Metallization and Superconductivity In Alkali Bromides and Iodides

[1] C. Nirmala Louis*, [2] A. Amalraj and [1] Y. Ramola

[1] Research Department of Physics, Holy Cross College, (Autonomous), Nagercoil, Tamil Nadu, India. *

[2] Department of Chemistry, St. Jerome's College, Anandhanadarkudy, Nagercoil, Tamil Nadu, India.

[1,2]Affiliated to Manonmaniam Sundaranar University, Tirunelveli, Tamil Nadu, India.

[1] nirmalalouis@holycrossngl.edu.in*

* Corresponding author

Abstract-We have analyzed the variation of structural changes, phase stability, metallization and superconductivity of some of the alkali bromides and alkali iodides compounds under pressure with reference to: structure - normal or high pressure, number of valence electrons, growth of delocalized anion d-electron number, using the band structure, density of states and superconductivity results obtained by FP-LMTO method. Also, we conclude that, since the dependence of Tc on electron-phonon enhancement factor □ is more, these materials come under the class of electron-phonon-mediated superconductors. The above observations lead us to confirm that the highest Tc value depends more on the ground state structure rather than the high-pressure structure. So, if we retain the ground state structure under high pressure or create conditions equal to this, then one may achieve high Tc in these materials.

I. INTRODUCTION

When materials are exposed to high pressure, their physical characteristics alter in a number of ways. Increased pressure causes a substantial reduction in volume, which leads to changes in electrical states and crystal structure. The recent development in diamond anvil cell enables the experimentalist to perform the investigation at very high value of pressure (5 Mbar) [1]. About twenty-three new elemental superconductors have already been found at high pressure and this number is increasing. New compounds are now added in this list. With the development of high-pressure experimental techniques, investigations on pressure-induced structural phase transition, insulator-metal transition and superconducting transition are getting the attention of all [2]. In particular, there is a great interest in the pressure induced metallization and superconductivity of simple alkali halides [3]. These results lead us to expect superconductivity in other alkali bromides and iodides under high pressure, especially those alkali bromides and iodides which have already become metals [4,5].

II. DETAILS OF THE CALCULATION

The physical properties of a material are expressed via the interrelation of the equation of state (EOS) between the thermo dynamical variables FP-LMTO computations are used to investigate the cohesive, structural, and vibrational characteristics of solids under pressure. The full potential linear muffin-tin orbital (FP-LMTO) technique [6] was used to produce band configurations corresponding to different pressures. The calculated total energies were fitted to the Murnaghan's equation of state (EOS), to determine the phase transition pressure and other ground state properties. The final energy

Corresponding Author: C. Nirmala Louis, Holy Cross College, (Autonomous), Nagercoil, Tamil Nadu, India. *

convergence is within 10^{-5} Ry. Also, we have analyzed the structural phase transition from NaCl □ CsCl structure, metallization and superconducting transition (with normal and high-pressure structures).

III. RESULTS AND DISCUSSION

3.1 Metalliztion Under Pressure

At normal pressure, alkali bromides and alkali iodides are wide gap insulators. As pressure rises, charge transfers from the s, p, and d states, widening the valence band and increasing the width of the empty conduction bands. These changes lead to the narrowing of the band gap and at particular pressure, there is a closing of band gap called metallization. In some materials, metallization takes place by the indirect closure of band gap between valence band maximum and conduction band minimum at different symmetry points. Materials become metals under pressure but before that they undergo structural phase transition from one phase to another phase. In some materials, metallization takes place by the direct closure of band gap between valence band maximum and conduction band minimum at the same symmetry point.

