



Short communication

Polymorphs of Li_3PO_4 and Li_2MSiO_4 ($M = \text{Mn, Co}$) The role of pressure

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ABSTRACT

The behavior of Li_3PO_4 and Li_2MSiO_4 ($M = \text{Mn, Co}$) compounds under high pressure/high temperature is investigated. $Pmn2_1$ - Li_3PO_4 remains stable up to the higher experimental limit of 80 kbar (900 °C). A sample of $\text{Li}_2\text{MnSiO}_4$ consisting of a mixture of $Pn2_1$ and $Pmnb$ polymorphs converts upon high pressure/high temperature treatment into the $Pmn2_1$ polymorph; the latter being stable at 80 kbar and 900 °C. A sample of $\text{Li}_2\text{CoSiO}_4$ - $P2_1/n$ transforms to the denser $Pmn2_1$ polymorph at 40 kbar/900 °C, but decomposes at higher pressure (60 kbar/900 °C). No evidence on any novel Li_2MSiO_4 polymorph is detected in any of the high-pressure products.

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1. Introduction

The Li_2MSiO_4 ($M = \text{Fe, Mn, Co, Ni}$) family is attractive as positive electrode for lithium batteries due to its improved safety and at least theoretical possibility to reversibly deintercalate two lithium ions from the structure. Li_2MSiO_4 compounds exhibit a rich polymorphism, adopting a variety of crystal structures built up from $[\text{SiO}_4]$, $[\text{LiO}_4]$ and $[\text{MO}_4]$ tetrahedral units. The electrochemistry of $\text{Li}_2\text{FeSiO}_4$, $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{CoSiO}_4$ towards Li^+/Li has been reported showing that these compounds are able to provide one electron per formula unit at average voltages of ca. 3.1 V, 4.2 V and 4.3 V, respectively [1–4]. Yang et al. succeeded to remove the two lithium ions from $\text{Li}_2\text{MnSiO}_4$ [3], though the electrode suffers a large polarization and a limited cycleability. Density Functional Theory investigations [5–7] associate the poor electrochemical performance of Li_2MSiO_4 materials to the instability of most M^{+3} and M^{+4} ions in the tetrahedral environment; MSiO_4

structures are prompt to transform into other forms consisting in octahedral $[\text{MO}_6]$ units. In this context, it would be desirable to prepare Li_2MSiO_4 polymorphs based on MO_6 octahedra. High pressure/high temperature (HP/HT) synthesis is a good route to increase the coordination number around cations. For instance, berlinite- FePO_4 (Fe in tetrahedral sites, bulk modulus $B \approx 25$ GPa [8]) transforms into a VCrO_4 -type structure under high pressure (Fe in octahedral sites) [9]. Although most orthosilicates have large bulk moduli (olivine- Fe_2SiO_4 $B = 113$ GPa, Phenakite- Be_2SiO_4 $B = 201.8$ GPa, garnet- $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ $B = 159$ GPa, and so forth) pressure driven polymorphic transformation are not rare [10,11 and references therein]. The calculated bulk modulus of $\text{Li}_2\text{MnSiO}_4$ is 85 GPa [12], meaning that this is a somewhat compressible structure. Aiming to produce Li_2MSiO_4 forms with M in octahedral sites, in this work we have investigated the behavior of Li_2MSiO_4 ($M = \text{Mn, Co}$) under high pressure/high temperature conditions. For completeness, we have also performed HP/HT experiments on Li_3PO_4 , which can be considered the parent compound of the Li_2MSiO_4 family [13]. As a parallel objective, we aim to establish the pressure-dependence of the stability of the various Li_2MSiO_4 polymorphs, information that we have recently reported for $M = \text{Mn}$ [12].

