RAMAN AND INFRARED INVESTIGATIONS OF COMPLEXES IN AURIVILLIUS PHASE

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by

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Certificate

This is to certify that the thesis entitled *Raman and infrared investigations of complexes in Aurivillius phase* submitted by Archana to the Indian Institute of Technology Delhi, for the award of the Degree of Doctor of Philosphy, is a record of the original bonafide research work carried out by her under my supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted in part or full to any other university or institute for the award of any degree or diploma.

New Delhi Prof. H.C. Gupta

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New Delhi Archana

Abstract

Aurivillius oxides are the materials with general formula $(Bi_2O_2)[A_{m-1}B_mO_{3m+1}]$. They consist of a regular intergrowth between $(Bi_2O_2)^{2+}$ sheets and $[A_{m-1}B_mO_{3m+1}]^{2-}$ perovskite-like layers, with *m* being the number of octahedra stacked along the direction perpendicular to the sheets, and A (Ca, Sr, Ba, Pb, Bi, Na, rare-earth ions, or mixtures of these) and B (Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} or Mo^{6+}) are the 12-fold and 6-fold coordination sites of the perovskite slab, respectively. This thesis mainly focuses on the lattice dynamical study of Raman and infrared wavenumbers of Aurivillius oxides using normal coordinate analysis based on the Wilson's GF matrix method. A short-range-force-constant-model (SRFCM) has been applied to study the vibrational properties of tantalates-based Aurivillius oxides $ABi_2Ta_2O_9$ (A=Ca, Sr, Ba), niobates-based Aurivillius oxides $ABi_2Nb_2O_9$ (A=Ca, Sr, Ba, Pb), tungstates-based Aurivillius oxides (Bi_2WO_6 & $Bi_2W_2O_9$) and molybdate-based Aurivillius oxide Bi_2MoO_6. Out of these oxides $BaBi_2Ta_2O_9$ crystallizes in tetragonal space group while all other present themselves in orthorhombic space group. Calculations of zone center phonons are made with stretching and bending force constants. The force constants are evaluated by fitting the calculated values of optical phonons at zone center to the available experimental results. By comparing the force constants in all these materials, we can conclude that Bi layer is rigid in Aurivillius oxides. All the Raman and infrared values are then assigned to their corresponding modes on the basis of group theoretical analysis. In tantalates- and niobates-based Aurivillius oxides, this assignment was done for the first time.

Calculated vibrational frequencies are found in good agreement with experimental results. The potential energy distribution (PED) has also been investigated for each normal mode and the contributions of different force constants to various frequencies are determined. The calculated interatomic interactions are then compared for the different structures in the same family in order to understand the physicochemical properties of these oxides.

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