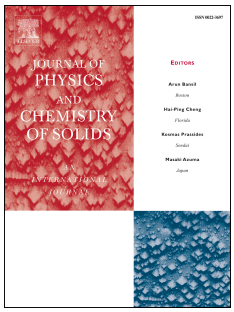
Accepted Manuscript



Effect of bromine deficiency on the lattice dynamics and dielectric properties of alpha-phase diisopropylammonium bromide molecular crystals

Ahmad Alsaad, Chris M. Marin, Nabil Alaqtash, Hsien-Wen Chao, Tsun-Hsu Chang, Chin Li Cheung, A. Ahmad, I.A. Qattan, Renat F. Sabirianov

PII: S0022-3697(17)31141-1

DOI: 10.1016/j.jpcs.2017.10.004

Reference: PCS 8234

To appear in: *Journal of Physics and Chemistry of Solids*

Received Date: 22 June 2017

Revised Date: 29 September 2017

Accepted Date: 2 October 2017

Please cite this article as: A. Alsaad, C.M. Marin, N. Alaqtash, H.-W. Chao, T.-H. Chang, C.L. Cheung, A. Ahmad, I.A. Qattan, R.F. Sabirianov, Effect of bromine deficiency on the lattice dynamics and dielectric properties of alpha-phase diisopropylammonium bromide molecular crystals, *Journal of Physics and Chemistry of Solids* (2017), doi: 10.1016/j.jpcs.2017.10.004.

Effect of Bromine Deficiency on the Lattice Dynamics and Dielectric Properties of Alpha-Phase Diisopropylammonium Bromide Molecular Crystals

Ahmad Alsaad,[1] Chris M. Marin,[2] NabilAlaqtash,[3] Hsien-Wen Chao,[4] Tsun-Hsu Chang,[4] Chin Li Cheung,[2] A. Ahmad,[1] I.A. Qattan,[6] and Renat F. Sabirianov[5]

[1]*Department of Physical Sciences, Jordan University of Science and Technology, P.O. Box 3030, Irbid 22110, Jordan*

[2]*Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588, United States*

[3]*Department of Physics, The Hashemite University, P.O. Box 330127, Zarqa 13133, Jordan*

[4]*Department of Physics, National Tsing Hua University, Hsinchu 300, Taiwan*

[5]*Department of Physics, University of Nebraska at Omaha, Omaha, NE 68182, United States*

[6]*Department of Applied Mathematics and Sciences, Khalifa University of Science, Technology and Research, P.O. Box 127788, Abu Dhabi, UAE.*

Keywords: Bromine Deficiency; Lattice Dynamics; Dielectric Properties; Alpha-Phase Diisopropylammonium Bromide; FT-IR and Raman vibrational spectra

Diisopropylammonium bromide (DIPAB) molecular ferroelectric crystals were synthesized and examined to exhibit a large electric polarization (~23μC/cm^2), a large dielectric constant in the α-phase. Although the PXRD pattern indicates that the α-DIPAB sample has an overall excellent crystallinity, our analysis of its FT-IR and Raman vibrational spectra suggests the presence of disorder in the synthesized crystals as indicated by the presence of broad features in the Raman spectrum. Using vdW+DF2 calculations, we identified the majority of vibrational modes in the experimental spectra and analyzed the ones due to Br-disorder. We found that the bromine (Br) deficiency strongly affects the electric properties of α-DIPAB. Particularly, the experimentally measured dielectric constant of α-DIPAB is large (~20), whereas the DFT-based calculations of the ideal DIPAB give much smaller values (~2-3). We find that Br-deficiency is responsible for large dielectric constant of the DIPAB crystal with calculated value of~15-20. Furthermore, we showed that the van der Waals forces have a slight effect on the structural parameters, only causing a small shift in the vibrational frequencies. The main vibrational features of the DIPAB crystal in the Raman spectrum were shown to be driven by covalent bonding in the DIPA molecules and hydrogen bonds between the molecules with Br.

1. Introduction

Ferroelectric materials are promising candidates for applications in piezoelectric, pyroelectric, optoelectronic and nonlinear devices. Particularly, organic ferroelectric materials are highly desirable due to their environmentally friendly (lead-free) compositions, light weight, and mechanical flexibility.[1,2] They have shown promises for a wide range of applications including memory chip, sensing,[3] actuation,[4] energy harvesting,[5] and fast switchable data