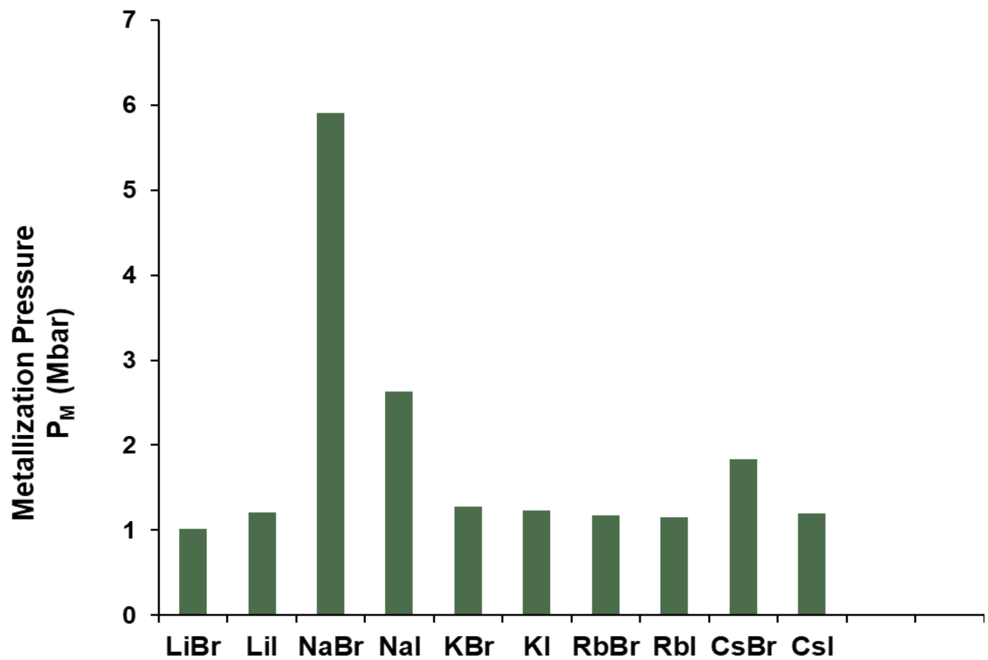


Figure.1. Metallization pressure in alkali bromide and alkali iodide compounds

Metallization pressure in alkali bromide and alkali iodide compounds are given in Figure.1. In this figure, NaBr shows highest metallization pressure when compared to other alkali bromides and alkali iodides (LiBr, LiI, NaI, KBr, KI, RbBr, RbI, CsBr and CsI). Another remark is sodium halides (NaBr and NaI) and CsBr show higher metallization pressure when compared to other alkali halides (LiBr, LiI, KBr, KI, RbBr, RbI and CsI).

Corresponding Author: C. Nirmala Louis, Holy Cross College, (Autonomous), Nagercoil, Tamil Nadu, India. *

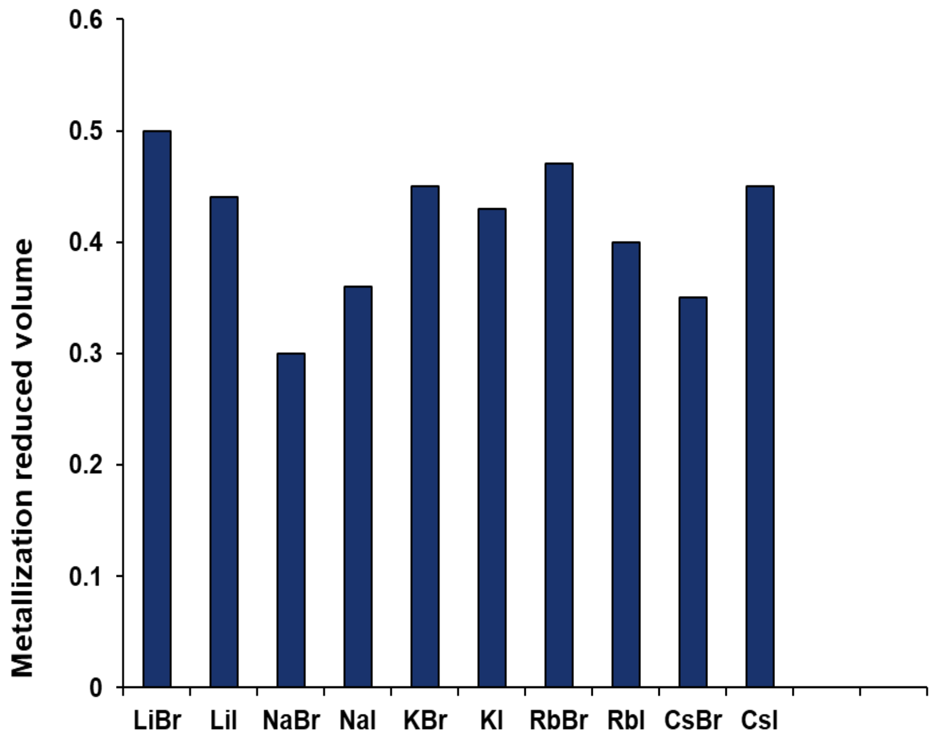


Figure.2. Metallization reduced volume in alkali bromide and alkali iodide compounds

Metallization reduced volume in alkali bromide and alkali iodide compounds are given in Figure.2. In this figure, NaBr shows lowest metallization reduced volume when compared to other alkali bromides and alkali iodides (LiBr, LiI, NaI, KBr, KI, RbBr, RbI, CsBr and CsI). Another remark is sodium halides (NaBr and NaI) and CsBr show lower metallization reduced voulme when compared to other alkali halides (LiBr, LiI, KBr, KI, RbBr, RbI and CsI).

