Coherence: A Scientific Journal
A Peer- Reviewed Journal of the Science Section
The Bhawanipur Education Society College
Vol.2, Issue 1 (2024) 24-31

Design and Applications of Superalkali Materials in Advanced Technology

Manisha Dey*
Indian Institute of Engineering Science and Technology, Botanical Garden Area, Howrah, West Bengal

Abstract

In the principality of materials science, the search for novel compounds with exceptional properties has been a driving force behind technological advancements. Among these intriguing materials, super-alkalis have come out to be a fascinating class, not following conventional chemical expectations and entrancing researchers with their extraordinary characteristics. Unlike their traditional alkali metal counterparts, super-alkali materials exhibit exceptional levels of alkalinity, increasing electron affinities and ionization energies that surpass those of lithium, sodium, and potassium. This unique trait stems from their complex atomic structures, which are often comprised of clusters that grant upon them their exceptional reactivity and stability. The term "super-alkali" confines not only their intensified chemical properties but also indicates their capability for revolutionizing various fields, from catalysis to energy storage and beyond, they have got numerous potentials. In this research, we dig into the principality of super-alkali materials, unwinding their perplexing nature and discovering the promise they hold for shaping the landscape of materials science and technology.

Keywords: Super-alkali, Non-linear optics, Hyperpolarizability, Ionization potential, alkalinity, electride characteristics.

1. Introduction

What are superalkali metarials?

In the advancement of novel materials, super-alkali materials are a class of compounds that has remarkable alkalinity, which signifies they have a higher electron affinity or a lower ionization energy than traditional alkali metals like lithium, sodium, and potassium. These materials typically consist of clusters of atoms that exhibit unique electronic structures that leads to their superalkalinity. The term "super-alkali" was formulated to describe the increased and remarkable chemical reactivity, and stability of these compounds when compared to conventional alkali metals.

* Correspondent Author: email: manishadey9088@gmail.com (M. Dey)

What are Nonlinear optical (NLO) metarials?

In the modern optical communication system, nonlinear optical (NLO) materials have become a revolutionary subfield via rapid replacement of electrons by photons (as an information carrier). These materials exhibit wide range of applications in optical science including optoelectronics, photonic, frequency doubler, laser-based technologies, etc.

A molecular formula $A_{k+1}C$ where A is an alkali metal atom and C is an electronegative atom with formal valence k has been found by Gutsev and Boldyrev [1] for obtaining even smaller Ionization potentials. Some examples of investigated super-alkalis are Li_2F, Li_3O, Na_3O, Li_3S, and Li_4N [2-4]. Some experimentally synthesized super-alkali species are Li_2F, Li_3O, Na_3O, and Li_3S [5,6]. Highest occupied molecular orbitals (HOMO) of these species have non-bonding or antibonding character. Superalkalis have interesting properties which can be used to form different novel compounds to enhance electro-optical properties [7,8]. Super-alkali compounds having extraordinarily smaller values of IE than alkali metal atoms [9-13] may be used as a source of excess electrons. The superalkali clusters exhibit potential reducing capability that can be adopted for synthesis of numerous charge transfer compounds. For example, via interaction of superalkali clusters with counter superhalogens, novel supersalts can be formed [14,15].

