Threefold representation of M-N-O systems as a guide to predict mechanosynthesis of M-N nanocrystals

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Abstract. A method is proposed to forecast how micrometric powders are converted into intermetallic nanocrystals by high-energy milling. Mixtures of MO-N or M-N as precursors were processed to obtain PbTe or PbSe. This transformation takes place by oxidizing highly reactive chalcogens such as Se or Te and reoxidation of PbO to form Pb complex chalcoxides. In the latter phases Te or Se share electrons to act as Te$^{IV}$ or Se$^{IV}$, PbTeO$_3$ or PbSeO$_3$. Once that state is completed, the reduction state manifests itself as an amorphous precipitation of phases. The final stage is traced as high purity nanocrystals.

1. Introduction
In view of a wide world of applications of intermetallic chalcogenides, a great effort is brought to researchers to explore and develop new process routes to produce efficiently high purity nanocrystals. Results have been published recently on several process routes, among those are: thermal decomposition of precursors, selective vapor deposition, organometallic chemical treatment of reactive species, controlled fusion and solidification of pure metals to render nanocrystalline phases (by Czochralski method) and high-energy milling (HEM) \[1-2\].

Undoubtedly, among those processes one must recognize that the last one is simpler than any other; and the high quality and purity of intermetallic compounds can be reached, provided physical and chemical parameters are controlled \[1, 3\].

It must be established clearly that by HEM one can produce alloying and mechanosynthesis of intermetallic phases. This means that by milling pure metals like Pb and Te or Se, or alternatively by milling mixtures of PbO and either Te or Se one can produce nanopowders of the type PbTe or PbSe, respectively. Under any of those circumstances, there are two basics mechanisms by which the transformation is induced, namely: thermo-mechanical and physic-chemical driving forces.
Therefore, to avoid presence of impurities a set of ZrO$_2$-spheres and a nylamid vial would be very favorable system components to be considered in the HEM-process. That is due to high impact resistance, wear resistance and also owning to their inert chemical nature [3-4].

A critical chemical factor to be considered in the synthesis of PbO + Te or PbO + Se, as expected; it is to eliminate the effect of the final oxygen potential. An implicit reason considered is that an oxide phase should dictate the maximum surface oxygen potential [1].

If the mecanosynthesis via the HEM is not underestimated as a process then, a sequence of effects can be described as: physical and chemical joined powders that constitute agglomerates as well as an incipient presence of chalcogenides as intermetallic compounds [1]. These events take place since very early in the grinding process; and so they indicate us that friction, fracture and low energy collisions give way to both Van der Waals junction forces and local transformation of intermetallic phases [1, 3].

Lead intermetallic chalcogenides such as PbTe or PbSe as well as pure Te or Se are highly reactive species. These acts as oxygen scavengers and their reactivity are favored by HEM [5].

Several researchers have evaluated a wide range of stoichiometric chemical complex compounds that can be framed within ternary ratios in the Pb–Te–O or Pb–Se–O systems. Among them, one can list the following: PbTeO$_3$, PbTeO$_4$, PbTe$_2$O$_8$, Pb$_2$Te$_3$O$_8$, Pb$_2$TeO$_5$ and Pb$_2$TeO$_7$. And, for complex selenium oxides almost equivalent phases including PbSeO$_3$ have also been reported [5-6]. Additionally, simpler species related to complex oxides are: ‘Pb$_2$O’ (it was traced as an amorphous non-stoichiometric compound), PbO, PbO$_2$, TeO$_2$, SeO$_2$ and TeO$_3$ (PbO$_2$ and TeO$_3$ were scarcely found; however their index of detection was unambiguously traced). Other oxides traced experimentally are those that do not necessarily obey stoichiometric ratios between Pb, Te and O or Pb, Se and O; instead amorphous or even vitreous phases can be traced.

