

Halogenide-sodalites: Thermal expansion, decomposition and the Lindemann criterion

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Regarding their topological information content and complexity, sodalites are the simplest porous zeolitic framework materials. The framework consists of alternating, corner sharing T¹O₄- and T²O₄-tetrahedra forming the so-called β-cages which are containing alkali- or earth-alkali cations and anions as templates.

The structural parameters during the compound's thermal expansion are expected to show a link to the sodalites decomposition temperature via the Debye temperature [1]. To clarify the interactions in different sodalites, framework and template ions were systematically varied. Twelve sodalites of different chemical compositions |Na₈X₂|[T¹M²O₄]₆ (T¹ = Al, Ga; T² = Si, Ge; X = Cl, Br, I) were synthesized and temperature-dependent X-ray experiments, as well as TGA-DSC measurements, were carried out.

The decomposition temperatures were determined from the TGA-DSC measurements and the temperature-dependent volumes obtained in Rietveld refinements were fitted with a Debye-Einstein-Anharmonicity model, yielding Debye- and Einstein-temperatures for each compound. They were used in equation 1, modified from the one given by Shelimova and Plachkova [2]:

$$\theta_{average} = K_L \sqrt{\frac{T_D}{\bar{A} \cdot V^{2/3}}} = K_L Y \quad (\text{Eq. 1})$$

where $\theta_{average}$ is the geometrical average of the obtained Debye- and Einstein-temperatures, T_D is the decomposition temperature, K_L the Lindemann constant, \bar{A} the average atomic mass and $V^{2/3}$ the average atomic distance. Plotting Y vs $\theta_{average}$ (figure 1) groups the compounds on three different lines of similar Lindemann constants instead of the expected one for isostructural compounds. No correlations between selected bond-lengths, chemical composition or other parameters to the Lindemann constants could be found, meaning the underlying reason for this grouping of the compounds has to be searched beyond the average structure. Thus, further experiments (total scattering, low-temperature diffraction) and computational methods (DFT, MD) are currently carried out to elucidate this correlation.

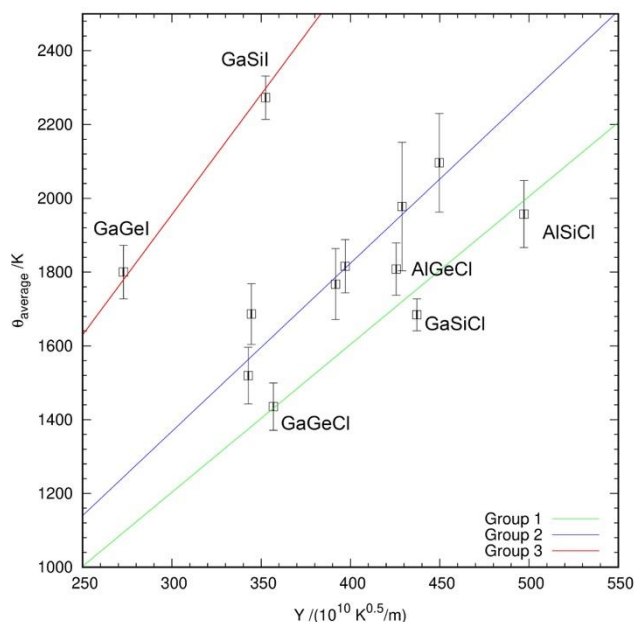


Figure 1: Plot of Y vs $\theta_{average}$. The linear equations for the three groups are given by the lines. $AlGeCl$ is included in group 1.

[1] K. Hoffmann, M.M. Murshed, R.X. Fischer, H. Schneider, T.M. Gesing, Synthesis and characterization of mullite-type $(Al_{1-x}Ga_x)_4B_2O_9$, Z. Kristallogr. Cryst. Mater. 229(10) (2014) 699-708. DOI:10.1515/zkri-2014-1785

[2] L.E. Shelimova, S.K. Plachkova, Estimation of the Debye Temperature of IV-VI Semiconductor Compounds and Rhombohedral $(GeTe)_{1-x}((Ag_2Te)_{1-y}(Sb_2Te_3)_y)_x$ Solid Solutions ($y = 0.6$), Physica Status Solidi (a) 104(2) (1987) 679-685. Doi:10.1002/pssa.2211040219