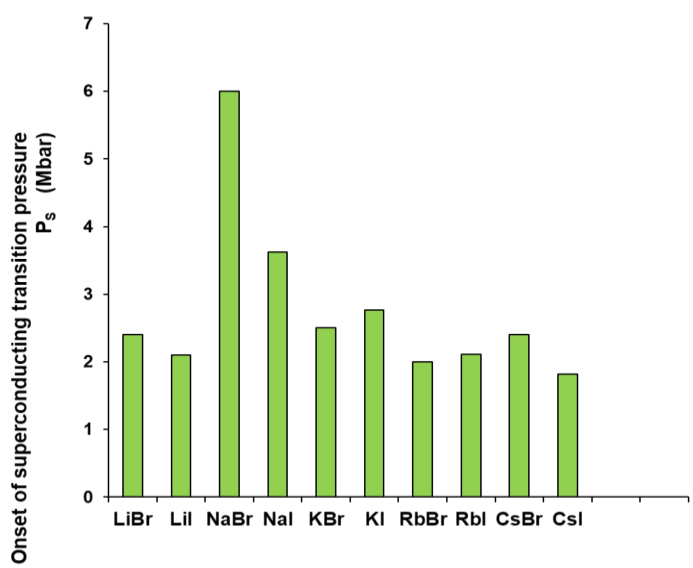
3.2 Superconducting Transition Under Pressure

The results of superconducting transition temperature (Tc) calculations performed for various materials under high pressure are used to critically analyze the route to high Tc. We have analyzed the phenomena of superconductivity for both normal and high-pressure phases of alkali bromide and alkali iodide materials. It is hoped that this analysis will enable us to make some generalization with respect to the path to high Tc superconductivity in ionic compounds. The Tc calculations are performed for different reduced volumes corresponding to NaCl, CsCl and hcp structures of alkali bromides and alkali iodides materials. The factors which determine superconducting behavior in materials are electron - phonon mass enhancement factor λ, electron-electron interaction parameter μ^*, Debye temperature θ_D, s, p$\rightarrow$ d electron transfer and the delocalized d electron. The value of highest Tc (Tc-max) is considered for analyzing path to high Tc in these compounds. The onset of superconducting transition pressure and maximum value of superconducting transition temperature in alkali bromides and alkali iodides compounds are studied.

Corresponding Author: C. Nirmala Louis, Holy Cross College, (Autonomous), Nagercoil, Tamil Nadu, India. *

Table.1. Onset of superconducting transition pressure and reduced volume and Maximum value of superconducting transition temperature in alkali bromide and alkali iodide compounds

Alkali bromide and alkali iodide compounds	Onset of superconducting transition pressure P_S (Mbar)	Onset of superconducting transition reduced volume VS	Maximum value of superconducting transition temperature Tc-max K	
			Normal pressure structure Tc-max K	High pressure structure Tc-max K
LiBr	2.4	0.4	3.179	0.653
LiI	2.1	0.39	8.864	0.8
NaBr	6	0.3	2.079	0.664
NaI	3.624	0.31	5.790	1.187
KBr	2.5	0.35	5.911	0.897
KI	2.77	0.37	2.151	0.107
RbBr	2.00	0.39	2.153	0.819
RbI	2.115	0.35	0.874	0.019
CsBr	2.4	0.32	4.602	2.467
CsI	1.82	0.4	2.110	2.150



Corresponding Author: C. Nirmala Louis, Holy Cross College, (Autonomous), Nagercoil, Tamil Nadu, India. *

Figure.3. Onset of superconducting transition pressure in alkali bromide and alkali iodide compounds

The onset of superconducting transition pressure, reduced volume and maximum value of superconducting transition temperature in alkali bromide and alkali iodide compounds are given in Table.1. The onset of superconducting transition pressure in alkali bromide and alkali iodide compounds are given in Figure.3. In this figure, NaBr shows highest onset of superconducting transition pressure when compared to other alkali bromides and alkali iodides (LiBr, LiI, NaI, KBr, KI, RbBr, RbI, CsBr and CsI). Another observation is sodium halides (NaBr and NaI) show higher onset of superconducting transition pressure when compared to other alkali halides (LiBr, LiI, KBr, KI, RbBr, RbI, CsBr and CsI).