The NLO materials with large first or second hyperpolarizabilities have recently attracted massive attention as they exhibit attractive features like increased thermal stability, and improved transparency, etc [16]. Due to small ionization potential and good reducing ability, the superalkali clusters can be used as NLO materials [17]. Among all the important applications of superalkali clusters which are being excess electron compounds, the most fascinating is their nonlinear optical behavior when bound to various inorganic as well as organic fullerene system [18,19]. The loosely bound excess electrons of superalkalis can exhibit dramatic effect on generating very high NLO properties. Super-alkali based electride molecules $(Na_3O)^+(e@C_{20}F_{20})^-$ and $(K_3O)^+(e@C_{20}F_{20})^-$ possess much larger β_0 than those obtained for $Na^+(e@C_{20}F_{20})^-$ and $K^+(e@C_{20}F_{20})^-$ [20], respectively. These molecules also have high stabilities arising from their high vertical detachment energies (VDE) and transition energies (ΔE). A novel class of inorganic salt alkalides $M^+(en)_3M'_3O^-$ (M, M' = Li, Na, K) designed by incorporating $M_3'O$ (M' = Li, Na, and K) superalkalis [21] shows that both superalkalides $M^+(en)_3M_3'O^-$ and alkalides $M^+(en)_3M_3'^-$ possess significantly large β_0 values although $M^+(en)_3M_3O^-$ complexes have higher stabilities. It has been shown that NLO property of $Li_3(NH_3)n$ (n = 1 – 4) complexes increases with increasing coordination number. Several possible isomers of alkalides $Li(NH_3)_nNa$ obtained by introducing Na atom into $Li_3(NH_3)_n$ complexes has also been considered to study NLO responses [22]. A series of inorganic electrides $Li_3O@Al_{12}N_{12}$ obtained by doping superalkali (Li_3O) on nanocages ($Al_{12}N_{12}$) show an interesting diffuse electron system. These electrides are energetically and electronically very stable and show excellent deep-ultraviolet transparency due to their large binding energies, HOMO–LUMO gaps and IE values [23].

2. Examples of Superalkali Materials:

Superalkali materials encompass a diverse range of compounds that exhibit extraordinary alkalinity and unique properties. Here are several examples of superalkali materials as follows:

- **Noble Gas Clusters:** Clusters formed by combining alkali metals with noble gases, such as LiHe, NaHe, or KHe, have been identified as superalkali materials. These clusters show remarkable electron affinity and can be used in various applications like gas-phase chemistry and quantum computing, etc.
- **Alkali Metal Oxides:** Compounds like Li_2O, Na_2O, and KO_2 are some examples of superalkali materials because of their high electron affinity and show unnatural stability. These materials have used to study their applications in energy storage systems and catalysis.
- **Lithium Fluoride Clusters:** Clusters that are composed of lithium and fluorine atoms, for example LiF3 or Li2F, are considered superalkali materials. These clusters exhibit remarkable alkalinity and have been examined for their capability as nonlinear optical materials and in electronic devices.
- **Sodium Hexafluoroantimonate ($NaSbF_6$):** This compound contains sodium and the hexafluoroantimonate anion, exhobit superalkali properties because of its remarkable electron affinity and unnatural stability. $NaSbF_6$ has been examined for its role in superacid chemistry and as a potential electrolyte in batteries.
- **Potassium Carbide (KC_2):** Another example of Superalkali is Potassium Carbide, which is marked by its by its remarkable alkalinity and electron affinity. KC_2 has been examined for their applications in solid-state chemistry and as a pioneer for carbon-based materials.
- **Sodium Hydride (NaH):** Sodium hydride is another example of superalkali material because of its remarkable alkalinity and reactivity. NaH has been examined for its potential use as a hydrogen storage material and as a strong reducing agent in organic synthesis.

Structures

Super-alkali materials generally show unique atomic structures that contribute to their remarkable properties. The accurate structure can vary depending on the specific composition of the material. However, there are some general trends:

- **Clustered Arrangement:** Rather than individual atoms, Super-alkali materials often consist of clusters of atoms. These clusters can contain a combination of alkali metals and other elements, such as oxygen or fluorine.

