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Synchrotron-based X-ray diffraction studies of carbonate hydroxylpyromorphite $Pb_{10}(PO_4)_6(OH)_2$

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The formula of apatites is represented as $M_{10}[XO_4]_6Y_2$, where M is occupied Ca and Pb, position Y by anions including OH, Cl, F, and position $[XO_4]$ accommodates ionic complexes such as $[PO_4]$, $[VO_4]$ and $[AsO_4]$. In calcium hydroxylapatites, $Ca_{10}(PO_4)_6(OH)_2$, substitutions of carbonate ion are common. Carbonates can be accommodated within the structure in two distinct crystallographic positions: type A, where CO_3^{2-} is located in the structural channel (substitution for OH) and type B substitution for PO_4^{3-} tetrahedron. Location of the carbonate ion in lead hydroxylapatite structure however, is still unknown.

In order to determine the nature of carbonate substitutions in hydroxylpyromorphite, $Pb_{10}(PO_4)_6(OH)_2$, two synthetic analogues were prepared via solution growth route - (1) carbonate-free (HPY-P) and (2) with the maximum theoretical substitution of CO_3^{2-} (HPY- CO_3). High-resolution X-ray diffraction measurements were carried out at the beamline 11-BM of the Advanced Photon Source, Argonne National Laboratory. Subsequent Rietveld refinement analyses were based on the structural model of carbonate-substituted calcium hydroxylapatite by Fleet et al. [1].

The results indicate that CO_3^{2-} in HPY is present in both structural positions. The calculated formula of the carbonated sample is $Pb_{10}(PO_4)_{5.85}[(CO_3)_{0.58}(OH)_{1.3}]$. The refined unit cell parameters for HPY-P and HPY- CO_3 are $a=9.8789$ Å, $c=7.4301$ Å and $a=9.8784$ Å, $c=7.7364$ Å, respectively.

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Photoelectron spectroscopy studies of double metal cyanide catalysts

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Double metal cyanide (DMC) catalysts, based on zinc hexacyanocobaltate (III) ($Zn_3[Co(CN)_6]_2 \cdot nH_2O$), are widely used for epoxide polymerization. Active catalysts could be prepared in the presence of a low molecular weight complexing agents as organic coordination ligands [1]. By adding various complex ligands the catalytic activity of the DMC catalyst can be improved [2,3]. However, despite of wide application in chemical industry, the mechanism of their catalytic activity is still discussing. Generally the Zn atoms are assumed to be the active centers in the DMC catalyst structure. It is still open question related to stability of the DMC catalysts at various experimental conditions. In order to get more experimental data in this point we used the X-ray photoelectron spectroscopy (XPS) technique to study the DMC catalyst before and after argon ion beam etching. The composition and chemical nature of elements within the surface region of both the reference zinc hexacyanocobaltate and catalyst samples were analysed. The samples prior to Ar^+ ion sputtering revealed the coexistence of native oxides of Co and Zn in addition to the main Zn-Co-CN compounds. Argon ion sputtering of both samples led to their partial destruction and formation of oxide states of Co and Zn. The contribution of Co-O states at the surface area of the argon sputtered catalyst is evidently larger than at the reference material. Character of Zn bonds is dominated by Zn-CN even after sputtering with 2 keV Ar^+ ions. The contribution of Zn-O states was found to be relatively small.

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