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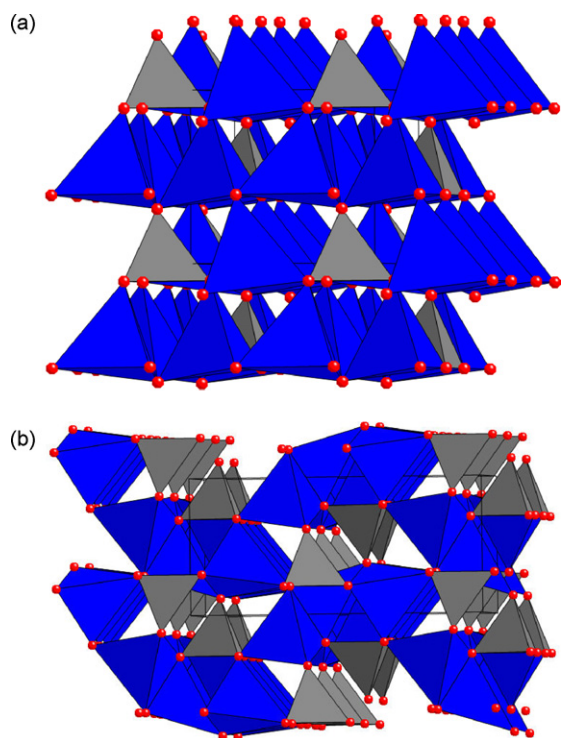


Fig. 1. Schematic representation of (a) β - Li_3PO_4 and (b) γ - Li_3PO_4 structures. Lithium in blue, phosphorous in grey and oxygen in red.

1.1. Structures

Li_2MSiO_4 compounds crystallize in several different polymorphs related to either the low temperature form or the high temperature form of Li_3PO_4 , denoted as β - Li_3PO_4 and γ - Li_3PO_4 , respectively. Fig. 1 shows the structure of both polymorphs. β - Li_3PO_4 (S.G. $Pmn2_1$) presents a structure consisting of only corner-sharing tetrahedra, in which all the tetrahedra point towards the same orientation along the c axis [14]. γ - Li_3PO_4 (S.G. $Pmnb$) is built up by both corner and edge sharing tetrahedra and with half of the tetrahedra pointing to opposite orientations along the c -axis than the other half [15]. Table 1 summarizes the polymorphs that are known for $\text{Li}_2\text{MnSiO}_4$, $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{CoSiO}_4$, which will be hereafter denoted by their corresponding space groups (S.G.).

2. Experimental

$\text{Li}_2\text{MnSiO}_4$ was prepared by dispersing 6 nm size SiO_2 particles (Cab-osil M5) in water and stabilizing them by citric acid (Aldrich).

Table 1
Lattice parameters for the reported polymorphs of Li_2MSiO_4 ($M = \text{Mn, Fe, Co}$).

a (Å)	b (Å)	c (Å)	β (°)	Volume (Å ³ /f.u.)	S.G.	Refs.
$\text{Li}_2\text{CoSiO}_4$						
6.253	10.685	4.929	90	82.33	$Pbn2_1$	[16]
6.28	5.36	4.94	90	83.14	$Pmn2_1$	[13]
6.20	10.72	5.03	90	83.57	$Pmnb$	[13]
6.284	10.686	5.018	90.60	84.23	$P2_1/n$	This work
$\text{Li}_2\text{FeSiO}_4$						
6.2661	5.3295	5.0148	90	83.72	$Pmn2_1$	[2]
$\text{Li}_2\text{MnSiO}_4$						
6.334	10.910	5.070	90.99	87.74	$P2_1/n$	[17]
6.312	10.765	5.011	90	85.12	$Pmnb$	[12]
6.3141	5.3702	4.9650	90	84.17	$Pmn2_1$	[12]

