

Reply to Comment on “Tuning of Photoluminescence and Local Structures of Substituted Cations in $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ Phosphors”

We are very thankful to Prof. Bogdan I. Lazoryak for his interest in our work on structure and photoluminescence tuning of $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphors¹ and his pertinent comments.² In his commentary, he raises the concern that the $\text{Sr}_2\text{Ca}(\text{PO}_4)_2$ and $\text{Ca}_{10}\text{Li}(\text{PO}_4)_7$ phases are not completely isostructural as they belong to the different symmetry groups. He suggests that the presence of the two-phase region is the reason for the nonlinear variation of the unit cell parameters. In addition, he suggests that Eu^{2+} cations cannot be located in the M4 sites.

First, we would like to start by saying that our results are reliable as they are based upon careful analysis of high quality XRD data (see Supporting Information), a type of analysis in which we have prior experience regarding the study of phase transitions and crystal structure analysis for these kinds of compounds.^{3,4} Prof. Lazoryak does not, however, have the original experimental data. As shown in Figure 1, compared with

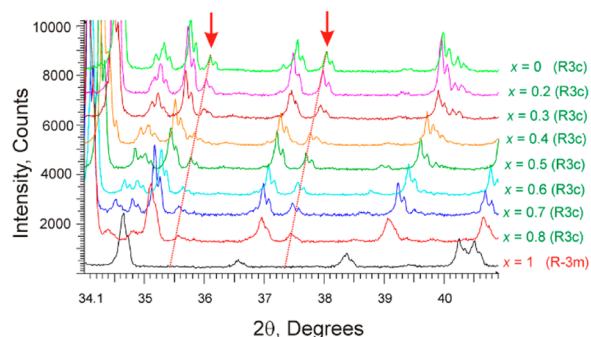


Figure 1. Partial XRD patterns ($34-50^\circ$) for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphors. Superstructure peaks of the $R3c$ phase which cannot be indexed by $R\bar{3}m$ phase are marked by red arrows. Dotted lines are plotted to guide the eye.

all powder patterns, it can be shown that the compounds with different composition ($x = 0-0.8$) have several superstructure peaks that cannot be indexed by the $R\bar{3}m$ phase. These peaks are very obvious, so we disagree that the difference between space group $R3c$ and $R\bar{3}m$ is very small. Moreover, Figure 2 being a good example, shows the powder pattern for $x = 0.8$ fitted by $R3c$ and $R\bar{3}m$ phases, respectively. It can be found that $R\bar{3}m$ is inappropriate for the composition $x = 0.8$, and the difference between $R3c$ and $R\bar{3}m$ is noticeable. On the other hand, compound $x = 1$ does not have these superstructure peaks, as depicted in Figure 1. Indeed, the powder pattern of $\text{Sr}_2\text{Ca}(\text{PO}_4)_2$ ($x = 1$) should be fitted by the $R\bar{3}m$ phase, but we fitted it by $R3c$ in our paper.¹ We agree that we made an error in our manuscript, but it does not change the main ideas and conclusions of our manuscript. It should be noted that the structures of $\text{Sr}_2\text{Ca}(\text{PO}_4)_2$ and $\text{Ca}_{10}\text{Li}(\text{PO}_4)_7$ are relatively well-known and previously published.^{5,6} Our investigations were focused on