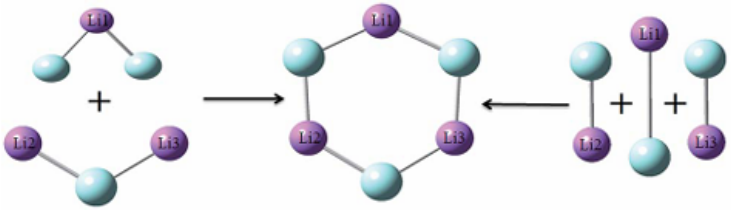

Figure 1: Equilibrium geometry of Li3F3 ring which can be formed by interaction of LiF2 and Li2F as well as trimerization of LiF

- **Cage-like Structures:** In some cases, super-alkali materials have the tendency to form cage-like structures in which the alkali metal atoms are confined within a framework of other atoms. These structures can provide stability to the material and allow for the blend of additional atoms or molecules.

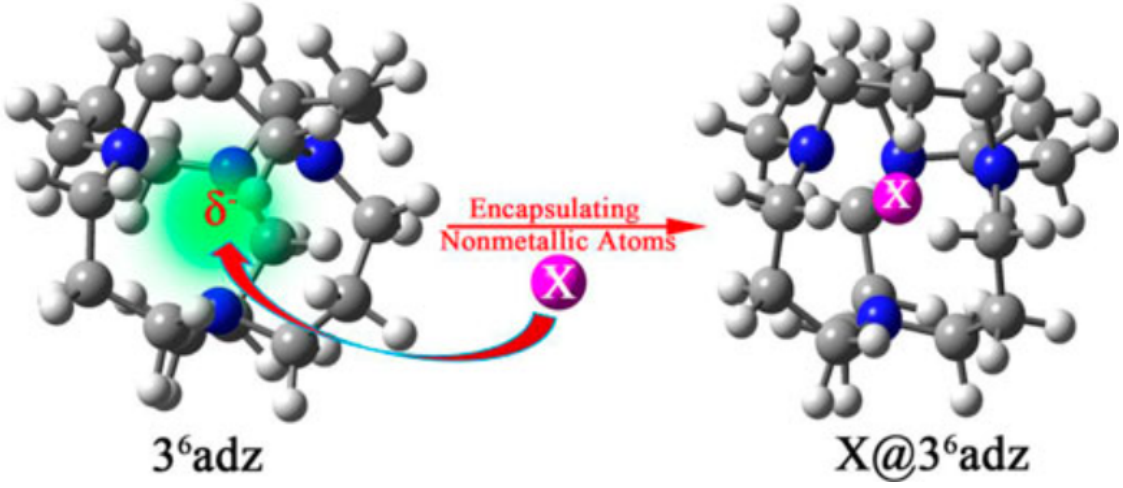

Figure 2: The schematic design strategy of X@36adz (X = H, B, C, N, O, F, and Si) based on the cage-like 36adz complexant. 36adamanzane (36adz)

Overall, the structure of super-alkali materials is complex and can vary depending on factors such as the specific elements involved, the bonding interactions between atoms, and the overall geometry of the cluster. Analyzing and examining these structures is important for unsealing the full potential of super-alkali materials in various applications.

3. Properties

Super-alkali materials possess several distinctive properties that set them apart from traditional alkali metals and other compounds. Here are some key properties of super-alkali materials:

1. **High Electron Affinity:** Super-alkali materials show remarkably higher electron affinity compared to conventional alkali metals which means they have a strong ability to attract and bind with electrons, making them apt for various electronic applications.
2. **Low Ionization Energy:** These materials remarkably have low ionization energies which means they readily release electrons to form ions. This property grants their high reactivity and stability in certain chemical environments.
3. **Large Alkalinity:** Super-alkali materials exhibit remarkable alkalinity, which refers to their ability to donate electrons or accept protons. This property is a consequence of their low ionization energy and high electron affinity.
4. **Diffuse Electrons:** Super-alkali materials often comprise diffuse electrons, which are electrons that are not tightly bound to any specific atom and instead spread out over a larger region within the material. This electron delocalization contributes to their unique electronic properties.