The onset of superconducting transition reduced volume in alkali bromide and alkali iodide compounds are given. LiBr, LiI and CsI shows highest onset of superconducting transition reduced volume when compared to other alkali bromides and alkali iodides (NaBr, NaI, KBr, KI, RbBr, RbI and CsBr). Another observation is sodium halides (NaBr and NaI) show lower onset of superconducting transition reduced volume when compared to other alkali halides (LiBr, LiI, KBr, KI, RbBr, RbI, CsBr and CsI).

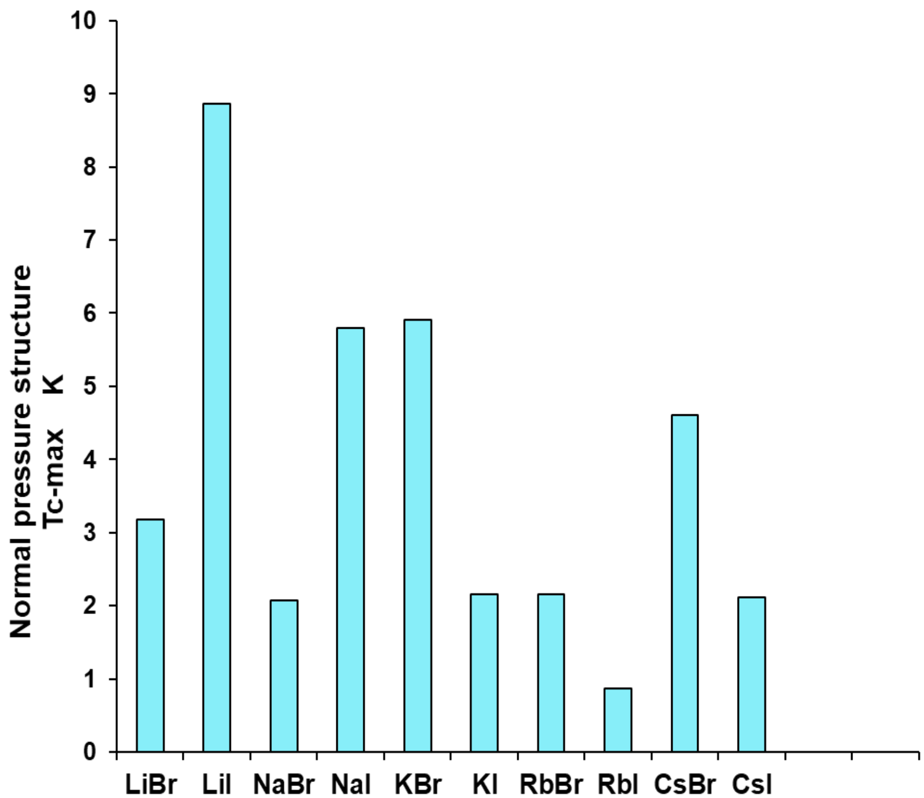


Figure.4. Maximum value of superconducting transition temperature in normal pressure structure of alkali bromide and alkali iodide compounds

The maximum value of superconducting transition temperature in normal pressure structure of alkali bromide and alkali iodide compounds are given in Figure.4. In this figure, LiI shows maximum Tc value of 8.864K. NaI and KBr shows maximum Tc value of 5.790 K and 5.911K respectively. CsBr shows maximum Tc value of 4.602K and LiBr shows 3.179K. Other alkali bromide and alkali iodide compounds (NaBr, KI, RbBr, RbI and CsI) show Tc value of less than 2K.

