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► To cite this version:

S. Clevers, V. Dupray, Florent Simon, G. Coquerel. Is Second Harmonic Generation a reliable tool for studying solid-solid phase transition and structural purity?. XXXVIII èmes JEEP, Mar 2012, Rouen, France. hal-01942447

HAL Id: hal-01942447

<https://normandie-univ.hal.science/hal-01942447>

Submitted on 24 Sep 2019

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Is Second Harmonic Generation a reliable tool for studying solid-solid phase transition and structural purity?

Simon Clevers^a, Valérie Dupray^a, Florent Simon^a and Gérard Coquerel^a

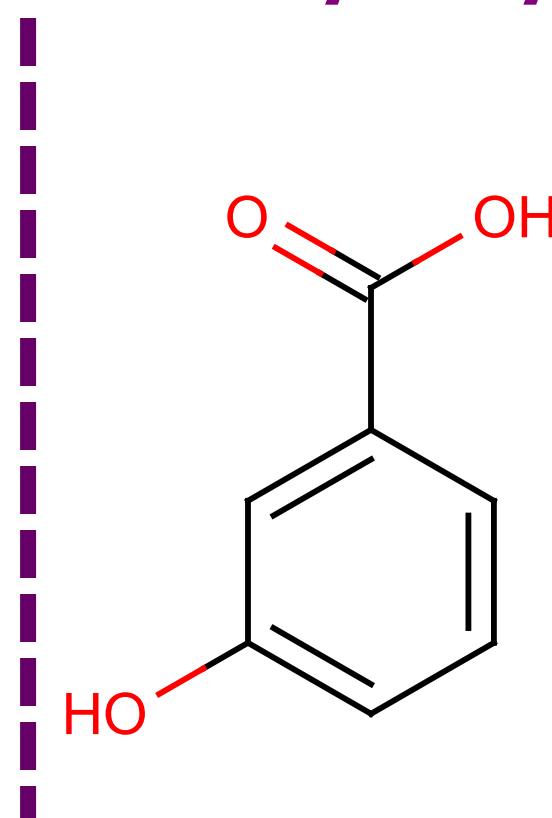
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Introduction

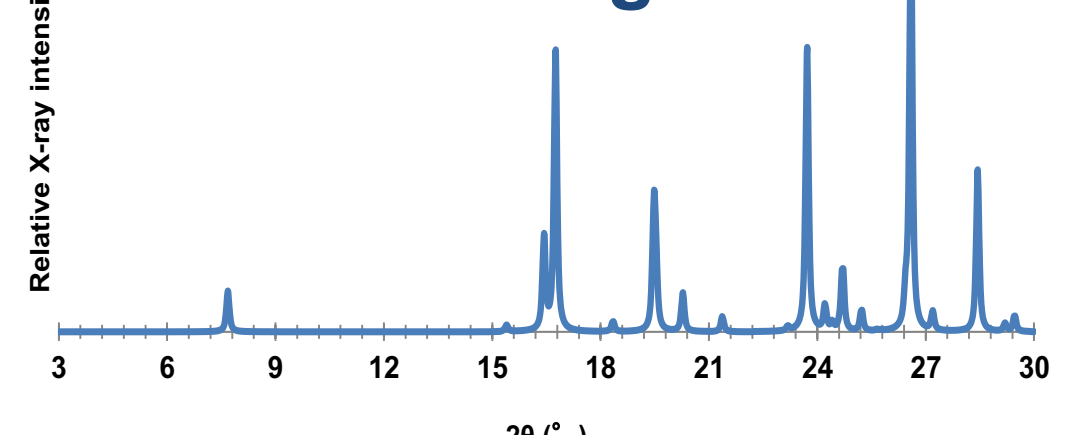
Second Harmonic Generation (SHG):

SHG is an optical process which can be used to detect the non-centrosymmetry of crystalline compounds^{1,2} (powder form). In order to study phase transitions, a device has been developed to perform SHG measurements versus temperature. The case of 3-hydroxybenzoic acid is considered.