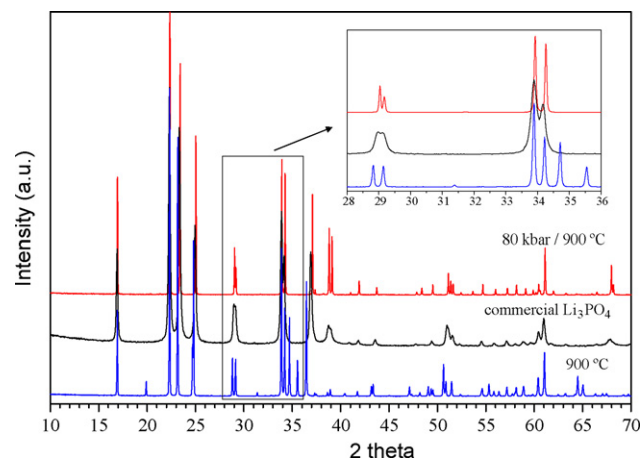


Fig. 2. XRD patterns of commercial Li_3PO_4 (black), a portion of it heated at 900°C (blue) and another portion treated at $900^\circ\text{C}/80\text{ kbar}$ (red).

LiNO_3 and Mn -acetate (both Aldrich) were used as a source for lithium and manganese. The suspension was dried, grinded with mortar and pestle and calcinated in the reductive atmosphere ($\text{Ar} + 5\text{ wt.}\% \text{H}_2$). The dry and grinded sample was slowly heated (2°C min^{-1}) to 900°C and after 10 h at 900°C it was cooled to room temperature with cooling rate 2°C min^{-1} . A sample of $\text{Li}_2\text{CoSiO}_4$ was prepared by combustion route using as reagents Li and Co nitrates, nanosized crystoballite and urea as fuel for the reaction. Afterwards the as-prepared powder was treated at 950°C for 48 h and quenched to room temperature. The Li_2MSiO_4 samples and commercial Li_3PO_4 (Aldrich) samples were subjected to high temperature-high pressure treatment in a belt-type press (hydrostatic pressure). Different conditions were applied, with pressure in the range 20–80 kbar and temperature between 600 and 900°C . After applying the pressure and temperature during 1 h the anvil is quenched to room temperature while pressure is slowly released.

The X-ray powder diffraction patterns (XRDP) of $\text{Li}_2\text{MnSiO}_4$ samples were collected on a STOE diffractometer operating in transmission geometry with $\text{Mo K}\alpha_1$ radiation $\lambda = 0.70926 \text{ \AA}$ (2θ range 2 – 55° , step size = 0.01°). The XRD characterization of $\text{Li}_2\text{CoSiO}_4$ and Li_3PO_4 samples was performed using a Bruker D8 high-

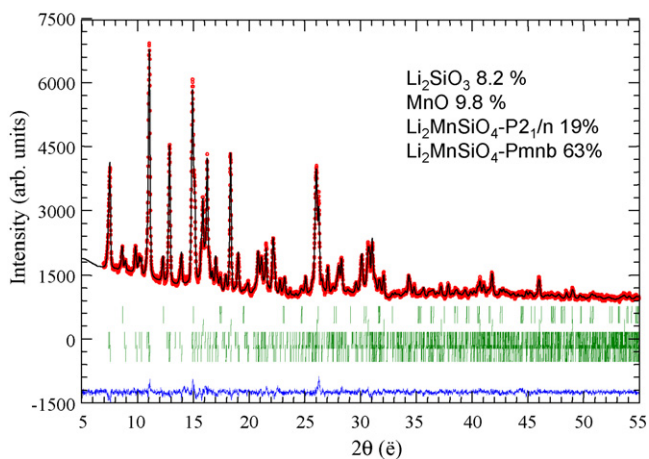


Fig. 3. Observed (red) and calculated (black) XRD patterns of as-prepared $\text{Li}_2\text{MnSiO}_4$ ($R_p = 2.38\%$, $R_{wp} = 3.01\%$). Blue is the difference. Vertical bars mark reflection positions of the four phases included in the refinement; from top to bottom Li_2SiO_3 , MnO , $P2_1/n$ - $\text{Li}_2\text{MnSiO}_4$ and $Pmnb$ - $\text{Li}_2\text{MnSiO}_4$.