5. **Electride Characteristics:** When the clusters are represented as M_2X, they can exhibit what's called "electride" characteristics. This means that in these clusters, the M atoms form bound alkali cations ($M2^+$) along with extra electrons. In these clusters, the highest occupied molecular orbital (HOMO) is important. Normally, in simple MX molecules (like NaCl), the HOMO is mainly the p atomic orbital of the X atom. But in M2X clusters, because of the repulsion from the X^- anion, the extra electron cloud is pushed above the M2 part by the X atom. The difference in energy levels between the HOMO and the lowest unoccupied molecular orbital (LUMO) tells us about the chemical reactivity of these clusters. This difference is called the HOMO–LUMO energy gap (E_{gap}). If this gap is large, the cluster is less reactive, and if it's small, it's more reactive. The E_{gap} value depends on the atomic numbers of M and X. Generally, clusters with higher E_{gap} values are less reactive, and those with lower values are more reactive. Specifically, as the atomic number of X increases, the E_{gap} increases, but as the atomic number of M increases, the E_{gap} decreases.

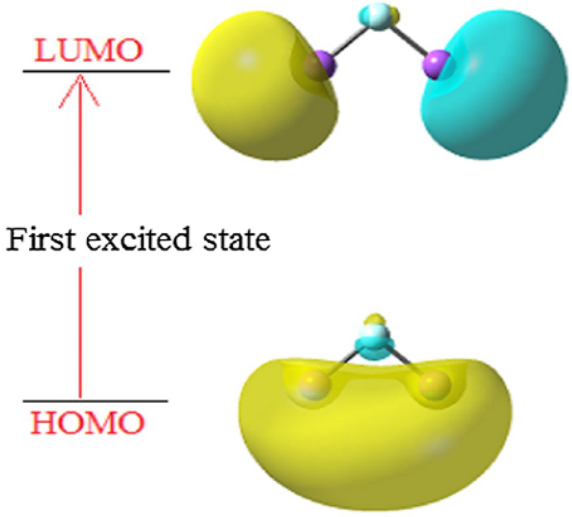

Figure 3: Electronic transition for determining excited state of M2X clusters (M = Li, Na; X = F, Cl)

6. **Potential for Energy Storage:** Some super-alkali materials have been examined for their capability as energy storage devices, for instance batteries and capacitors, because of their remarkable alkalinity and electron mobility.

Altogether, the differentiable combination of remarkable electron affinity, low ionization energy, and charecteristic electronic structure makes superalkali materials compelling subjects for research across various scientific disciplines.

4. Major Area of Applications

Super-alkali materials provide a wide range of potential applications across various fields due to their unique properties. Some of the key applications include:

- **Nonlinear Optics:** Super-alkali materials have promising applications in nonlinear optics because

of their large nonlinear optical coefficients. They can be utilized in devices such as frequency doublets, modulators, and optical switches for telecommunications and laser technology.

To examine the nonlinear optical (NLO) behavior of M2X clusters, TD-DFT calculations were employed by the researchers. They focused on the distinction between the ground state and a vital excited state to determine the NLO property called β_o.

β_o is a measure of NLO behavior and it depends on:

$$\beta_0 = \Delta\mu . f0 / \Delta E^3$$

The distinction in dipole moments between the ground state and the key excited state.
The strength of the transition is called the oscillator strength (fo).
The third power of the transition energy (ΔE).

In M_2X clusters, the crucial excited state is the first one, that involve the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This transition is similar to moving an electron cloud.

For example, in Li_2F clusters, the transition involves moving the electron cloud from where there are extra electrons (HOMO) to the LUMO, which mainly require lithium (Li) atoms. The energy difference (ΔE) and transition strength (f_o) in M_2X clusters are compared with those in other materials, like electrides and Li-doped fluorocarbon chains, to examine their NLO behavior.

There is an energy difference (ΔE) and transition strength (f_o) in M_2X clusters, even though it might be smaller compared to other materials, their βo values are remarkably increased. This means that, although some parameters are smaller, the vital energy difference (ΔE) plays an impactful role in increasing their NLO responses.