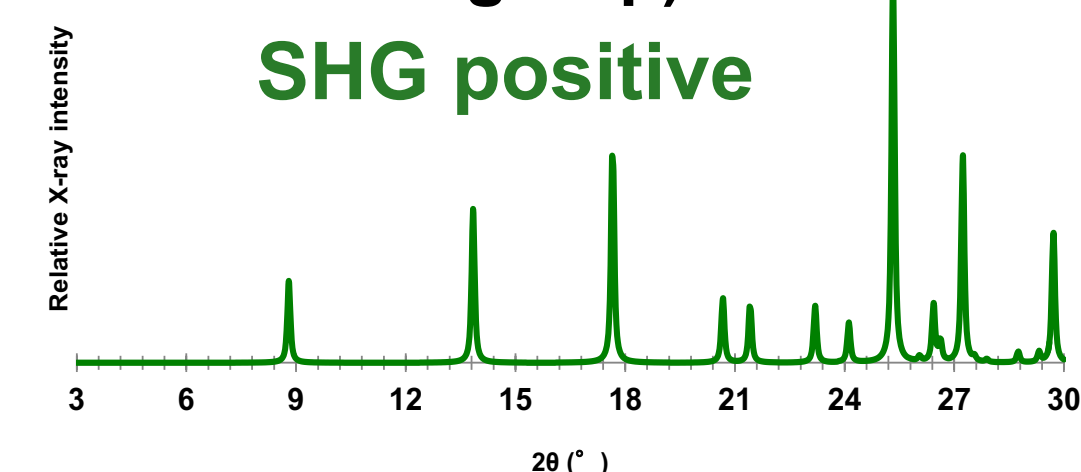
3-Hydroxybenzoic acid (MHBA) exhibits two polymorphic forms :



A stable form P2₁/c (Centrosymmetric group) **SHG negative**



A metastable form Pna2₁ (Non centrosymmetric space group) **SHG positive**



