

三元硒化物 $\text{La}_4\text{In}_{4.66}\text{Se}_{13}$ 之合成及陽離子填佔在 Na-La-M-In-Se 系統中之研究

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摘 要

在本論文中，所有化合物都是以該比例的元素態反應物在 825°C 的溫度下合成。單晶解析的結果顯示，此些化合物的空間群皆為 *Pbam*，斜方晶系，並與兩種已知物 $\text{La}_4\text{In}_5\text{S}_{13}$ 及 $\text{Pb}_4\text{In}_2\text{Bi}_4\text{S}_{13}$ 為相同之結構。

$\text{La}_4\text{In}_{4.66}\text{Se}_{13}$ 的晶格常數為 $a = 12.434(4) \text{ \AA}$, $b = 22.168(7) \text{ \AA}$ and $c = 4.1946(12) \text{ \AA}$, $R1/wR2 = 0.0432/0.1107$ 。結構上主要是由 InSe_6 以鄰邊共享的方式連結，並在端點的地方與 InSe_4 相接形成二維的層狀結構後，再以 La-Se 的離子鍵將層與層串連起來。單晶數據的結果顯示，其中一八面體的中心位置是僅被三分之二的 In 填佔。我們分別建構三種不同的分子模型去瞭解此化合物的電子結構，結果顯示 $\text{La}_4\text{In}_{4.66}\text{Se}_{13}$ 應為一電子傳導效率不佳的半導體。

一系列的四元硒化物在以 NaCl 為助熔劑的反應中得到，如 $\text{Na}_2\text{La}_4\text{In}_4\text{Se}_{13}$ ，晶格常數為 $a = 21.36(1) \text{ \AA}$, $b = 26.39(1) \text{ \AA}$, $c = 4.151(2) \text{ \AA}$, $R1/wR2 = 0.0320/0.0650$ 。而摻雜金屬的化合物，包含 Mg、Ca、Sr、Mn、Pb 亦是在類似的反應中製備而成。此系統中的化合物都是相同的結構，藉由六個 InSe_6 八面體及兩個 MSe_6 八面體所形成的單元 $\text{M}_2\text{In}_6\text{Se}_{26}$ ，以兩個不同的方向堆疊所組成。比較金屬位置上的電子密度，我們可以了解金屬離子是根據其環境的喜好及鍵結類型與 Na、La 混合填佔在所有的金屬位置上。

Synthesis of ternary selenide $\text{La}_4\text{In}_{4.66}\text{Se}_{13}$ and cation site preference study on Na-La-M-In-Se System

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ABSTRACT

In this dissertation, the title compounds were synthesized at 825°C by stoichiometric ratios of elements. Single crystal study reveals two structure types of known compound $\text{La}_4\text{In}_5\text{S}_{13}$ and $\text{Pb}_4\text{In}_2\text{Bi}_4\text{S}_{13}$ are obtained and all crystallizes in the space group *Pbam* of the orthorhombic system.

$\text{La}_4\text{In}_{4.66}\text{Se}_{13}$ with cell dimension $a = 12.434(4) \text{ \AA}$, $b = 22.168(7) \text{ \AA}$ and $c = 4.1946(12) \text{ \AA}$, $R1/wR2 = 0.0432/0.1107$, which is mainly structured by edge shared InSe_6 octahedra with InSe_4 tetrahedra connected at the corners, forming 2-D layers linked by La-Se ionic bonding. Single crystal analysis reveals that one of the metal octahedra sites is occupied by 2/3 of In. Three molecule models were constructed to understand the electronic structure. The result indicates that the $\text{La}_4\text{In}_{4.66}\text{Se}_{13}$ should be a semiconductor with low electron transference efficiency.

A series of quaternary chalcogenides, such as $\text{Na}_2\text{La}_4\text{In}_4\text{Se}_{13}$ with cell dimension $a = 21.36(1) \text{ \AA}$, $b = 26.39(1) \text{ \AA}$, $c = 4.151(2) \text{ \AA}$, $R1/wR2 = 0.0320/0.0650$, were found in the reaction using NaCl as flux and doped by Mg、Ca、Sr、Mn、Pb in similar process. The structure of these compounds are the same, which is composed by two directional $\text{M}_2\text{In}_6\text{Se}_{26}$ units that formed by six InSe_6 octahedra and two MSe_6 octahedra. From the comparison of electron density on metal sites, the result indicates that doped metal ions are mix-occupied with Na

and La in all metal sites depending on environmental preference and types of bonding.

