Synthesis and Characterization of $K_2RE_2Bi_2Se_9$ (RE=La, Ce, Nd, Yb) as Potential Thermoelectric Materials

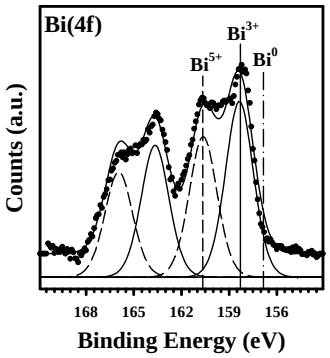
The College of New Jersey

Benny C Chan, Chemistry Department, The College of New Jersey, Ewing, NJ 08628

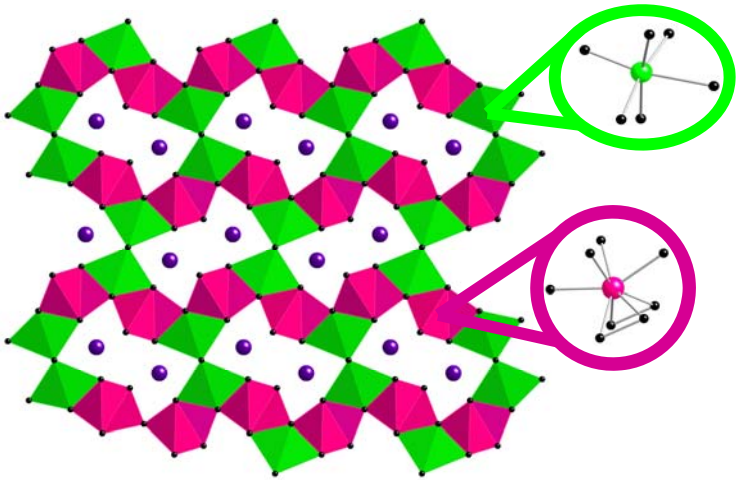
Chalcogenides have numerous applications including optoelectronics, catalysis, magnetism, and thermoelectrics. Our research studies synthetic strategies to prepare novel chalcogenides. We have based our compounds on the well known bismuth tellurides and selenide compounds. Our general hypothesis is that the disruption of the rock salt-like structures of bismuth chalcogenides will improve the thermoelectric properties. The hypothesis was demonstrated in the literature through Kantazidis' compounds in the Cs-Bi-Te composition space. We have furthered the disruption of the structure by adding a rare earth element that has a higher coordination environment than Bi but lower than Cs or K. The reaction was accomplished by reacting K_2Se_2 with RE, Bi, and additional Se at 750 C. The structures change slightly between La and the rest of the REs. We believe the size difference between the REs result in a slight contraction of the RE-Se bond lengths and distorts the Bi sites to remove the glide planes from the Pbam space group to form the $P2_12_12$ space group.

Comparison of Unit Cells

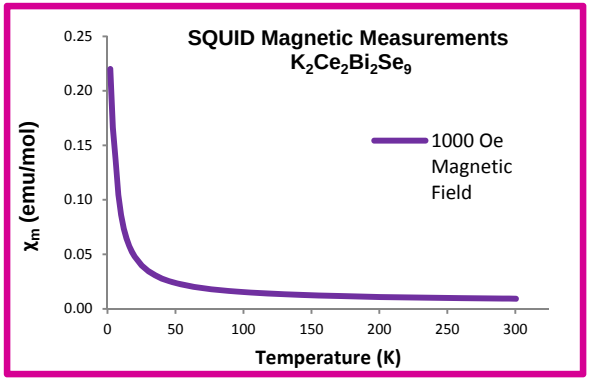
Compound	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Vol. (Å^3)	Space Group	R Value
$K_2La_2Bi_2Se_9$	11.546	17.776	4.302	90	90	90	883	Pbam	0.0285
$K_2Ce_2Bi_2Se_9$	11.486	17.788	4.269	90	90	90	872.1	$P2_12_12$	0.0316
$K_2Nd_2Bi_2Se_9$	11.437	17.78	4.232	90	90	90	860.6	$P2_12_12$	0.033
$K_2Yb_2Bi_2Se_9$	11.453	17.814	4.228	90	90	90	862.6	$P2_12_12$	0.0473



We performed XPS to study the oxidation states, curiously, we have discovered the Bi is in multiple oxidation states, +3 (55.6%) and +5 (44.4%). The crystallography is modeled as a +3 oxidation state. We are continuing our study of the structure by doing bond valence calculations and additional magnetic studies to confirm the mixed oxidation states.



The structure consists of wave-like slabs of octahedral Bi (green) and bicapped trigonal prisms of La (pink) polyhedra. The potassium ions (purple spheres) sit inside of the channels made by the slabs.



Magnetic susceptibility demonstrates the compound exhibits temperature independent paramagnetism where electrons have moved into the conduction band. The magnetic moment was determined to be 2.66 which is consistent with Ce^{3+}. The XPS results suggest that the Bi is responsible for the delocalized electrons. These materials should be studied further for thermoelectric properties.