A known irreversible phase transition from the non-centrosymmetric metastable form (**SHG Positive**) to the centrosymmetric stable form (**SHG negative**) occurs at circa 160° C³.

The SHG device can be used to track this phase transition.

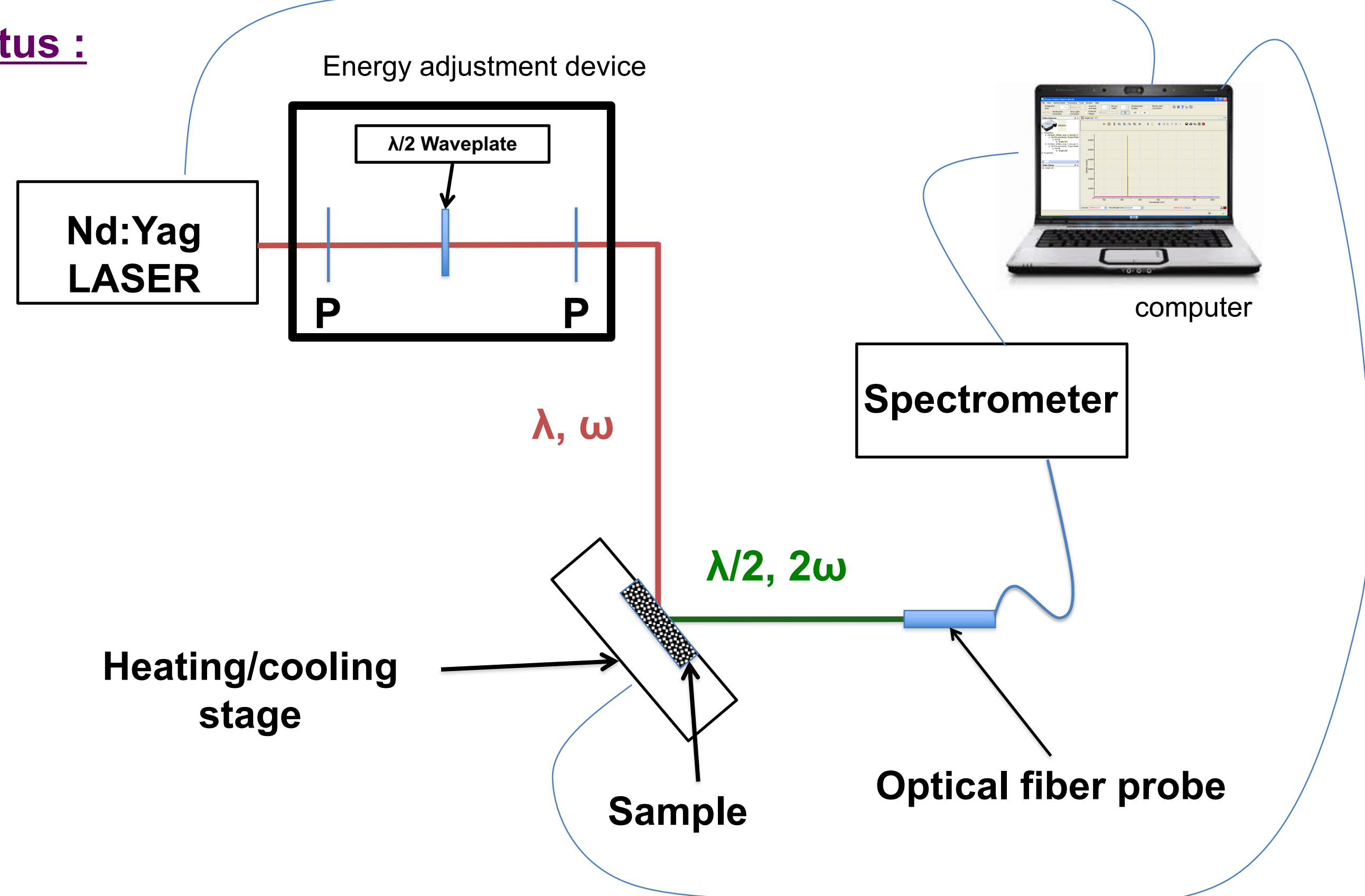
Aim of this study :