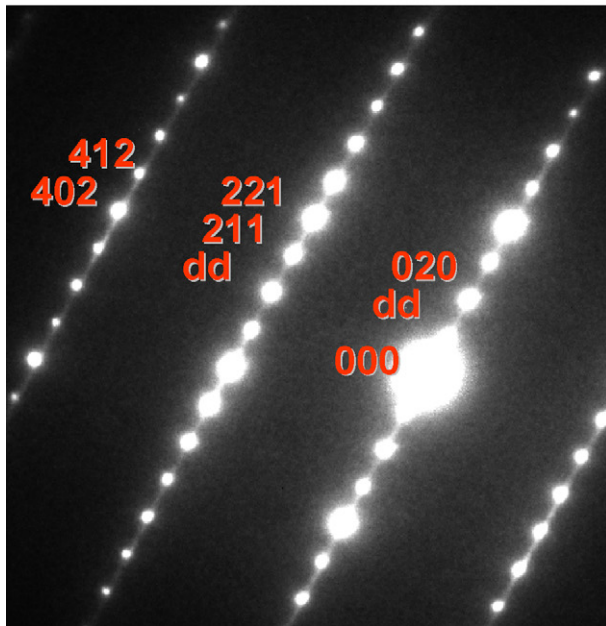
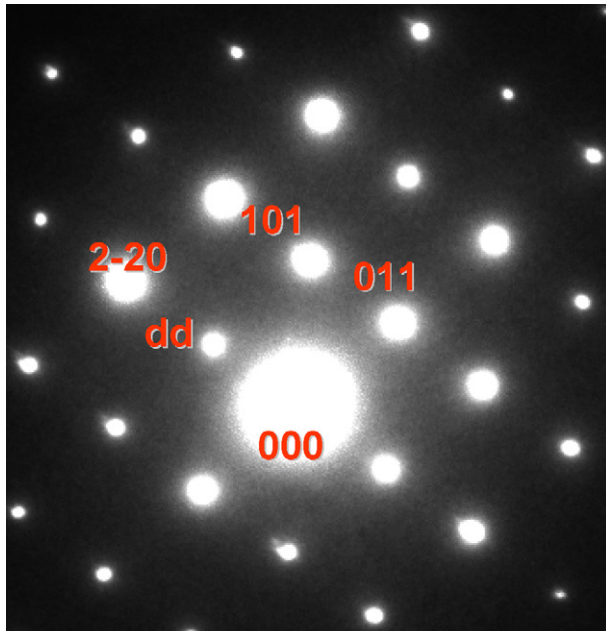


Fig. 4. SAED patterns of as prepared $\text{Li}_2\text{MnSiO}_4$. Indexation has been done using the $Pmnb$ cell of Table 1. Extra spots are due to double diffraction (dd).

resolution X-ray powder diffractometer, with monochromatic $\text{Cu K}\alpha 1$ ($\lambda = 1.5406 \text{ \AA}$) radiation obtained with a germanium primary monochromator, and equipped with a position sensitive detector (PSD) MBraun PSD-50M. The data were collected in the 2θ range between 10° and 70° in steps of 0.015° . For the Co-containing samples the relatively high background and the low quality of the patterns are due to strong fluorescence of this metal. The treatment of XRD patterns was carried out using the FullProf program [26]. Atomic coordinates and thermal displacement parameters were considered but only lattice parameters were refined. A Tecnai F20 ST transmission electron microscope was used to conduct a selected area electron diffraction (SAED) characterization of the as prepared $\text{Li}_2\text{MnSiO}_4$.

