1. INTRODUCTION

1.1 Solid-state metathesis:

Solid state chemistry involves a vast number of synthesis methods, some of which use solvents to promote the reactions but the conventional approach to the synthesis of solid state materials involves solventless techniques and is known as solid state or ceramic synthesis’. In this process the starting materials are subjected to a series of repeated grinding, heating and cooling stages, so as to overcome the solid state diffusion barrier. Unlike solutions that have well-mixed components and fast diffusion rates, in solids, diffusion of ions is slow, even at elevated temperatures. Ideally starting material particles should be as small as possible with high surface areas. Solid state reactions can often take several hours to progress and require high temperature. Inspite of these limitations majority of solid-state materials are still synthesized using the ceramic method. Synthesis of select solid state materials can be achieved at lower temperature compared to ceramic method by means of either fast self-propagating solid state reactions involving self propagation, exothermic reactions or solid state metathesis (SSM) reactions of the type,

\[ \text{MCl}_n + \text{Na}_n\text{E} \rightarrow \text{ME} + \text{nNaCl} \]

\( (\text{M} = \text{transition, main group, lanthanide or actinide metal}; \ \text{E} = \text{molybdate, tungstate, vanadate, pinictide, chalogenides}) \)

based on the advantage of reaction enthalpy given out in a specific reaction. Typically, in a SSM process a high lattice energy bye product is formed along with the desired product and the reaction enthalpy provides the driving force for the process. The
reactions can be initiated at a point source by a heated filament, match or flame or they can be ignited in bulk by heating in a furnace or microwave oven or by mechanochemical means. Reaction proceeds by propagation of a solid state synthesis that occurs in the material transforming initial reactants to final products. The synthesis can be quite spectacular and in some cases take the form of a solid-flame. The criteria for a reaction to propagate depends on factors such as reaction exothermicity, heat capacity of the reagents and products, as well as density and type of containment vessel. It has been empirically observed that an SSM reaction will propagate with a synthesis wave if the calculated exothermicity of the reaction is high enough to melt the co-formed salt [1]. If this is the case, the reaction is exothermic enough such that successive layers will be ignited in turn and the reaction will propagate. Wide ranges of metal oxides, nitrides, borides, pnictides and chalcogenides have been prepared by metathesis reactions.

SSM has been successful to synthesize compounds that are often difficult to produce conventionally. Alkali or alkaline-earth metal main group compounds are combined with halides to form oxides [2-8], sulphides [4, 9], selenides [4, 9], tellurides [4], nitrides [10-16], phosphides [17-19], arsenides [18], antimonides [18], carbides [20,21], silicides [22], borides [16,23,24] and aluminides [25]. Additionally, nanostructured materials such as nanotubes [26], nanocrystals [27,28] and high-surface-area materials [29] are also produced. These reactions provide a novel tool for preparing difficult-to-synthesize materials. Although the precursor is usually a halide, an oxide can be used as well. For example, that MgSiN₂ was synthesized by reacting SiO₂ with Mg₃N₂ [14].
The important parameter in solid-state metathesis reactions is the formation of stable byproduct. For example, combining GaI$_3$ with Li$_3$N to produce GaN, as given in equation has a $\Delta H_{\text{rxn}}$ of $-515$ kJ.

$$\text{GaI}_3 + \text{Li}_3\text{N} \rightarrow \text{GaN} + 3\text{LiI}$$

This is more than four times as energetic as the elemental reaction Ga + 0.5N$_2$ → GaN ($\Delta H = -110$ kJ).

The phase produced is often determined by the rate of the reaction [25] and the reaction rate can be tuned to control the crystallite size of the products formed [10]. Diluents or fast reaction times can be used to produce nanoscale powders or materials with high surface areas [10]. Reaction temperatures are controlled through the choice of halide, alkali or alkaline-earth metal [30].

Alkali halides usually have lower heats of formation than alkaline earth halides, so reactions utilizing alkaline-earth metals will generally result in higher reaction temperatures. The upper limit of the reaction temperature is usually governed by the boiling point of the salt produced. Alkaline-earth salts have higher melting and boiling points, thereby increase the upper limit of the reaction temperature.

