Oral Contributions

[MS19 - 05] Structural variety of novel Pb and Bi selenites

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Selenium-containing lead and bismuth compounds are of special interest since of their geochemical and mineralogical abundance. During the last decade there has been a surge of research activity in the study of PbO/Bi_2O_3–MxO_y–SeO_2 (*M* = Cu^{2+}, Ni^{2+}, Fe^{3+}, V^{5+}; x=1,2; y=1,3,5) ternary system. The asymmetric $[SeO_3]^{2-}$ selenite groups with stereochemically active s^2 lone electron pair, and Pb^{2+}/Bi^{3+} cations with highly irregular coordination increase the chance to achieve non-centrosymmetric crystal structures. This may give rise to the discovery of novel polar materials with various applications. Here, we report on the synthesis, characterization, and structure of eight novel lead and bismuth selenites containing different transition metals.

The crystals of three novel lead selenites with nickel α–$PbNi(SeO_3)_2$ (**I**), *β*–$PbNi(SeO_3)_2$ (**II**), and $PbNi_2(SeO_3)_2(SeO_2OH)2$ (**III**), and two lead vanadate selenites $Pb4(V_3O_8)_2(SeO_3)_3$ (**IV**), and $Pb_2(VO_2)(SeO_3)_2Cl$ (**V**) were obtained by hydrothermal method from aqueous solutions of PbO, SeO_2, and NiO (for **I–III**) or V_2O_5 (**IV**, **V**). The compound $Mn_2(Bi_2O)(SeO_3)_4$ (**VI**) was prepared in a similar manner from aqueous solution of SeO_2, BiOCl, Mn_2O_3, and MnO_2. The reactions were performed in 23 mL Teflon-lined Parr reaction vessels heated in Thermo Scientific mechanical convection oven up to 200°C (**I**, **V**, **VI**), 220°C (**II**), 180°C (**III**), 210°C (**IV**). The products of novel selenites consisted of greenish-yellow platy crystals of **I–III** and reddish-brown prismatic crystals of **IV–VI** up to 300 μm in maximal dimension. The crystals of two novel bismuth selenites $Bi_6(SeO_3)4Cl_{10}$ (**VII**), and $MnBi(SeO_3)_2Cl$ (**VIII**) were prepared by the solid-state reaction method. The mixture of Bi_2O_3, $BiCl_3$, SeO_2, and Mn_2O_3 powders was pressed into a disk, which was subsequently sealed in an evacuated silica-glass tube and heated at 400°C. The products consisted of transparent (**VII**) and brown platy crystals (**VIII**) ranging in maximal dimension up to 400 μm.

Crystals selected for data collection were mounted on a Bruker DUO four-circle diffractometer equipped with an APEX II CCD detector and monochromated MoKα radiation. The structures were solved by direct methods.

Traditional inorganic crystal chemistry based upon the concept of cation-centered polyhedra is applied to the most of the selenites reported herein. However, the structure of **VI** is described as consisting of strongly bonded structural units formed by oxocentered coordination polyhedra. Structural investigations revealed that the structures under consideration are based upon structural units of various shape and dimensionality.

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