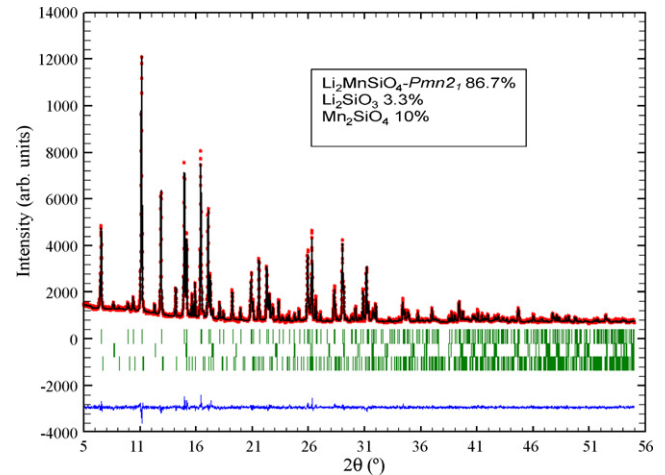


Fig. 5. Observed (red), calculated (black) XRD patterns and their difference (blue) of HP- $\text{Li}_2\text{MnSiO}_4$ prepared at 6 kbar and 600°C ($R_p = 11.5\%$, $R_{wp} = 9.76\%$, $R_{exp} = 8.86\%$). Vertical bars mark reflection positions of the three phases included in the refinement: $Pmn21$ - $\text{Li}_2\text{MnSiO}_4$ top, Li_2SiO_3 middle and Mn_2SiO_4 bottom.

3. Results and discussion

3.1. Li_3PO_4

The XRDP of commercial Li_3PO_4 (Fig. 2) corresponds to β - Li_3PO_4 (ICSD-10257). As expected, a portion heated at 900°C converts to the high temperature polymorph, γ - Li_3PO_4 (ICSD-25816). The XRDP of other portion treated at 80 kbar/ 900°C can be interpreted based on the β - Li_3PO_4 cell, but with an improved crystallinity. This indicates that pressure prevents the transformation of β - Li_3PO_4 ($77.78 \text{ \AA}^3/\text{f.u.}$) to the high temperature form, γ - Li_3PO_4 ($79.42 \text{ \AA}^3/\text{f.u.}$). This is to say, pressure favours the formation of the denser polymorph.

3.2. $\text{Li}_2\text{MnSiO}_4$

The X-ray diffraction patterns of as-prepared $\text{Li}_2\text{MnSiO}_4$ (see Fig. 3) can be interpreted as a coexistence of $Pmnb$ and $P2_1/n$ $\text{Li}_2\text{MnSiO}_4$ polymorphs in a ratio 63:19 w/w. Crystalline impurities can be identified and indexed as MnO (ICSD-76086) and Li_2SiO_3 (ICSD-853). Refined lattice parameters for the majority polymorph

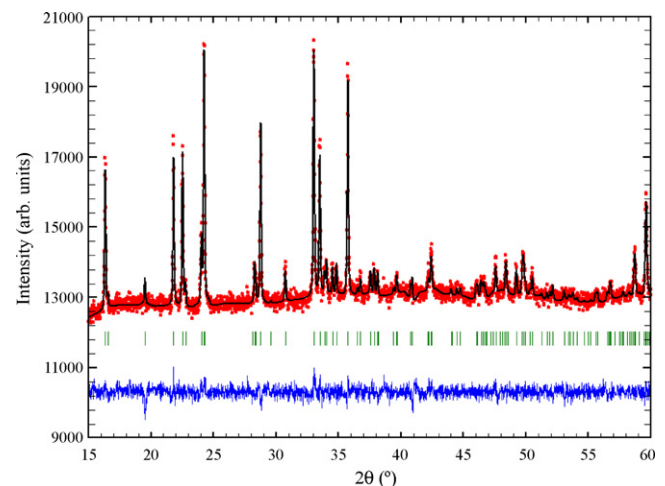


Fig. 6. Observed (red), calculated (black) XRD patterns, and their difference (blue), of as-prepared $\text{Li}_2\text{CoSiO}_4$ ($R_p = 0.46$, $R_{wp} = 0.20$, $R_B = 0.08$, $R_{exp} = 0.17$).

are listed in Table 1. Fig. 4 shows typical SAED patterns of this sample, that can be indexed based on the $Pmnb$ -cell. This result is in agreement with the SEAD characterization published by Dominko et al. [1], while the most of XRD characterizations have suggested $Pmn2_1$ as the most likely form of $\text{Li}_2\text{MnSiO}_4$.