To evaluate the potential of SHG signal measurements to detect the phase transitions by comparison with other usual techniques such as Differential Scanning Calorimetry (DSC), X-Ray Powder Diffraction (XRPD). Two samples are studied : a commercial MHBA (normally constituted of the stable form) and a pure metastable product obtained by recrystallization in acetone.

Principle of SHG:

A laser beam is sent on the sample at the fundamental frequency ω
 ⇒ If the sample is non centrosymmetric a SHG signal is detected at twice the fundamental frequency.
 ⇒ According to the Kurtz and Perry method¹ the signal is compared to a reference signal. In our case, samples were compared to KDP.

Apparatus :

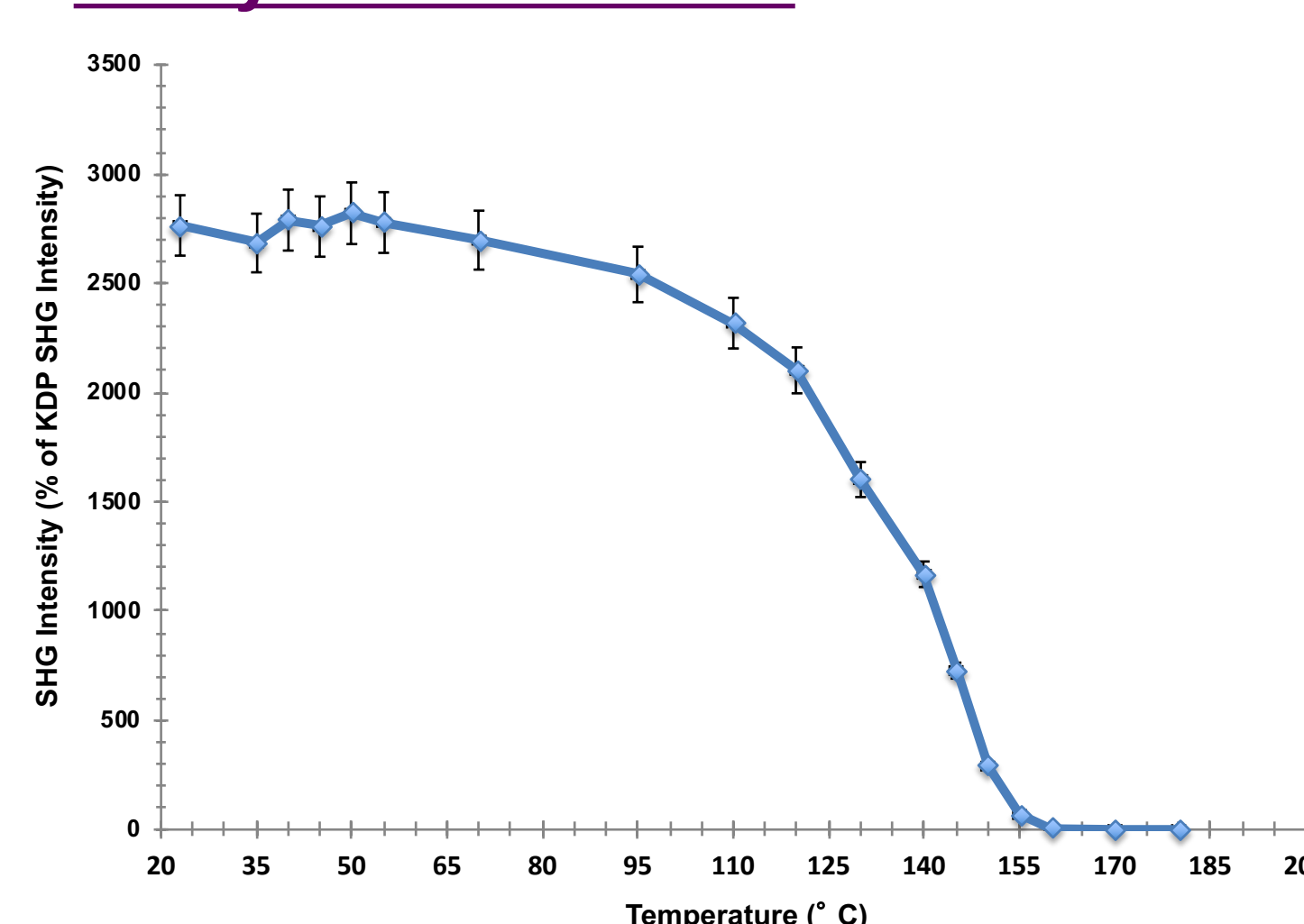


- ⇒ The powder sample is placed in an heating/cooling stage (computer controlled).
- ⇒ The SHG signal is measured versus temperature using a spectrometer.

Thermo-SHG

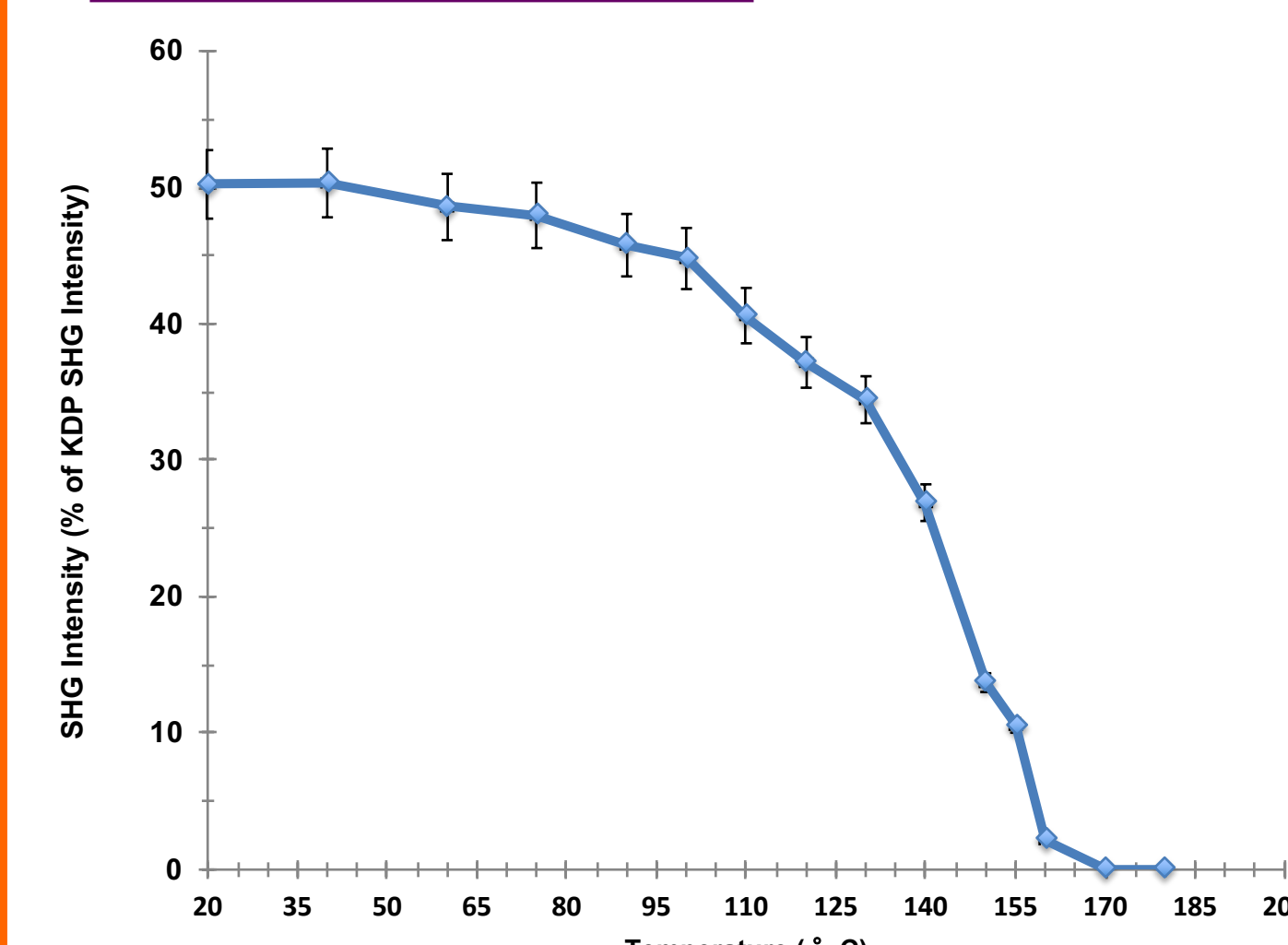
Results:

