

Modulated phases in the $\text{LiCdVO}_4\text{-LiCd}_4(\text{VO}_4)_3$ system. Relationships with the olivine-type structure.

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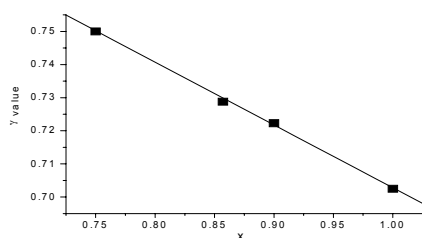
Olivine-type compounds are the subject of great interest as candidate materials for lithium-ion batteries since the discovery of insertion-deinsertion properties of lithium in LiFePO_4 [1]. The ideal formula unit of olivine-type compounds is $\text{AA}'\text{BO}_4$. The structure can be described in terms of hexagonal stacking of closed packed O_4 layers with A, A' cations and B cations in two octahedral sites and one tetrahedral site, respectively.

A solid solution $(1-x)\text{LiCdVO}_4 - x\text{Li}_{1/3}\text{Cd}_{1/3}\square_{1/3}\text{CdVO}_4$ has been observed for $0 \leq x \leq 1$. Two domains of the solid solution have been distinguished. The first one for $0 \leq x \leq 0.6$ corresponds to the LiCdVO_4 sub-structure of the Na_2CrO_4 -type [2]. For $0.7 \leq x \leq 1$ satellites peaks are observed which correspond to a modulated structure.

LiCdVO_4 and $\text{LiCd}_4(\text{VO}_4)_3$ [3] are isostructural to Na_2CrO_4 but in the case of the last compound some extra peaks have been observed in the diffraction pattern. LiCdVO_4 ($x=0$) crystallizes in Cmcm space group with $a=5.911$, $b=8.975$ and $c=6.513$ Å. In the structure the cadmium atoms occupy the octahedral site, lithium and vanadium atoms are in tetrahedral sites. The structures in the domain $0.7 \leq x \leq 1$ have been solved for $x=3/4$, $6/7$ and 1 . All these phases are modulated with an one-dimensional incommensurate $\mathbf{q}$ -vector $\mathbf{q} = \gamma\mathbf{c}^*$ and γ values of 0.75 , 0.733 and 0.703 respectively. The superspace group is $\text{Xmcm}(00\gamma)$ where X stand for $(\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})$ centring. A linear relation between the $\mathbf{q}$ -vector and the composition x has been evidenced (see figure).

According to the general formula $\text{Li}_{1-2x/3}\text{Cd}_{x/3}\square_{x/3}\text{CdVO}_4$ of the solid solution, the structures shows a different distribution of Li/Cd/ $\square$ on the tetrahedral A-type position. The main result is a strong occupation modulation of lithium and cadmium in one tetrahedral site, which can be described by a crenel function. This occupancy modulation is associated to appears together with a displacive modulations. The comparison with the structural results of the commensurate case with $x=3/4$ confirms a disordered model for the Li/Cd/ $\square$ distribution.

~~These two types of modulation induce the incommensurability of the structure.~~



[1] Pahdi, A. K., Nanjundaswamy K., S., and Goodenough, J. B.

(1997) *J. Electrochem. Soc.*, 144, 1188.

[2] Niggli A. (1954). *Acta Cryst.*, 7, 776.

[3] Ben Amara, M., PhD thesis, (1979), Université de Bordeaux 1.