So, researchers used calculations to estimate how M2X clusters behave in nonlinear optics. They found that even though some parameters might be smaller compared to other materials, the vital energy difference impactfully increases and remarks their NLO responses.

- **Quantum Computing:** The remarkable electron affinity and unnatural stability of super-alkali materials make them attractive for their utilization in quantum computing. They could capably serve as quits, the fundamental units of quantum information processing, because of their potential to maintain quantum states over longer periods.
- **Energy Storage:** Some super-alkali materials have been surveyed for use in energy storage devices such as batteries and super-capacitors. Their remarkably high alkalinity and electron mobility make them efficient for surpassing the energy density and efficiency of these devices.
- **Catalysis:** Super-alkali materials show remarkable chemical reactivity, making them potentially important catalysts for various chemical reactions. They could be used in processes such as hydrogenation, oxidation, and carbon-carbon bond formation in organic synthesis and industrial applications.
- **Photonics:** The nonlinear optical properties of superalkali materials make them befitting for use in photonics applications, including optical amplifiers, laser systems, and photonic integrated circuits. They could grant the development of faster and more efficient optical communication systems.

Overall, the diverse range of applications of super-alkali materials peaks their capability to advance various technological fields and contribute to the development of next-generation devices and technologies.

5. Conclusion

In conclusion, the research on super-alkali materials shows a wealthy arras of properties and applications that hold assurance for facilitating science and technology. By their unique electronic structure, marked by their remarkable high electron affinity and low ionization energy, super-alkali materials provide a wide range of options across multiple disciplines.

The analysis done in this paper marks the importance of super-alkali materials in various fields for example nonlinear optics, quantum computing, energy storage, catalysis, sensor technology, photonics, and materials science, etc. These materials exhibit outstanding properties, which include large nonlinear optical coefficients, stability against fragmentation, and sensitivity to electronic and chemical environments, making them consummate for a wide range of applications.

As researchers kept exploring and tried to understand the complexities of superalkali materials, further findings are apprehended that will push the boundaries of scientific understanding and technological innovation. By utilizing the unique properties of superalkali materials, we can develop advanced materials, devices, and technologies that point uncertain challenges and development towards a more reliable and proximate future.

References

[1] Gutsev, Go L., and A. I. Boldyrev. "DVM Xα calculations on the electronic structure of “superalkali” cations." *Chemical Physics Letters* 92.3 (1982): 262-266.

[2] Gao, Zhen, Xinlu Cheng, and Minjia Zhao. "Ab initio diffusion quantum Monte Carlo study of the structural and electronic properties of small lithium-chloride LinCl (0, 1+)(n= 1–7) clusters." *Computational and Theoretical Chemistry* 1214 (2022): 113781.

[3] Honea, Eric C., et al. "Localization of an excess electron in sodium halide clusters." *Physical review letters* 63.4 (1989): 394.

[4] Honea, Eric C., Margie L. Homer, and Robert L. Whetten. "Electron binding and stability of excess-electron alkali halide clusters: Localization and surface states." *Physical Review B* 47.12 (1993): 7480.

[5] Nešković, Olivera M., et al. "Ionization energies of hypervalent Li2F, Li2Cl and Na2Cl molecules obtained by surface ionization electron impact neutralization mass spectrometry." *Rapid communications in mass spectrometry* 17.3 (2003): 212-214.

[6] Yokoyama, Keiichi, et al. "Ionization energies of hyperlithiated Li2F molecule and LinFn− 1 (n= 3, 4) clusters." *Chemical Physics Letters* 330.3-4 (2000): 339-346.

[7] Li, Ying, Di Wu, and Zhi-Ru Li. "Compounds of superatom clusters: preferred structures and significant nonlinear optical properties of the BLi6-X (X= F, LiF2, BeF3, BF4) motifs." *Inorganic chemistry* 47.21 (2008): 9773-9778.

