Comment on: “Nucleation and Growth of BaF$_{x}$Cl$_{2-x}$ Nanorods”

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In a recent paper, Xie et al$^1$ reported on the nucleation and growth of BaF$_{x}$Cl$_{2-x}$ nanorods. In this comment, we wish to draw attention to pertinent experimental results that shed more light on the observed morphology and structure of the nanorods discussed in reference [1]. In an independent paper, Zhang et al$^2$ present the synthesis and characterization of Ba$_3$ClF$_7$ microrods.

The composition BaF$_2$Cl given in references [1,2] should be corrected. In the Ba/F/Cl system, three compounds have been characterized from single-crystal data: BaFCl$^3$, Ba$_{12}$F$_{19}$Cl$_5$ and BaF$_7$Cl$_2$.$^4$ The matlockite-type compound BaFCl can be obtained under different synthesis conditions, and Ba$_{12}$F$_{19}$Cl$_5$ forms in a flux only at high temperature. At high fluorine concentrations and at relatively low temperatures, the compound Ba$_7$F$_{12}$Cl$_2$ can be obtained in the form of hexagonal needles: melt synthesis with an NaCl/LiCl flux gives an ordered and a disordered modification$^5$ with space group $P6_3/m$ and $P6_3/m$, respectively. Between 160°C and 250°C under hydrothermal conditions, and by gel growth at room temperature, an ordered structure$^6$ and a superstructure$^7$ can be obtained, respectively.

Synthesis conditions given in references [1,2] are consistent with the conditions for the formation of Ba$_7$F$_{12}$Cl$_2$. The powder pattern given in reference [1] was indexed by using unconfirmed powder diffraction data$^8$ and should be indexed with the structural data given for ordered Ba$_7$F$_{12}$Cl$_2$ (Figure 1); an experimental FWHM of 0.03° and a presumed crystal size of about 60 nm according to the fast growth conditions was included in the pattern simulation (Powder-Cell).$^9$ The rod-like shaped nano-units given in reference [1] are in agreement with the hexagonal needle shape (Figure 2) obtained during crystal growth and might explain the $a/c$ ratio of the nanocrystalline material formed on precipitation.

A powder sample, kindly provided by Prof. Yadong Li, was measured additionally by X-ray diffraction using a STOE Stadi P diffractometer with capillary equipment and CuK$_{α1}$ radiation. Rietveld refinements (Topas 4.2)$^{10}$ for this sample yielded the following phase composition: Ba$_{12}$F$_{12}$Cl$_2$ ($a=10.6281(3)$ Å, $c=4.17940(14)$ Å) 66 wt %, BaFCl 20 wt %, NaF 12 wt %, and BaF$_2$ 2 wt %. The average crystallite sizes in nm (with e.s.d. values of the last digits in parentheses) based on the Scherrer method were: Ba$_{12}$F$_{12}$Cl$_2$ 166(4), BaFCl 96(5), NaF 97(8) and BaF$_2$ 30(2).

As a further comparison of the samples using another experimental technique, we have obtained Raman spectra. Figure 3 compares the Raman spectra of the sample provided by Professor Li and an assembly of single crystals of

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Ba$_7$F$_{12}$Cl$_2$ prepared in our laboratory. The spectra are quite similar; the small shift of the band around 220 cm$^{-1}$ is related to polarization effects, as our crystals are slightly oriented.

A common feature of the crystal structures of BaFCl, Ba$_2$F$_3$Cl$_3$, and Ba$_3$F$_7$Cl$_2$ is that the Ba atoms have a coordination number of 9. In the crystal, however, the arrangement is quite different. In Ba$_2$F$_3$Cl$_3$ and Ba$_3$F$_7$Cl$_2$ as well as in the corresponding lead compounds Pb$_3$F$_7$Cl$_2$ and Pb$_3$F$_7$Br$_2$, the propeller shape arrangement of the halides in the structure as well as the short lattice constant $c$ favors a needle shape crystal habitus for all synthesis methods.

Barium halides are interesting hosts for optical applications. Ba$_3$F$_7$Cl$_2$ is a host for the rare-earth element Eu$^{2+}$ and acts as an intense white phosphor. The channel-type structure allows the replacement of Ba$^{2+}$ and Cl$^{-}$ with other ions and interstitial sites can be occupied. Detailed order/disorder studies on single crystals of substituted Ba$_3$F$_7$Cl$_2$ are still in progress. Nanocrystalline barium fluoride chloride samples might reveal further interesting optical properties.

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