Independently of the pressure (20, 40, 60, 80 kbar) and temperature (between 600 and 900 °C) that was applied to the as prepared $\text{Li}_2\text{MnSiO}_4$ sample, the patterns of all the HP products can be properly indexed based on the unit cell of $Pmn2_1$ - $\text{Li}_2\text{MnSiO}_4$ (see Table 1). Fig. 5 shows the Rietveld refinement of the HP- $\text{Li}_2\text{MnSiO}_4$ obtained at 60 kbar and 600 °C. The HP/HT treatment reduces the amount of Li_2SiO_3 and MnO impurities present in the as prepared sample, whereas new intensity peaks attributable to the formation of Mn_2SiO_4 appear. One can conclude that the high pressure/high temperature treatment allows to fully transform the $Pmnb$ and $P2_1/n$ polymorphs into the denser $Pmn2_1$ one; the latter remains stable at 80 kbar and temperature of 900 °C.

3.3. $\text{Li}_2\text{CoSiO}_4$

Fig. 6 shows the X-ray diffraction pattern of as-prepared $\text{Li}_2\text{CoSiO}_4$. It can be interpreted based on a cell crystallizing in the

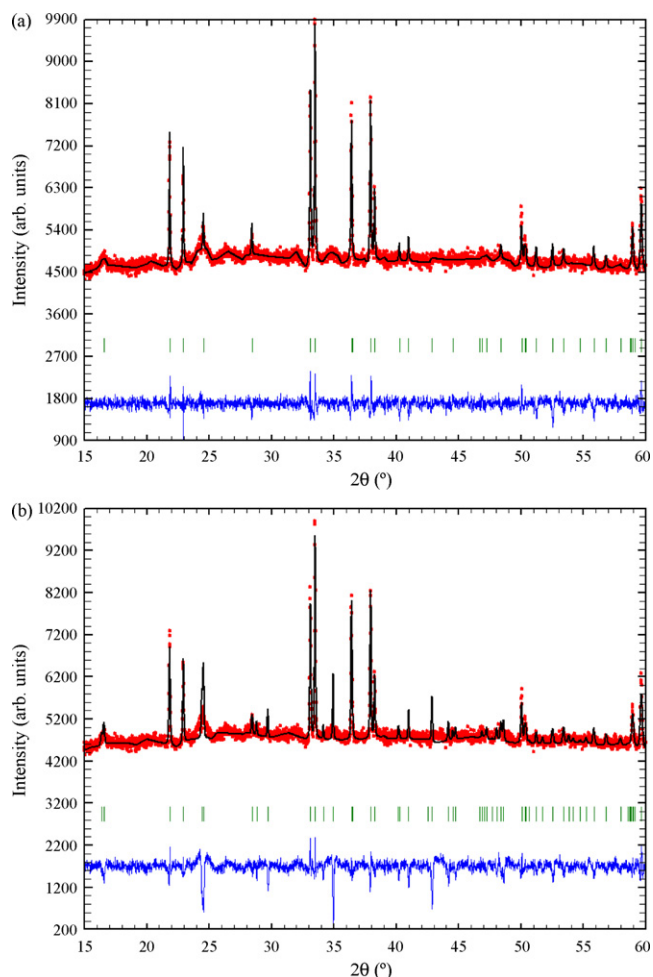


Fig. 7. Observed (red), calculated (black) XRD patterns, and their difference (blue), of HP- $\text{Li}_2\text{CoSiO}_4$ prepared at 40 kbar. (a) pattern indexed based on the $Pmn2_1$ polymorph, with refined lattice parameters $a = 6.2634(3)$ Å, $b = 5.3469(2)$ Å, $c = 4.9312(2)$ Å ($R_p = 0.62$, $R_{wp} = 0.35$, $R_B = 0.11$, $R_{exp} = 0.24$, $\chi^2 = 2.17$) and (b) pattern indexed based on the $Pbn2_1$ polymorph with refined lattice parameters $a = 6.2630(4)$ Å, $b = 10.6928(7)$ Å, $c = 4.9310(3)$ Å ($R_p = 0.65$, $R_{wp} = 0.46$, $R_B = 0.09$, $R_{exp} = 0.24$, $\chi^2 = 3.26$).