[8] Yang, Hui, et al. "Structural properties and nonlinear optical responses of superatom compounds BF4-M (M= Li, FLi2, OLi3, NLi4)." *International Journal of Quantum Chemistry* 112.3 (2012): 770-778.

[9] Alexandrova, Anastassia N., and Alexander I. Boldyrev. "σ-Aromaticity and σ-antiaromaticity in alkali metal and alkaline earth metal small clusters." *The Journal of Physical Chemistry A* 107.4 (2003): 554-560.

[10] Veličković, Suzana R., et al. "Experimental and theoretical investigation of new hypervalent molecules LinF (n= 2–4)." *Chemical Physics Letters* 448.4-6 (2007): 151-155.

[11] Jena, Puru. "Beyond the periodic table of elements: The role of superatoms." *The journal of physical chemistry letters* 4.9 (2013): 1432-1442.

[12] Tong, Jing, et al. "Low ionization potentials of binuclear superalkali B2Li11." *The Journal of chemical physics* 131.16 (2009).

[13] Paduani, C., and Andrew M. Rappe. "Assemblage of superalkali complexes with ever low-ionization potentials." *The Journal of Physical Chemistry A* 120.32 (2016): 6493-6499.

[14] Giri, Santanab, Swayamprabha Behera, and Puru Jena. "Superalkalis and superhalogens as building blocks of supersalts." *The Journal of Physical Chemistry A* 118.3 (2014): 638-645.

[15] Jha, Ruchi, Santanab Giri, and Pratim K. Chattaraj. "Effect of confinement on the behavior of superhalogen and superalkali." *Computational and Theoretical Chemistry* 1206 (2021): 113491.

[16] Santos, Francisco A., et al. "Nonlinear optical materials: predicting the first-order molecular hyperpolarizability of organic molecular structures." *Photonics*. Vol. 10. No. 5. MDPI, 2023.

[17] Ahsin, Atazaz, and Khurshid Ayub. "Superalkali-based alkalides Li3O@[12-crown-4] M (where M= Li, Na, and K) with remarkable static and dynamic NLO properties; A DFT study." *Materials Science in Semiconductor Processing* 138 (2022): 106254.

[18] Talapatra, Gautam B., et al. "Nonlinear optical properties of the fullerene (C60) molecule: theoretical and experimental studies." *The Journal of Physical Chemistry* 96.13 (1992): 5206-5208.

[19] Muhammad, Shabbir, et al. "Insighting the functionally modified C60 fullerenes as an efficient nonlinear optical materials: a quantum chemical study." *Materials Science in Semiconductor Processing* 141 (2022): 106421.

[20] Wang, Jia-Jun, et al. "The interaction between superalkalis (M 3 O, M= Na, K) and a C 20 F 20 cage forming superalkali electride salt molecules with excess electrons inside the C 20 F 20 cage: Dramatic superalkali effect on the nonlinear optical property." *Journal of Materials Chemistry* 22.19 (2012): 9652-9657.

[21] Tu, Chunyun, et al. "Constructing (super) alkali–boron-heterofullerene dyads: an effective approach to achieve large first hyperpolarizabilities and high stabilities in M 3 O–BC 59 (M= Li, Na and K) and K@ n-BC 59 (n= 5 and 6)." *Physical Chemistry Chemical Physics* 16.4 (2014): 1597-1606.

[22] Mai, Jinmei, et al. "A novel class of compounds—superalkalides: M+(en) 3 M 3′ O−(M, M′= Li, Na, and K; en= ethylenediamine)—with excellent nonlinear optical properties and high stabilities." *Physical Chemistry Chemical Physics* 17.43 (2015): 28754-28764.

[23] Sun, Wei-Ming, et al. "Theoretical study on superalkali (Li 3) in ammonia: novel alkalides with considerably large first hyperpolarizabilities." *Dalton Transactions* 43.2 (2014): 486-494.