Recrystallized MHBA



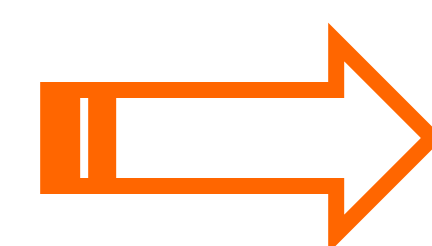
- Exhibits SHG signal
- SHG intensity decreases progressively with the temperature
- 90% of the signal is lost between 100° C and 160° C.
- The SHG signal disappears completely at 170° C. (mean heating rate 2K/min)

Commercial MHBA



- Results similar to the recrystallized product results: Inconsistent with the centrosymmetric space group assignment.
- The commercial compound exhibits a low SHG signal (55 times less intense than the recrystallized product).

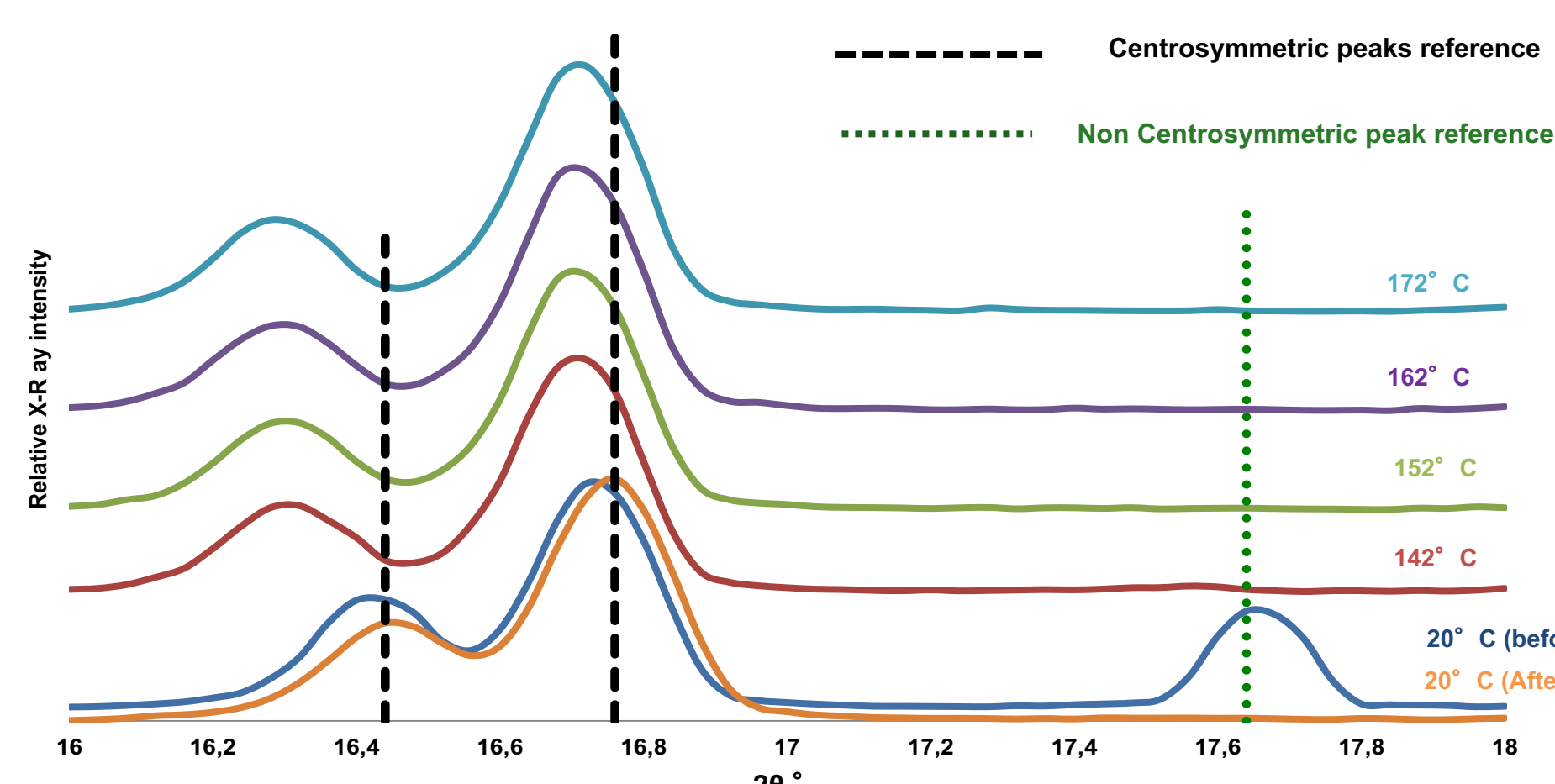
⇒ The commercial sample contains a SHG positive compound = small amount of metastable noncentrosymmetric form



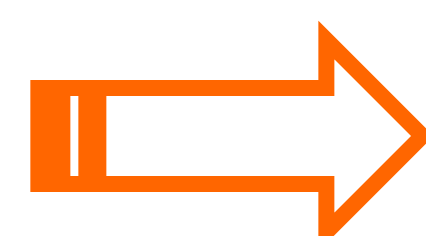
- SHG allow the monitoring of the polymorphic transition of MHBA from its metastable to its stable form
- SHG can probe the structural purity of the sample and track the conversion of a small amount of metastable form.