Another set of experimental and theoretical data has been reported on lead telluride reactivity measured in respect of different oxygen partial pressures [5-6]. Thus, the following set of reactions was postulated

\[
\begin{align*}
PbTe + 2 O_2(g) &= PbTeO_4 \\
PbTe + \frac{3}{2}O_2(g) &= PbTeO_3 \\
PbTe + O_2(g) &= PbTeO_2
\end{align*}
\]

2. Development of the proposal

The first hypothesis under which the experimental campaign was designed was that where a mixture of a chemically stable oxide plus an avid element for oxygen, under the influence of HEM, one might induce an overall reducing effect. Thus, mechanical energy dissipated as heat, fracture in addition of plastic deformation could become driving forces to start transformation of precursors onto intermetallic phases [1, 3-4]. Henceforth, an ideal way to represent that proposal would be represented by:

\[
MO(s) + N(s) \xrightarrow{\Delta E_m} MN(s) + \frac{1}{2} O_2(g)
\]

where: M represents Pb and N can be Te or Se. \(\Delta E_m\) stands for energy supplied by HEM.

Since micropowders of MO and N are subjected to random collisions rates, only the most efficient impacts are expected to act as a spark to initiate chemical transformations. This specific reaction condition is reached in the milling system when both temperature and gaseous chalcogens phases are in close contact with ultrafine or nanosized PbO powders. Thus, provided there are no other oxides and solely PbO is reduced, then as thermochemically expected from any intermetallic formation, energy would be continuously released, therefore a thermally self-sustained process would be expected [1].
Under these process conditions, a chemical starting point would be considered as the initial transient condition that will give way to a steady state transformation process.

However, such proposal is partially valid, since evolution of chemical conditions traced during milling indicate us that in addition of PbO other single and complex oxides can also be present [1-4]. Due to its importance, this finding will be closely approached in a further section.

Other research works along these lines, have also proposed that processing pure metals to obtain lead chalcogenide can be represented by the following reaction [5, 7]:

\[
M(s) + N(s) \xrightarrow{\Delta\mu_a} MN(s)
\]

To this point, it is important to cite that out of the MN(s) phases obtained by the HEM, it is expected to reach very high purity nanocrystals. Therefore, a massive transformation from pure metals, as given by reaction (5), does not necessarily satisfy that stringency mentioned previously. It is acknowledged that very small oxygen partial pressures as those reached under experimental atmosphere conditions, would decidedly affect precursors as well as products considered in reactions (1-5).

In view of these findings, a modified reaction scheme was proposed to take into account an intermediate stage. This proposal is represented by the following scheme, as shown in figure 1.

![Scheme of the HEM process considered as a batch reactor.](image)

**Figure 1.** Scheme of the HEM process considered as a batch reactor.

### 3. Experimental and theoretical results

By comparing mechanical metallurgical versus physicochemical responses in the HEM-process, it was found that the former factor was quite modest as compared to the later one. In view of that, an acute analysis was centered on chemical transitions induced by thermally activated process.

The first and decisive point to be considered about the physicochemistry of transformations from micropowders as precursors to nanocrystalline phases of high purity is that: (i) powders were charged under atmosphere conditions (this statement means that an initial oxygen potential given by PbO plus Te was already present in the system) and (ii) it was not attempted to remove humidity from ZrO₂-spheres neither from internal walls of the vial [3-4]. Therefore, reasons to perform experiments through these conditions were that an oxide (PbO) was as one of the precursors.

During milling through which precursors were subjected, to achieve the mechanosynthesis of either PbTe or PbSe via the HEM, gaseous phases enriched in either Te or Se were identified. These appeared on surfaces of the milling media (ZrO₂-spheres). Appearances of these deposits were either bright metallic or grayish, thus indicating a condition of either metal or oxide vapors [8], see figures 2 and 3. By processing PbO plus Te, it is expected to relate those phases with Te₂ (g) or Te₂O₂ (g) while the twofold system PbO plus Se they correspond to Se₆ (g) and SeO (g) [9-10]. As a consequence, the
partial pressure of chalcogen gaseous phase should override gradually the oxygen partial pressure in the vial [1].

Additionally, regarding early tracing of intermetallic phases, it is a clear indication as to how a chemical transition from PbO and Te is promoted by the fractured surface in contact with chalcogens gaseous phases [3].