The heavier the halogen used, generally the lower the reaction temperature. This can be useful for the synthesis of compounds that are unstable at high temperatures. For example, it is easier to obtain GaN from GaI$_3$ than GaCl$_3$ in a reaction with Li$_3$N [11] due to the differences in heats of formation of LiI ($\Delta H = -270.4$ kJ/mol) vs LiCl ($\Delta H = -408.5$). Conversely, the synthesis of some materials is favored by high temperatures.
Another effective method for lowering a reaction temperature is by using diluents
[31]. This can be realized by adding inert salts, such as the byproduct salt itself, to the
reaction mixture. This process can be improved for nitrides by adding low-melting or
vaporizing nitrogen containing compounds (like NH₄Cl or LiNH₂) [11]. Not only do
these compounds act as a heat sink, they also supply nitrogen to the reaction as well.

Reaction temperature can also be reduced by controlling the heat loss. In this way,
these reactions can be effectively scaled up without producing destructive amounts of
heat. This can be achieved by specifically designing the reaction vessel [11] or by
controlling the amount of heat produced by slow addition of precursors into the reactor.
If a hotter reaction is desired, either selection of suitable starting materials or
performing these reactions at an elevated temperature, is necessary.

Solid-state metathesis (SSM) reactions developed over the past two decades offer an
effective method for synthesizing materials that are difficult to make by conventional
methods. Solids with different crystal structures have been formed to be highly useful
since they facilitate tailor making of materials suitable for specific purposes.

1.2 Crystal structure description:

1.2.1 ABO₄ type compounds:

(i) Scheelite and Wolframite:

Wolframite and Scheelite are two common structural types for ABO₄ type of
compounds. The Wolframite structure may be described as made up of hexagonally
close packed oxygens with certain octahedral sites filled by A and B cations in an
ordered way. The oxygens are not close packed in the Scheelite structure and the co-
ordination number of the A cation is eight while the B cation is in approximate
tetrahedral co-ordination to oxygen. The scheelite structure may be regarded as cubic close-packed array of A$^{2+}$ and BO$_4^{2-}$ units which are ordered. The oxygens are three coordinated to cations in both the scheelite and wolframite structure. However, in scheelite each oxygen is bound to two A cations and one B cation, where as in the wolframite structure half are coordinated to two B cations and half are coordinated to two A cations. Crystal structures of scheelite and wolframite are depicted in Fig.1.1(a) and Fig.1.1(b) respectively.

**Fig.1.1(a):** A perspective view of the scheelite structure. The large black circles represent the A atoms, the grey circles represent the W atoms, and the small black circles represent the O atoms. The A-O and W-O bonds are shown.
In the AWO$_4$ type of compounds, if A$^{2+}$ has a small ionic radius, <0.77 Å (Mg, Zn) it will form the monoclinic wolframite structure, while larger A$^{2+}$ cations with ionic radius >0.77Å (Ca, Ba) form the tetragonal scheelite structure. Monoclinic ZnWO$_4$ is also a known material named sanmartinite [32]. The crystal structure of CaWO$_4$ is tetragonal with two formula units per primitive cell [33] and consists of calcium surrounded by eight oxygens. The isolated tetrahedral of WO$_4$ are nearly regular with four equal W-O distances. AWO$_4$ type oxides have attracted a great deal of interest in the recent years due to their use as laser host materials [34], scintillators [35], oxide ion conductors [36], microwave applications [37] and also as magnetic materials [38]. AWO$_4$ type divalent transition metal compounds have been reported to be useful for humidity sensors [39], photocatalysts [40], photochromic [41] and as photoanodes [42]. MnWO$_4$ has been the subject of extensive studies due to its multiferroic, electrochemical and ionic properties [43-46] and it is a high-gain Raman laser [47,48].
ii) BiVO₄ and LaVO₄:

BiVO₄ naturally called as the mineral pucherite with an orthorhombic crystal structure [49]. However, BiVO₄ prepared under laboratory conditions does not adopt the pucherite structure but crystallizes either in a scheelite or a zircon-type structure (Fig.1.2) [50]. The scheelite structure can have a tetragonal crystal system (space group: I₄₁/a with a = b = 5.1470 Å, c = 11.7216 Å) or a monoclinic crystal system (space group: I₂/b with a = 5.1935 Å, b = 5.0898 Å, c = 11.6972 Å, and β = 90.3871°) [51] while the zircon-type structure has a tetragonal crystal system (space group: I₄₁/a with a = b = 7.303 Å and c = 6.584 Å) [52].

