Structural, Electric and Dynamic Properties of $(\text{Pyrrolidinium})_3[\text{Bi}_2\text{I}_9]$ and $(\text{Pyrrolidinium})_3[\text{Sb}_2\text{I}_9]$: New Lead-Free, Organic–Inorganic Hybrids with Narrow Band Gaps

Autorzy

Magdalena Rowińska

Anna Piecha-Bisiorek

Wojciech Medycki

Piotr Durlak

Ryszard Jakubas

Anna Gągor

Rok wydania

2023

Czasopismo

Molecules

Numer woluminu

28

Strony

3894/1-3894/15

DOI

10.3390/molecules28093894

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Hybrid organic–inorganic iodides based on Bi(III) and Sb(III) provide integrated functionalities through the combination of high dielectric constants, semiconducting properties and ferroic phases. Here, we report a pyrrolidinium-based bismuth (1) and antimony (2) iodides of (NC4H10)3 [M2 I9] (M: Bi(III), Sb(III)) formula which are ferroelastic at room temperature. The narrow band gaps (~2.12 eV for 1 and 2.19 eV for 2) and DOS calculations indicate the semiconducting characteristics of both materials. The crystal structure consists of discrete, face-sharing bioctahedra [M2 I9] 3− and disordered pyrrolidinium amines providing charge balance and acting as spacers between inorganic moieties. At room temperature, 1 and 2 accommodate orthorhombic Cmcm symmetry. 1 displays a complex temperature-induced polymorphism. It is stable up to 525 K and undergoes a sequence of low-temperature phase transitions (PTs) at 221/222 K (I ↔ II) and 189/190 K (II ↔ III) and at 131 K (IV→III), associated with the ordering of pyrrolidinium cations and resulting in Cmcm symmetry breaking. 2 undergoes only one PT at T = 215 K. The dielectric studies disclose a relaxation process in the kilohertz frequency region, assigned to the dynamics of organic cations, described well by the Cole–Cole relation. A combination of single-crystal X-ray diffraction, synchrotron powder diffraction, spin–lattice relaxation time of 1H NMR, dielectric and calorimetric studies is used to determine the structural phase diagram, cation dynamics and electric properties of (NC4H10)3 [M2 I9].

Słowa kluczowe

organic–inorganic metal halides, pyrrolidine, bismuth(III) iodides, band structure, phase transitions

Licencja otwartego dostępu

Adres publiczny

http://dx.doi.org/10.3390/molecules28093894

Strona internetowa wydawcy

http://www.mdpi.com/journal/metals