Thermochemical stabilities of these phases were confirmed by identifying them with data reported in the literature [9-10]. Temperature ranges through which theoretical data was disclosed were those traced by an infrared thermometer; the overall highest temperature registered was around 550 K.

Based on other reports on thermal responses during milling an educated guess would lead us to propose that powders could reach thermally as twice as that value [1, 11].

Among the complex oxide phases plentifully identified in the Pb–Te–O system was the stoichiometric PbTeO₃ phase. In the Pb–Se–O system, as shown in figure 4, the equivalent phase was PbSeO₃, other complex phases in the PbO–TeO₂ subsystem have a quasi-similar composition; however, they were amorphous and did not have well defined Pb:Te:O composition ratios [1, 3].

By using either conventional analytical techniques such as XRD or electron microscopy techniques as SEM, TEM or HRTEM and even XPS as well, other phases like PbO₂, TeO₂ and SeO₂ were identified [1, 3, 8, 12], see figure 4. Additionally, under high (pulse) energy discharges by the TEM-electron gun, non-crystalline as well as non-stoichiometric phases in terms of Pb:Te:O or Pb:Se:O ratios were induced. These species, however, showed ratios closely related to PbTeO₃ or PbSeO₃, respectively.

Just before any discussion is derived out of these findings and also previously to make any proposal related to a chemical mechanism; we believe, it is very important to establish that chemical analysis referred to oxides, others than PbO, are traced on surfaces of powders. It means that any composition effects between precursors, gases species and powders and between gases (oxygen and gaseous chalcogens) solely represent local and superficial powder chemical changes [8].

Through these postulates, one can infer that if mixtures of precursors such as PbO plus both Te or Se then plastic deformation and fracture as well as chalcogen vapor phases may be found during HEM [1, 8]. Therefore, if the thermal potential becomes a strong driving force to induce chemical transition then fresh fractured surfaces, in close contact with gaseous chalcogens phases, will become local efficient mass exchangers.

4. Development of the proposal or model
To frame all possible stable single and complex phases, as earlier was proposed to account for the Pb–Se–O system [1], a ternary system was disclosed, see figure 5. There, pure substances were located on

![Figure 2. Gray oxide deposited on ZrO₂-spheres as vapor during milling of PbTe nanoparticles.](image1)

![Figure 3. Bright oxide deposited on ZrO₂-spheres as vapor during milling of PbSe nanoparticles.](image2)
their apexes. Each side of the triangle includes three binary sides namely: Te–O, Pb–O and Te–Pb. 
The Te–O side includes phases like \( \frac{1}{2} \) Te2O2, TeO2 and TeO3. The Pb–O axis includes PbO and PbO2; 
and the remaining Pb–Te axis, solely includes the PbTe. However, the most important subsystem is 
that relating two oxides, PbO and TeO2. Thus, by using an equivalent analogy, it becomes evident that 
an analysis based on compositions of precursors as well as on data shown in the figures 1–4 would not 
be enough to propose a chemical model. However, by taking, for example all data previously disclosed 
as single and complex oxides referred to the Pb–Te–O system then a PbO–TeO2 subsystem can be 
used to frame most of the complex oxide phases traced in this work, see figure 5. Through this 
approach a very clear sequence of changes that might evolve during milling can be located as 
stoichiometric phases, see figure 5. Additionally, other secondary subsystems like those where the 
dimer gaseous phase, \( \frac{1}{2} \) (Te2O2), is related to PbO2 or where the intermetallic, PbTe, is connected to 
pure oxygen or the richest oxide, TeO3, related to pure Pb, all of them can be adequately represented in 
the Pb–Te–O ternary system, as shown in figure 5.

If a closer analysis is carried out, on the ternary representation of this system, it is evident that all 
of the most common species related between those extreme chemical couples (a–c), is the PbTeO3 
phase. As earlier described, if phase transformations are evaluated as cumulative collision as well as 
statistical cumulative chemical events, one can postulate that the PbTeO3 phase can be the average 
chemical effect which in turn will determine the average oxygen potential.