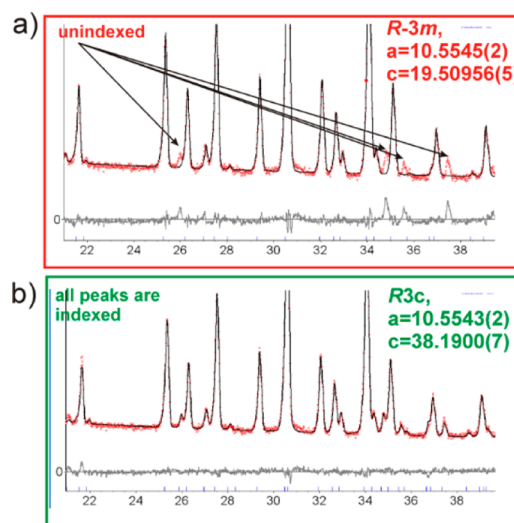


Figure 2. Partial XRD patterns ($21-40^\circ$) of the compound at $x = 0.8$ fitted by (a) $R\bar{3}m$ phase and (b) $R3c$ phase. The arrows marked the unindexed peaks owing to the incorrect choice of $R\bar{3}m$.

compounds with $x = 0.2-0.8$, as their structures were previously unknown, and we correctly define their symmetries as $R3c$. We also believe that there is a phase transition from $R3c$ to $R\bar{3}m$ in the range of $0.8-1$, but we had no points within this region; data associated with this region do not affect our results.

Second, we agree that the Rietveld refinements of some samples ($x = 0.2, 0.3, 0.4$) [Supporting Information of previous manuscript]¹ show some discrepancy with respect to the calculated and observed intensities, which may be the reason for a two-phase system. However, the Rietveld refinement of two phases does not appear to work in this case. Even if one phase has 58 refined parameters, two phases will have two times more parameters, and the number of observed reflections will stay the same. The situation is complicated by the fact that there is no peak splitting of these hypothetical two phases (Figure 3). The noticeable shift of strong peaks ($2\theta \sim 0.1^\circ$) from $x = 0$ to 1 and small fwhm of peaks ($\sim 0.07-0.15^\circ$) imply that the mix of two phases, even with similar concentrations (for example, x and $x' = x + 0.1$), should show peak splitting. However, we only observe peak broadening, meaning that these two phases should be of similar concentrations. Even if we delete the data points for the $x = 0.2, 0.3, 0.4$ data, assuming their questionable quality, and the residual red points ($x = 0, 0.5, 0.6, 0.7, 0.8, 1$), which previously had very good Rietveld refinement [Supporting Information of previous manuscript],¹ we still observe nonlinear behavior $V(x)$ (Figure 4). Therefore, the reason for nonlinearity $V(x)$ is not a

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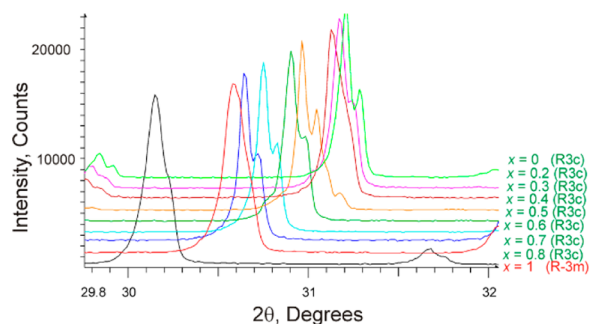


Figure 3. Partial XRD patterns (corresponding to the strongest peaks) for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphors.

two-phase system but some another property of this crystal system, which is why we have proposed this vacancy mechanism.

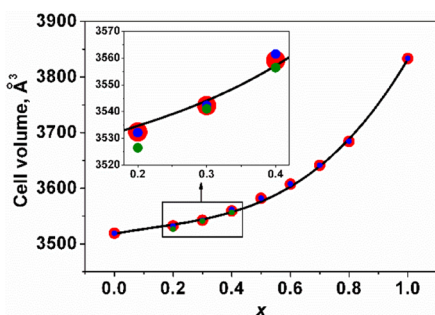


Figure 4. Cell volume dependence $V(x)$ (big red circles) obtained previously and fitted by a quadratic polynomial (black line); exclusion of $x = 0.2, 0.3$, and 0.4 points does not change nonlinear behavior of $V(x)$. Small blue circles represent cell volume of the first phase, and green circles represent cell volume of the second phase, which were obtained after Le Bail profile fitting. Inset shows a zoomed part of $V(x)$, and the small difference between cell volumes of the first and second phases is seen. Cell volume of $x = 1$ was doubled because the $R\bar{3}m$ phase has a c -axis two times smaller.