Corresponding Author: C. Nirmala Louis, Holy Cross College, (Autonomous), Nagercoil, Tamil Nadu, India. *

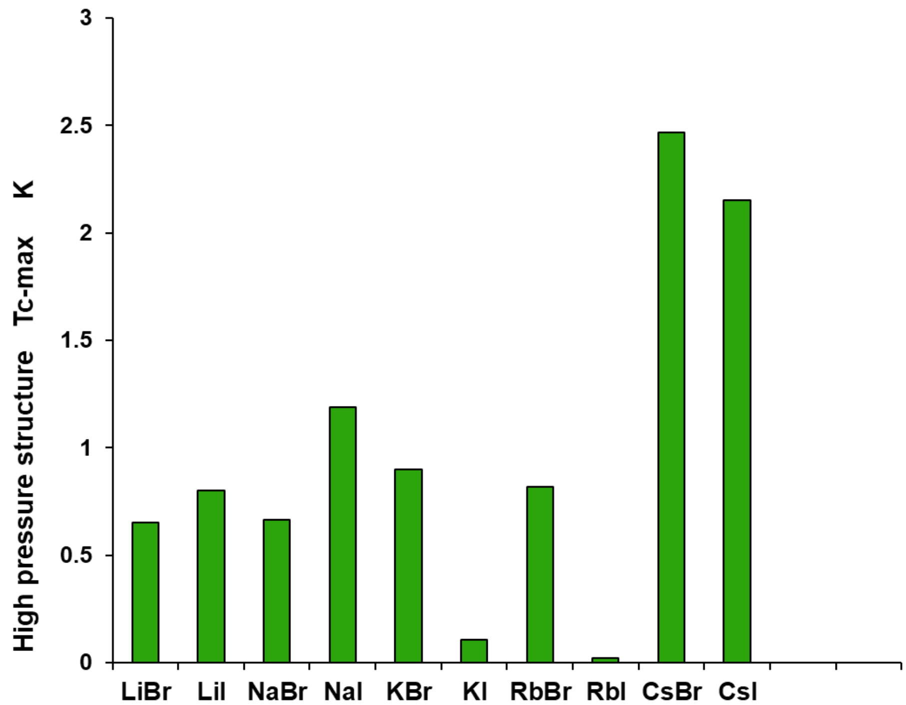


Figure.5. Maximum value of superconducting transition temperature in high pressure structure of alkali bromide and alkali iodide compounds

The maximum value of superconducting transition temperature in high pressure structure of alkali bromide and alkali iodide compounds are given in Figure.5. In this figure, CsBr shows maximum Tc value of 2.467K and CsI shows 2.15K. NaI and RbBr shows maximum Tc value of 1.187K and 0.819K respectively. KI and RbI shows very low Tc value of 0.107K and 0.019K respectively. Other alkali bromide and alkali iodide compounds (LiBr, LiI, NaBr, and KBr) show Tc value of less than 1K.

If alkali bromides and alkali iodides compounds are retained in the normal state structure under high pressure then the superconducting transition temperature Tc value is comparatively high. A careful observation shows that, increase of □ value and growth of delocalized anion d-electron number (more itinerant than its previous status) enhances Tc. Also, phonon frequency softening (decreasing of $□_{D)}$ is considered to contribute to the decrease of □ and hence Tc. The calculated Tc values depend more sensitively on the changes in □ rather than on $□_D$ and $□^{*.}$ So, we conclude that, alkali bromides and alkali iodides compounds are electron-phonon-mediated superconductors under high pressure. Those alkali halides with NaCl structure at normal pressure (LiBr, LiI, NaBr, NaI, KBr, KI, RbBr and RbI) have larger Tc value and those alkali halides with CsCl structure at normal pressure (CsBr and CsI) have smaller Tc value. But when the size of the alkali metal increases Tc decreases in normal pressure structure. It is noted that those alkali halides with NaCl structure at normal pressure (LiBr, LiI, NaBr, NaI, KBr, KI, RbBr and RbI) have smaller Tc value and those alkali halides with CsCl structure at normal pressure (CsBr and CsI) have higher Tc value. Similar to normal pressure structure Tc value, high pressure structure Tc decreases, when the size of the alkali metal increases. This reflects the fact that the structural and band gap arrangements of these compounds at high pressure have a significant influence in their superconducting (high Tc-max) behavior.

Corresponding Author: C. Nirmala Louis, Holy Cross College, (Autonomous), Nagercoil, Tamil Nadu, India. *

IV. CONCLUSION

In summary, we have investigated the pressure dependent band structure, density of states, metallization, structural phase transition and superconductivity of cubic rocksalt (NaCl structure) type alkali bomides and iodides using FP-LMTO method. These materials become metal and then superconductor under high pressure, but before that it undergoes structural phase transition from NaCl to CsCl structure. It is also confirmed that structural phase transition, metallization and superconductivity do not occur simultaneously in alkali bomides and iodides.

V. ACKNOWLEDGEMENT

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