

## Elucidation of Fast Fluoride Ion Conduction in $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$

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$\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  shows a by several orders of magnitude increased ionic conductivity compared with the parent materials,  $\text{BaF}_2$  and  $\text{CaF}_2$  [1]. Using experimental techniques and molecular dynamics simulation we concluded that the origin of this conductivity increase is most likely an excess volume which reduces the activation energy for the fluoride ion migration. The excess volume is caused by geometric frustration, *i.e.*, the impossibility to build a perfect fluorite structure by distributing the differently sized  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  over the cation sites which reduces the packing density of the system [2]. As a consequence,  $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$  exhibits the properties of a superionic fluorite<sup>1</sup> already at low temperature, which comprise: a disordered anion sublattice, excess volume, high ionic conductivity, low activation energy and collective ion transport [3]. The emergence of collective (or cooperative) ion transport can be understood as the melting of the anion sublattice [4] due to a sufficiently low migration activation energy, causing the high ionic conductivity and non-linear volume increase in pure fluorites.

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- [2] Is Geometric Frustration-Induced Disorder a Recipe for High Ionic Conductivity?, A. Düvel, P. Heitjans, P. Fedorov, G. Scholz, G. Cibin, A. V. Chadwick, D. M. Pickup, S. Ramos, L. W. L. Sayle, E. K. Sayle, T. X. T. Sayle, D. C. Sayle, J. Am. Chem. Soc., accepted, 2017.
- [3] Superionics: Crystal Structures and Conduction Processes, S. Hull, Rep. Prog. Phys. 67 (2004) 1233.
- [4] String-like Cooperative Motion in Homogeneous Melting, H. Zhang, M. Khalkhali, Q. Liu, J. F. Douglas, J. Chem. Phys. 138 (2013) 12A538.

<sup>1</sup>Superionic conduction in a fluorite emerges when it is heated beyond circa  $0.8 \cdot T_{\text{melt}}$ .