Third, based upon the suggestions of Prof. Lazoryak, we also performed simple Le Bail fitting using two phases for ($x = 0.2, 0.3, 0.4$) and using one phase for all other cases ($x = 0, 0.5, 0.6, 0.7, 0.8, 1$). The difference plots were very good (Figures 5a–i). The obtained cell volume dependence per x is shown in Figure 4. One can see that new data (blue circles depict cell volume of first phase; green circles, second phase) almost coincide with previously obtained data (big red circles), and the $V(x)$ remains nonlinear. Moreover, according to our expectations, the differences of cell volumes for the first and second phases are small, which implies a small difference between their x values. Rietveld refinement of the two phases with small differences is impossible in our case. Therefore, our previous Rietveld refinements of patterns $x = 0-0.8$ using only one phase was a good way to solve this problem, because the obtained average crystal structure can represent all observed phases (two or bigger) with small concentration differences, which exist between the samples.

Finally, we also disagree that the obtained XRD patterns could be used only to define the lattice parameters of the Le Bail method since the experimental data for these solid solution structures (9000–15000 counts) are insufficient for revealing subtle peculiarities of their structure. Decisions regarding the Rietveld refinement and especially the possibility of using the obtained data to make speculations should be found on

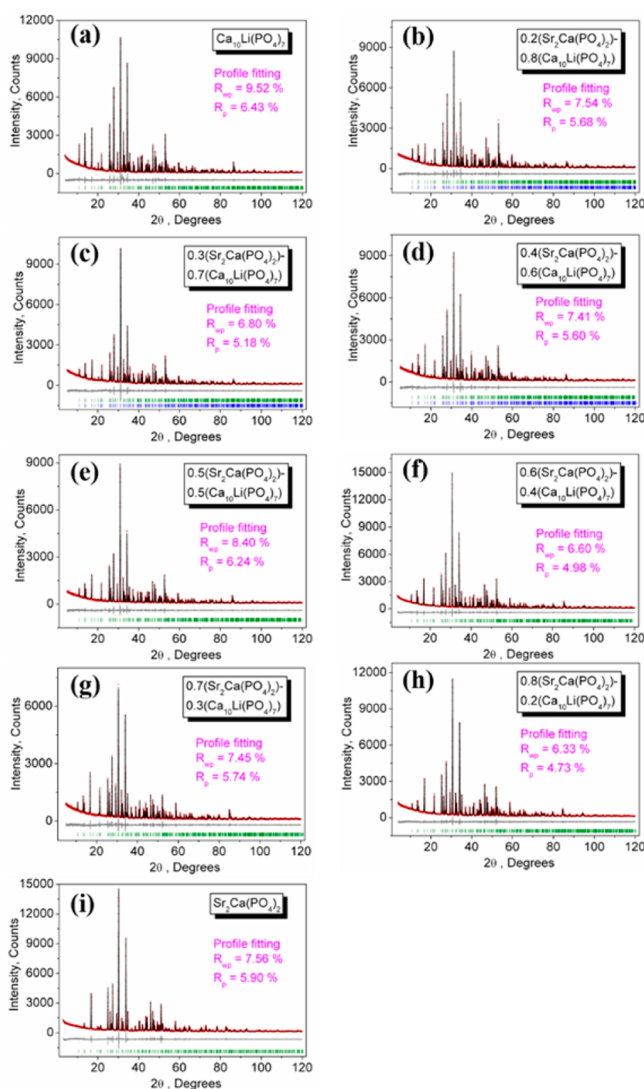


Figure 5. Difference plot of Le Bail profile fitting phases: (a) $x = 0$ by one phase $R\bar{3}c$; (b) $x = 0.2$ by two phases $R\bar{3}c$; (c) $x = 0.3$ by two phases $R\bar{3}c$; (d) $x = 0.4$ by two phases $R\bar{3}c$; (e) $x = 0.5$ by one phase $R\bar{3}c$; (f) $x = 0.6$ by one phase $R\bar{3}c$; (g) $x = 0.7$ by one phase $R\bar{3}c$; (h) $x = 0.8$ by one phase $R\bar{3}c$; and (i) $x = 1$ by one phase $R\bar{3}m$.