It is worth to emphasize that through most of the milling process this phase was that which satisfies 
the stoichiometric ratios of 1:1:3, respectively. This finding clearly reveals that tellurium in this phase 
is acting as a tetravalent atom.

![Figure 4. XPS spectrum of Se 3d core level [8].](image)

To complete a description of the physicochemical role played by the PbTeO3, a dynamic 
equilibrium is proposed where the threefold phase set: PbO–PbTe–PbTeO3 could coexist during 
milling. It is worth to point out that an equivalent approach was tested and proved for the triple set of 
components for the PbO–PbSe–PbSeO3 system [1], see figure 4. The only difference found between 
these systems is that the gaseous phase in the Pb–Te–O system involves \( \frac{1}{2} \) Te2O2 (g) instead SeO (g) 
and Te2 (g) instead Se6 (g), see figure 4.

This assemblage of values constitutes a thermodynamical arrangement that here represents the 
quasi-steady state transformation. Hence, most of the milling process will be regulated by either the 
PbO–PbTe–PbTeO3 or the PbTe–PbTeO3–\( \frac{1}{2} \)Te2O2, as dictated by the Gibbs phase rule [8].
Figure 5. Ternary representation of powder products at different milling times.

Figure 6. Ternary representation of the dynamic equilibrium condition developed during milling.

The last step to which nanopowders are subjected to would be those where highly crystalline phases are obtained. It is quite feasible that this final transition stage can be attributed to the total removal of the oxygen potential effect. Therefore, if partial pressures of oxygen are diminished to their lowest extent, it means that partial pressures given by the chalcogens gaseous phases would be definitely larger than oxygen atmospheric pressure.

5. Final remarks

By HEM microsize precursors like PbO in addition of either Te or Se can mechanosynthesized to render intermetallic compounds like PbTe or PbSe, respectively. Through this process, PbO is incipiently reduced by Te, and as expected Te is slightly oxidized during early stages of milling. Once, energy conditions due to effective collisions between powder and milling media rise the temperature of the milling system, gaseous chalcogens phases like Te_2 (g), TeO_2 (g) and Se_6 (g) as well as SeO (g) are formed in the Pb–Te–O and Pb–Se–O systems, respectively.

However, the effect of the reduction of PbO plus those oxygen contributions of physisorbed or chemisorbed oxygen or humidity as well as that oxygen trapped when powders were charged in the vial, all of them locally promote high oxygen potentials on surface of powders.

The average oxygen potential developed on surface of powders is that represented by the PbTeO_3 phase as shown on the ternary diagram in figure 5 (point 4).

Once this oxygen potential is surmounted by either Te_2O_3 (g) or SeO (g) then Te_2O_3 (g)/Te_2 (g) or SeO (g)/Se_6 (g) ratios become quite effective on reducing the PbTeO_3 and PbSeO_3, respectively.
It is important to point out that the reoxidation phenomenon as an average value represented by the PbTeO$_3$ involves higher valence (4+) oxides like PbO$_2$ or TeO$_2$ or even TeO$_3$ (6+). Additionally, lower oxygen potentials than that given by the PbTeO$_3$ would be phases involved like Te$_2$O$_2$ (g) or SeO (g). As a direct consequence of these findings chemically the PbTeO$_3$ can act as a pivot point with changes of Te-valences induces metastable non-stoichiometric phases on transformations.

Additionally, if oxygen content is not fully removed from nanoparticles then crystals would not be faceted; instead these would manifest themselves as quasi-spherical shaped particles. Thus, highly crystalline nanoparticles will be traced only when even traces of oxygen are totally removed.

A final remark to be mentioned is that related to the kinetics of the mechano-synthesis of these chalcogenides. It is that referred to the presence of Te$_2$O$_2$ (g) against Se$_6$ (g) or SeO (g). Lead tellurides due to Te$_2$O$_2$ (g) induces the PbTe rate of transformation in almost one half time that to transform PbSe.

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