Poster Sessions

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When does the chirality of NaClO₃ crystals arise in solution growth?

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Chiral symmetry breaking in sodium chlorate ($NaClO_3$) crystallization from a solution was reported by Kondepudi et al. (1990) [1]. The chiral $NaClO_3$ crystal has cubic crystal system and space group of $P2_13$. When Kondepudi et al. evaporated $NaClO_3$ solution without any mechanical disturbance, they obtained equal numbers of L- and D-crystals in the solution. In contrast, from a stirred solution almost only one type of crystals was obtained. This significant bias in chirality is termed as chiral symmetry breaking. Some theoretical models have been proposed for the mechanism of the chiral symmetry breaking, however, the mechanism has not been elucidated yet. To obtain the direct evidence of chiral symmetry breaking, we carried out in-situ observation of the crystallization process by using a polarization microscope. As a result, we found that non-cubic metastable crystals appeared at first, and then, transformed to cubic crystals by a solid-solid phase transition or a solution-mediated phase transition [2].

On the assumption that the metastable crystal is achiral, we conclude that the chirality of $NaClO_3$ crystal arises when the phase transition occurs. However, it is unknown whether the metastable crystal is chiral or achiral because the crystal structure has not been analyzed in the literature till date. Thus, in the present paper, we reported the result of a single-crystal X-ray diffraction experiment for the metastable crystal.

The metastable crystal was prepared by drop evaporation method as follows. A drop (6 μl) of a $NaClO_3$ solution saturated at room temperature (293K) was put onto a cover glass. The metastable phase crystallized in the drop as the solution evaporated. After the crystal grew up to 200 μm in size, the drop were replaced with glycerin. Afterwards, the crystal and the drop of glycerin were frozen by liquid nitrogen. The frozen drop is the specimen for the X-ray diffraction experiment. X-ray diffraction data was collected in oscillation mode by imaging plate type single-crystal X-ray diffractometer (R-AXIS IV++, Rigaku). To keep specimen frozen during the experiment, we kept the temperature around the specimen at -266±1 K by Cryostream (Oxford).

From the X-ray diffraction, we determined the lattice constant, crystal system, and space group of the metastable phase as follows; a=8.42 (Å), b=5.26 (Å), c=6.70 (Å), β=109.71(°), monoclinic, and $P2_1/a$, respectively. These values are very similar to that of $NaClO_3(I)$, which was reported as a high temperature phase of $NaClO_3$ crystal in melt growth (a=8.78 (Å), b=5.17 (Å), c=6.83 (Å), β=110 (°), monoclinic, and $P2_1/a$) [3]. Therefore, it is highly possible that the metastable phase we obtained from the solution is the same as the $NaClO_3(I)$ phase. In addition, we found that the metastable crystal is achiral because a crystal having a space group of $P2_1/a$ is achiral. From these results, we concluded that chirality of the cubic $NaClO_3$ crystal arises when the phase transition occurs.

The achiral metastable crystals have not been considered in the $NaClO_3$ crystallization from the solution. The phase transition from the achiral phase to the chiral phase may lead to a new understanding for the chiral symmetry breaking.

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Functionalized ZnO nanostructures for gas sensing and photovoltaic applications

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Zinc oxide (ZnO) is an incredibly versatile material that in its nanostructured form is studied for a large number of applications in optoelectronics, photovoltaics, gas and bio-sensing, piezoelectric devices, photocatalysis, spintronics, etc.

Recently this group has successfully reported the optimized not-catalyzed synthesis processes for producing single morphologies of ZnO nanostructures (i.e. nanowires [1], aligned nanorods [2], and nanotetrapods [3]) among the many different ones that are generally obtained in vapor phase reactions. The proper combination of metal thermal evaporation and controlled oxidation has produced good quality nanostructures, whose properties were not affected by contamination from catalysts or precursors.

The great potential of these nanostructures, however, can be fully explored only once they are functionalized with different organic or inorganic materials for tailoring their intrinsic properties towards the final application.

In this work authors report some meaningful examples of surface functionalization of their ZnO nanostructures by inorganic (calcogenides) and organic (phthalocyanines and porphyrins) semiconductors for applications in gas sensing, photovoltaics and photocatalitic degradation of water and gas pollutants. Although different techniques were used (an optimized chemical bath deposition – CBD – process and a supersonic molecular beam deposition – SuMBD – apparatus), in both cases particular attention has been devoted to the interface formation in the coupled compounds, in order to obtain working heterostructures where charge carriers can be efficiently separated and transferred.

The obtained functionalized ZnO nanotructures have been characterized accurately by electron microscopy (SEM and TEM), x-ray diffraction (XRD) and optical measurements (optical absorption, photoluminescence, and cathodoluminescence). The heterostructures properties have been also studied by functional characterizations such as chemoresistive gas sensing tests, photocurrent and photocatalytic activity measurements. The correlation between structural and functional properties has then been discussed.

In the case of functionalization with CdS, for example, a thickness dependent effect of charge transfer to the ZnO nanostructure has been demonstrated, together with an enhancement of the photocatalytic properties, and the modification of the gas sensing response mechanisms.

In the case of functionalization with organics, different emission spectra have been observed together with different morphologies of the obtained depositions. These phenomena have been discussed in terms of distinct molecular bonding of phthalocyanines and porphyrins at the interface with the oxide nanostructures.

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