Morphotropism in anhydrous sulfate halides: the case of belousovite-related compounds

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Anhydrous sulfate halides of transition metals exhibit a broad range of compositions, structures and properties, and attract increasing interest due to their prominent contributions in mineralogy. In materials chemistry, most attention is paid to sulfate fluorides [1]. Synthetic derivatives of other halogens, namely Cl, Br and I, are rare and have been addressed mainly among compounds of copper due to their attractive magnetic properties [2]. At the same time, the past decade has witnessed a series of illustrative examples when minerals proved to be archetypic not only for synthetic materials [3] but also for numerous isostructural families [4]. Examples are also rapidly accumulating when synthetic extension of these families results in rich polymorphism and/or morphotropism; some of these are reviewed in [5].

In this work [6] we present an interesting example of morphotropic series which includes fourteen new inorganic compounds with general formula $A\text{Zn}(\text{TO}_4)X$ ($A = K, \text{Rb, Cs, Ti, NH}_4$; $T = S, \text{Se}; X = \text{Cl, Br, I}$), structurally related to belousovite $K\text{Zn}(\text{SO}_4)\text{Cl}$ – recently discovered sulfate mineral [7] from the fumaroles of the Tolbachik volcano (Kamchatka). All these compounds have been prepared via melt and evaporation techniques by reacting $AX$ and $\text{ZnTO}_4$ either at high temperatures or in hot aqueous solutions (Fig. 1). The apophyllite-type layers in these structures undergo different corrugations, most pronounced in the case of $\text{CsZn}(\text{SO}_4)\text{I}$. In addition, during the study two species unrelated to belousovite, namely $\text{Na}_4\text{Zn}(\text{SO}_4)_2\text{Cl}_2$ and $\text{Cs}_2\text{Cd}_3(\text{SO}_4)_4$, were found with framework crystal structures having different topology and belonging to new structure types.

Figure 1. General strategy for the synthesis of belousovite-type compounds.