

Poster Presentations

[MS39-P04] **Synthesis and crystal structure of $\text{Fe}_6\text{Ca}_2(\text{SeO}_3)_9\text{Cl}_4$ - a porous oxohalide.**
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Transition metal oxohalide compounds containing p-block elements in low oxidation states carrying a stereochemically active lone-pair have proved to be a group rich in unusual crystal structures. Examples of lone-pair elements are Se^{4+} , Te^{4+} , Sb^{4+} , Bi^{4+} , etc., that adopt an asymmetric or one-sided coordination due to the presence of a stereochemically active electron lone-pair which do not participate in bonding but occupies a volume similar to that of an oxygen [1-2] that result in voids in the crystal structure. The lone pair cations are found to most often form bonds only to oxygen in oxohalide due to their high Lewis acid strength and small radius while the transition metal cations bond to both oxygen and halides. As a result, the combination of stereochemically active lone pair and the halide ions which often have low coordination number can act as “chemical scissors” to open up the structures and increase the possibilities for low-dimensional arrangements of transition metals. By utilizing this concept, a number compounds with unusual low-dimensional crystal structures have been synthesized, which may even show interesting physical properties such as magnetic frustration [3] or nonlinear optical second harmonic generation (SHG) [4]. There are mainly two types of structures among M-L-O-X compounds (M = transition metal cation, L = p-block lone pair element such as Se^{4+} , Te^{4+} , or Sb^{3+} , X = halide anion). One of them is often layered with only weak van der Waals interactions in between the layers. Another type exhibits 3D open framework having channels or voids where lone-pairs and halides are located and shows similar structural feature as the well-known porous materials such as zeolites. Therefore, it would

be very interesting from catalysis point of view if guest molecules could be introduced into the channel system that contains rich transition metals as active sites during catalysis reactions. Unfortunately, these channels are not accessible to guest species because most part of the non-bonding region is occupied by lone-pair electrons and halogen ions, the rest free space has only 3 ~ 4 Å left in diameter. The present study was carried out to utilize alkaline earth metal as extra building unit in structure construction. Herein, a porous oxohalide, $\text{Fe}_6\text{Ca}_2(\text{SeO}_3)_9\text{Cl}_4$, has been synthesized by chemical vapour transport reactions using conc. HCl as Cl-source and transporting agent. It crystallizes in the hexagonal space group $P6_3/m$ with unit cell parameters $a = 12.118(2)$ Å, $c = 12.703(4)$ Å, $Z = 2$. The Fe^{3+} ions have octahedral $[\text{FeO}_6]$ and more uncommon $[\text{FeO}_4\text{Cl}_2]$ coordination's, the Ca^{2+} ions coordinate an $[\text{CaO}_6]$ octahedron, the Se^{4+} ions show classic one-sided $[\text{SeO}_3]$ coordination. The crystal structure is an open framework having one dimensional channels extending along $[001]$ that the chlorine atoms and lone pairs on Se^{4+} are facing. The channels in this framework structure are unusually large compared to other oxohalide compounds and also accessible to guest molecules. Water vapor sorption measurements show an uptake of 9 wt% at 293 K.

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