estimation of standard uncertainties obtained after refinement. In our case, the $d(\text{P}-\text{O})$ bond lengths have a relatively large esd ($\sigma \sim 0.015-0.03 \text{ \AA}$), and the 3σ confidential interval is wide and is comparable to the interval 0.08 \AA of ideal values $d(\text{P}-\text{O}) = 1.5-1.58 \text{ \AA}$. We therefore did not use information about $d(\text{P}-\text{O})$ bond lengths in our speculation. Sr/Ca ion occupation has smaller esd's ($\sigma \sim 0.008-0.02$) and a larger interval of possible values $\text{occ} = 0 \dots 1$. The obtained occupation values, therefore, have good reliability, and we used them in our speculations. Moreover, their behavior with respect to x showed a good trend without large random oscillations. On the other hand, the low reliability of Li localization prevented us from proving or disproving the disordering of Li ions by two close positions in $\text{Ca}_{10}\text{Li}(\text{PO}_4)_7$. We used the simplest model of isostructural compounds $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ with one ordered K ion⁷ and put Li ion in this $6a(0, 0, z)$ site. The occupation of Li was fixed according to the chemical formula without any refinements. We did not use Eu^{2+} ions in our refinement due to the low doping concentration level in comparison with the σ of obtained occupations.

In conclusion, we are very grateful to Prof. Lazoryak for showing us one mistake in the choice of a space group of the compound with $x = 1$. It should be $R\bar{3}m$, instead of $R3c$. This mistake does not influence the final results and conclusions because our investigations are focused on unknown compounds with $x = 0.2-0.8$. All compounds with $x = 0-0.8$ were correctly assigned to $R3c$ symmetry due to the existence of the well-developed system of superstructure peaks. These compounds cannot be a mixture of two phases ($R3c + R\bar{3}m$) because of the absence of main peak splitting. Some peak broadening of compounds with $x = 0.2, 0.3, 0.4$ can be described by two $R3c$ phases ($R3c + R3c$) with a small difference of x , but their structures cannot be refined simultaneously in our case. Therefore, we suggest that Rietveld refinement using one average phase is a good way to solve this problem. Moreover, the nonlinear behavior of cell volumes $V(x)$ could not be explained by two phase systems ($R3c + R3c$), and the proposed vacancy mechanism remains valid. Refinements of structural models ($x = 0.2-0.8$) do not give very precise coordinates of P and O ions, but the occupancies of Sr/Ca ions is reliable, and we believe that all these parameters are worthy to be shown.

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■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.7b01261](https://doi.org/10.1021/acs.chemmater.7b01261).

Raw XRD data for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor with $x = 0$ (PDF)

Raw XRD data for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor with $x = 0.2$ (PDF)

Raw XRD data for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor with $x = 0.3$ (PDF)

Raw XRD data for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor with $x = 0.4$ (PDF)

Raw XRD data for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor with $x = 0.5$ (PDF)

Raw XRD data for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor with $x = 0.6$ (PDF)

Raw XRD data for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor with $x = 0.7$ (PDF)

Raw XRD data for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor with $x = 0.8$ (PDF)

Raw XRD data for $x\text{Sr}_2\text{Ca}(\text{PO}_4)_2-(1-x)\text{Ca}_{10}\text{Li}(\text{PO}_4)_7:\text{Eu}^{2+}$ phosphor with $x = 1.0$ (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

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