In the scheelite structure, each V ion is coordinated by four O atoms in a tetrahedral site and each Bi ion is coordinated by eight O atoms from eight different VO₄ tetrahedral units [51]. Fig.1.2(a) shows the four-coordinated V center and the eight coordinated Bi center alternating along the [001] direction. Each O atom in this structure is coordinated to two Bi centers and one V center, holding the Bi and V centers together forming a three dimensional structure. The only difference between the tetragonal and monoclinic scheelite structure is that the local environments of V and Bi ions are more significantly distorted in the monoclinic structure, which removes the four-fold symmetry necessary for a tetragonal system. In the zircon-type structure, V is still stabilized by four O atoms and Bi is coordinated by eight O atoms [Fig1.2(b)]. However, each Bi is surrounded by only six VO₄ units because two VO₄ units provide two O atoms to Bi.

Lanthanum orthovanadates, LaVO₄ crystallize in two polymorphs, that is, tetragonal phase (t) with zircon structure and monoclinic phase (m) with monazite structure. With
increasing ionic radius, $\text{Ln}^{3+}$ ions shows strong tendency toward monazite-structured ortovanadate due to its higher oxygen coordination number of 9 as compared with 8 of the zircon one. Its structural characteristics indicates $m$-LaVO$_4$ belongs to $C_{2h}^5P_{21}/n$ where as $t$-LaVO$_4$ belongsto $D_{4h}^{19}I4I/amd$ spacegroup.

**Fig1.2:** (a) Crystal structure of tetragonal scheelite type BiVO$_4$

*(red: V, purple: Bi, and gray: O)*
1.2.2 ABO$_3$ type compounds: BaSnO$_3$, BaZrO$_3$, LaFeO$_3$, BiFeO$_3$:

Perovskite is the name of the mineral calcium titanate. Most of the useful ceramics such as BaSnO$_3$, BaZrO$_3$, BiFeO$_3$, LaFeO$_3$, K(Ta, Nb)O$_3$ have perovskite type structure. These oxide ceramics have the general chemical formula ABO$_3$. Where A is a cation with a larger ionic radius, B with a smaller ionic radius and O is oxygen. Most of the ferroelectrics with perovskite type structure are compound with either A$^{2+}$ B$^{4+}$ O$_3$ or A$^{+1}$ B$^{5+}$ O$_3$ type. No ferroelectric has been reported for A$^{3+}$ B$^{3+}$ O$_3$, even though there are many compounds with that formula. A perovskite structure is essentially a three dimensional network of BO$_6$ octahedra as shown in Fig.1.3(a). It may be regarded also
as a cubic close packed arrangement of A and O ions with B ions filling the octahedral interstitial positions. The packing situation of this structure may be characterized by a tolerance factor defined as follows.

\[ t = \frac{(R_A+R_O)^2}{2} \cdot \frac{1}{(R_B+R_O)} \]

where \( R_A, R_B \) and \( R_O \) are the ionic radii of A, B and O ions respectively. When \( t \) is equal to 1, the packing is said to be ideal. In general, to form a stable perovskite structure one requires that \( 0.9 < t < 1.1 \). Besides the ionic radii, other factors, such as polarizability and bond type must also be taken into consideration while predicting the stability of a structure.

Fig. 1.3 (a) Three dimensional net work of \( BO_6 \) octahedra.
Fig. 1.3(b): Cubic perovskite of \( ABO_3 \) unit cell. Blue spheres represent the \( A \) cations, yellow spheres represent the \( B \) cations, and red spheres represent oxygen anions forming an octahedra.
References:


