrO₃.



Crystals of NaBrO₃ in presence of Na₂S₂O₆ (molar ratio 0,3%).

➔ No expected cubic crystals at high temperature and high supersaturation. Crystallization is not well controlled.

➔ Na₂S₂O₆ seems to lead to twinned crystals.

➔ **Effect on handedness ?**

PROSPECTS

❖ **Synthesis and characterization of Na₂S₂O₆**

- Improve yield of synthesis and recrystallization

❖ **NaBrO₃/ Na₂S₂O₆ system**

- Reconsider experimental conditions to well control of NaBrO₃ crystallization
- What will be the effect of Na₂S₂O₆ on expected cubic crystals of NaBrO₃ ? Will effects be the same (twins by inversion) than on NaClO₃ cubic crystals ?

ACKNOWLEDGMENTS

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