Comparison with X-Ray Powder Diffraction

Commercial MHBA



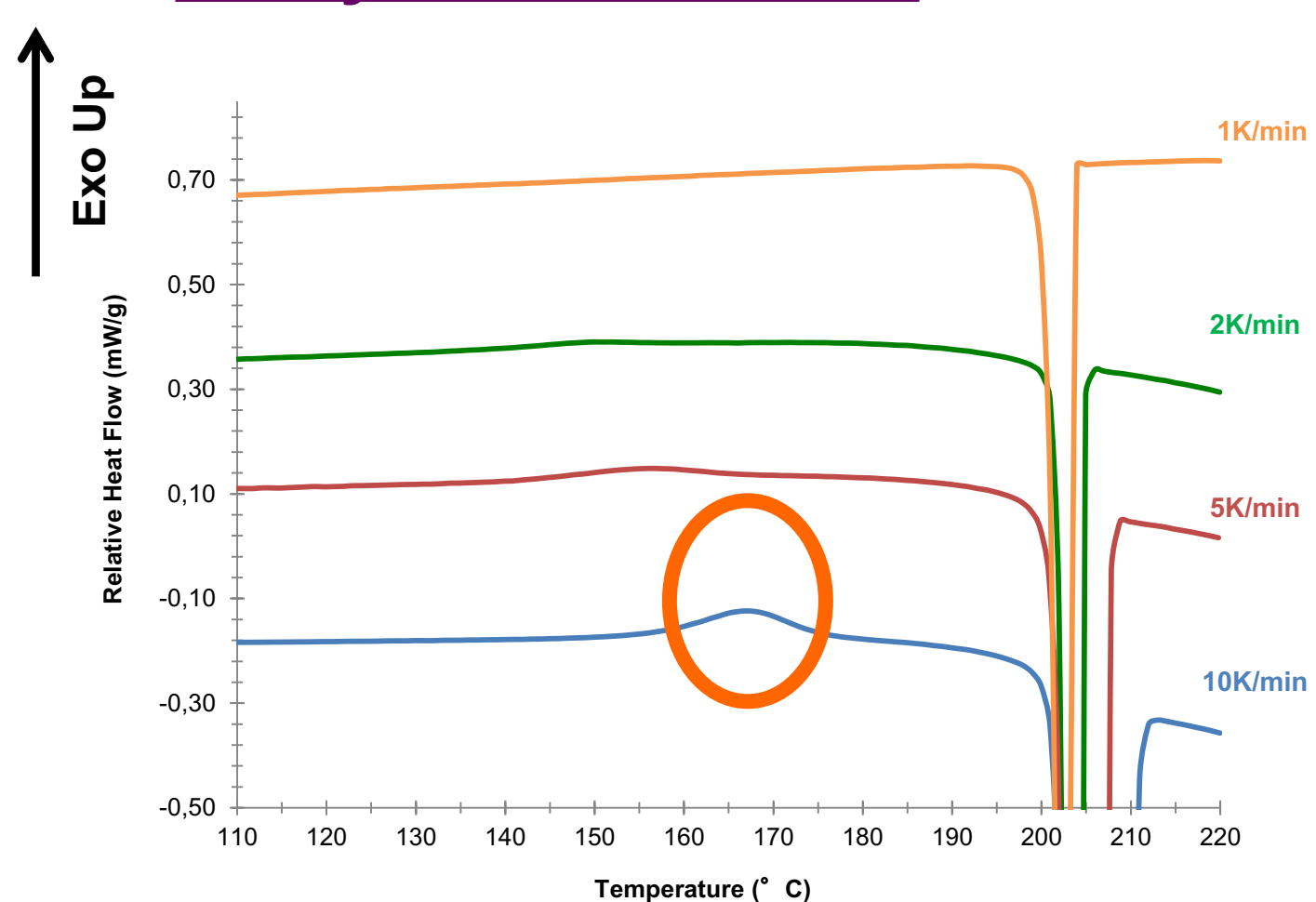
- XRPD confirms that :
 - the 2 polymorphic forms are present in commercial MHBA.
 - the structural impurity highlighted by SHG corresponds to the metastable form.
- Non centrosymmetric peak reference disappears between 142° C and 152° C



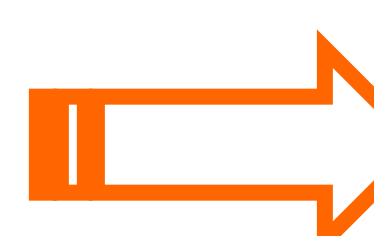
SHG and XRPD are complementary techniques

Comparison with Differential Scanning Calorimetry

Recrystallized MHBA



- In two cases : Average onset fusion peak ≈ 201.7° C
- Recrystallized MHBA DSC scans exhibit a weak exothermic event around 167° C (at 10K/min) attributed to the crystallization of the metastable (Pna2₁) form into the stable form (P2₁/c).
- DSC curves of commercial MHBA exhibit no heat exchange corresponding to a phase transition. In the case of commercial product, this technique can not detect the phase transition.



DSC is unable to detect the phase transition in the case of the commercial product

Conclusion

- ⇒ Possibility to follow a phase transition by SHG measurements.
- ⇒ High sensitivity of SHG compared to DSC.
- ⇒ In favorable cases SHG is a very sensitive probe to assess the structural purity.

Further Work

Understanding the possible relationship between the lattice thermal expansion (highlighted by a peak shift in TR-XRPD) and the SHG signal and determine more accurately the temperature of the solid-solid phase transition.