
Conference or Workshop Item:

Calligaris, GA, Lai, X, Roberts, KJ orcid.org/0000-0002-1070-7435 et al. (1 more author) (2017) Lattice strain analysis on habit-modified [S2O6]2−-doped NaBrO3 crystals. In: Abstracts of the XXIV IUCr Congress, 21-28 Aug 2017, Hyderabad, India.

https://doi.org/10.1107/S2053273317086375

Lattice strain analysis on habit modified $S_2O_6^{2-}$-doped $NaBrO_3$ crystals

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Crystallization processes are constantly being developed to match the rising industry needs such as better flow ability, compressibility and dissolution properties, to name a few, which in turn can be enhanced by crystal habit modification process where normally impurities are intentionally added during the crystallization process. Furthermore, crystal habit modification by impurity incorporation provides a good scenario to study fundamental aspects of the surface chemistry role in the crystal growth mechanism since even low levels of impurity can lead to substantial changes in the final morphology. Once incorporated, impurity can act either by blocking the movement of step/kink surface sites or disturbing the proper molecular packing of the next growing layer [1]. However, structural changes in crystal habit modification due to impurity incorporation still lacks investigations on lattice distortions that could bring new insights for both fundamental science and industrial crystallization process.

Sodium bromate ($NaBrO_3$) grown under moderate supersaturation crystalizes in the space group $P2_13$ ($a = 6.7072$ Å) and presents a habit mainly ruled by the tetrahedral faces of the "positive" {111}-form (defined by {111}, $\{1\bar{1}\bar{1}\}$, $\{\bar{1}1\bar{1}\}$ and $\{\bar{1}\bar{1}1\}$ faces) with the presence of the less important "negative" tetrahedral $\{\bar{1}\bar{1}\bar{1}\}$-form (with $\{\bar{1}\bar{1}\bar{1}\}$, $\{\bar{1}11\}$, $\{1\bar{1}1\}$ and $\{11\bar{1}\}$ faces). These symmetric but non-equivalent faces have a polar behavior from the $P2_13$ group and so present distinct surface chemistry that will rule the impurity incorporation selectivity between such faces.

In this work, large nearly perfect single crystals of $NaBrO_3$ were grown with and without the presence of habit modifying sodium dithionate ($Na_2S_2O_6$) impurities from 50 up to 2000 ppm in molar ratio. Changes in the final habit have been observed, with the $\{\bar{1}\bar{1}\bar{1}\}$-form prevailing over the {111}-form at level of 500 ppm or higher.

Sulphur incorporation has been confirmed by X-ray fluorescence on all doped samples. X-ray Powder Diffraction (XPD) has shown similar profiles between pure and doped samples and thus indicates that the dopant was well incorporated by the host lattice. However, surface microtopography revealed an increase of the roughness as well as the presence of growth steps hillocks as the dopant level goes higher, which in turn indicates the occurrence of dislocations lines during the crystal growth, not detected by XPD. Studies on $S_2O_6^{2-}$-doped $NaClO_3$ crystals supports an incorporation mechanism in which one SO_3^- group substitutes the ClO_3^- ion, whilst the other SO_3^- causes high disturbance in the upcoming layers and its growth rate. This assumption is going to be verified for the $NaBrO_3$ system using X-ray Multiple Diffraction (XRMD) technique that has enough sensitivity to detect minor distortions along the crystal lattice. The (000)(002)(111) and $(000)(002)(\bar{1}\bar{1}\bar{1})$ Bragg-Surface Diffraction (BSD) [2] cases are able to probe the lattice along two orthogonal directions inside the same growth sector and hence, identify any anisotropic strain caused by the $S_2O_6^{2-}$ ion. BSD ω:ϕ mappings (coupled scans along both incident (ω) and azimuthal (ϕ) angles) are also useful to evaluate the mosaicity level along the in-plane and out-of-plane directions whilst maintain the Dynamical Diffraction regime [3].

References:

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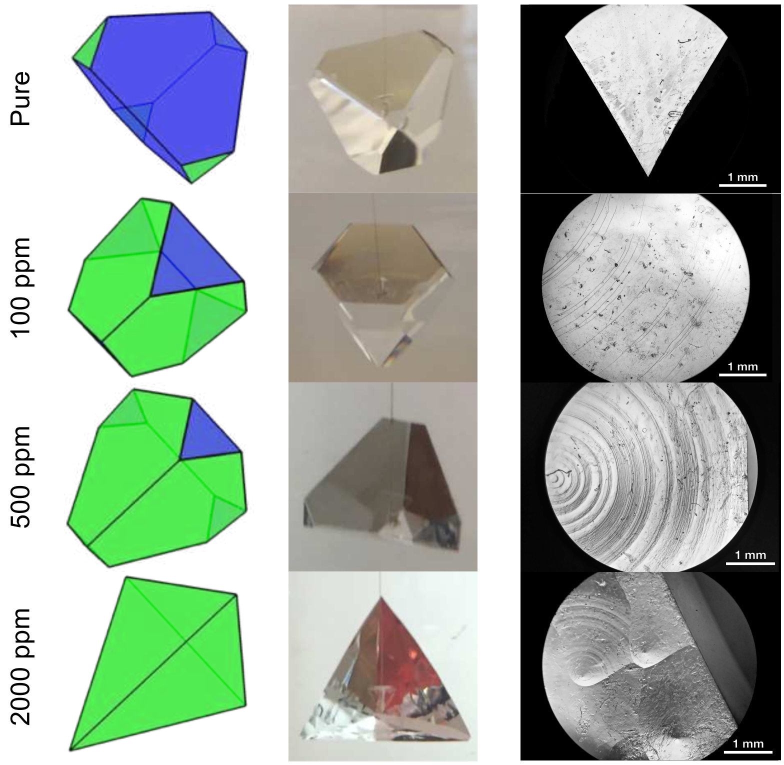

Figure 1. The evolution on changing crystal habit of $NaBrO_3$ crystals as a function of the $S_2O_6^{2-}$ concentration. The {111}- and {$\bar{1}\bar{1}\bar{1}$}-form faces, in blue and green respectively, swap importance in the final habit in function of the impurity level. Surface microtopography from the {$\bar{1}\bar{1}\bar{1}$}-form faces show the roughness increase as the dopant level rises.