$P2_1/n$ S.G., whose refined lattice parameters are listed in Table 1. No impurities are detectable in the XRDP. Interestingly, although the existence of the $P2_1/n$ - $\text{Li}_2\text{CoSiO}_4$ polymorph was reported in the late seventies (γ - $\text{Li}_2\text{CoSiO}_4$ in Ref. [13]), to the best of our knowledge no information about the lattice parameters had been reported to date. Portions of as prepared $\text{Li}_2\text{CoSiO}_4$ were subjected to 40 and 60 kbar and 900 °C. At 40 kbar the $P2_1/n$ polymorph was transformed into a phase of orthorhombic symmetry. The profile fitting of the XRD data of this sample is shown in Fig. 7, based on the $Pmn2_1$ polymorph (Fig. 7a) and on the $Pbn2_1$ polymorph (Fig. 7b). Although both refinements are feasible, the former gives better agreement factors. Both cells have a smaller volume than the $P2_1/n$ one, ($82.55 \text{ Å}^3/\text{f.u.}$ for $Pbn2_1$, $82.57 \text{ Å}^3/\text{f.u.}$ for $Pmn2_1$ compared to $84.23 \text{ Å}^3/\text{f.u.}$ for $P2_1/n$) confirming that HP treatment favors the formation of a denser polymorph. At 60 kbar and 900 °C $\text{Li}_2\text{CoSiO}_4$ decomposes producing substantial amounts of Li_2SiO_3 . Some amount of the unreacted and partially amorphized $\text{Li}_2\text{CoSiO}_4$ is also present.

4. Conclusions

The first aim of this work is to prepare novel Li_2MSiO_4 ($M = \text{Mn, Co}$) compounds consisting on MO_6 octahedra. Samples of known Li_2MSiO_4 polymorphs (M in tetrahedral sites) were treated under high pressure/high temperature conditions. Up to a maximum pressure of 80 kbar no evidence of any novel polymorph has been observed. For $M = \text{Co}$ the material decomposed below 80 kbar, with a considerable amount of Li_2SiO_3 detectable in the XRDP. This discards the possibility of preparing novel high-pressure polymorphs. Li_3PO_4 and $\text{Li}_2\text{MnSiO}_4$ are stable at 80 kbar making appealing a further investigation up to higher pressures. The different behavior upon pressure of $\text{Li}_2\text{CoSiO}_4$ compared to $\text{Li}_2\text{MnSiO}_4$ does not come as surprise. Olivine LiMXO_4 compounds transform under pressure to a Na_2CrO_4 -like structure ($X = \text{As}$ [18]) or spinel structure ($X = \text{P}$ [19]) when $M = \text{Fe, Co}$ or Ni , while no transformation is observed for $M = \text{Mn}$. The half-close shell of Mn^{2+} ions renders more stable structures.

The second objective of this work was to elucidate the stability range of Li_2MSiO_4 polymorphs as a function of pressure. We have firstly demonstrated that pressure stabilizes the denser polymorph of the parent compound Li_3PO_4 . High-pressure experiments have been performed over $Pbmn + P2_1/n$ - $\text{Li}_2\text{MnSiO}_4$, and $P2_1/n$ - $\text{Li}_2\text{CoSiO}_4$. We have shown that these polymorphs transform to the denser $Pmn2_1$ polymorph below 40 kbar. This shows the utility of high-pressure experiments to prepare pure $Pmn2_1$ - Li_2MSiO_4 compounds starting from less dense polymorphs.

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