

On the thermo-elastic behaviour and phase-stability of Cs-bearing open-framework aluminosilicates

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In the last decades, synthetic Cs-aluminosilicates have been prepared in search for suitable crystalline phases as potential solid hosts for ^{137}Cs γ -radiation sources to be used in sterilization applications, or for fixation and deposition of other radioactive isotopes of Cs. We have investigated the thermo-elastic behaviour, the phase-stability and the main P/T -induced deformation mechanisms of three Cs-bearing open-framework silicates: CsAlSiO_4 (ABW topology, $a \sim 9.446$, $b \sim 5.439$, and $c \sim 8.927$ Å, space group $Pc2_1n$), $\text{CsAlSi}_5\text{O}_{12}$ (CAS topology, $a \sim 16.753$, $b \sim 13.797$ and $c \sim 5.023$ Å, space group $Ama2$), and $(\text{Cs,Na})\text{AlSi}_2\text{O}_6 \times n\text{H}_2\text{O}$ (pollucite, ANA topology, $a \sim 13.68$ Å, space group $Ia-3d$).

The high-pressure experiments of the aforementioned materials were performed under hydrostatic conditions with a diamond anvil cell, by *in-situ* single-crystal or powder X-ray diffraction. The *in-situ* high-temperature experiments were performed by single-crystal and powder X-ray diffraction using heating stages. Axial and volumetric bulk moduli (along with their P -derivatives) and axial and volumetric thermal expansion coefficients were obtained.

The experiments show that these three compounds remain crystalline at least up to 8-9 GPa (at room- T) and up to 1000°C (at room- P). This result is surprising if we consider their microporous nature. Pollucite only shows a P -induced phase-transition at a modest pressure (~ 0.7 GPa). Its high-pressure polymorph shows an almost isotropic elastic behaviour (*i.e.* $K_{T0}(a):K_{T0}(b):K_{T0}(c) = 1.10 : 1 : 1.09$). The elastic response of Cs-CAS is more anisotropic (*i.e.* $K_{T0}(a):K_{T0}(b):K_{T0}(c) = 1 : 1.50 : 2.36$). In contrast, Cs-ABW appears to be one of the most anisotropic crystalline materials, with $K_{T0}(a) : K_{T0}(b) : K_{T0}(c) = 19 : 12 : 1$. The elastic anisotropy of these materials at high-pressure reflects the configuration of the channels, and follows a general principle concerning the HP-behavior of microporous materials: the open-framework structures tend to accommodate the effect of pressure, by cooperative rotation of the tetrahedra, usually increasing the ellipticity of the channel systems and maintaining the original elliptical configuration, without any “inversion” in ellipticity.

At high-temperature, only Cs-CAS undergoes a phase-transition: at 773 K, a displacive transition from the acentric low- T space group $Ama2$ to the high- T centrosymmetric $Amam$ occurs. The anisotropic P -behaviour of Cs-ABW is observed even at high- T , with a negative thermal expansion coefficient along [100] and almost no expansion along [010].

Moreover, the chemical stability of the three Cs-bearing compounds is surprising. Pollucite, for example, retains Cs better than several other Cs-bearing materials when immersed into a fluid phase, even under hydrothermal conditions. This behavior can be ascribed to the topological configuration of the Cs-polyhedron and its bonding environment, to the small dimension of the sub-nanopores, where the Cs-sites lie, and to the high flexibility of the ANA framework type.

On the basis of their high thermo-elastic and chemical stability, the three aforementioned Cs-bearing materials, especially Cs-ANA, may be considered as functional materials usable for fixation and deposition of radioactive isotopes of Cs, or as solid hosts for ^{137}Cs γ -radiation source to be used in sterilization applications.