Reduced Local Symmetry in Lithium Compound Li$_2$SrSiO$_4$ Distinguished by an Eu$^{3+}$ Spectroscopy Probe

Lei Chen,* Peng Cheng, Zhao Zhang, Liangrui He, Yang Jiang, Guobao Li,* Xiping Jing, Yan’guang Qin, Min Yin, Ting-Shan Chan, Bin Hong, Shi Tao, Wangsheng Chu, Zhi Zhao, Haiyong Ni, Holger Kohlmann, and Oliver Oeckler*

Research on lithium compounds has attracted much attention nowadays. However, to elucidate the precise structure of lithium compounds is a challenge, especially when considering the small ions that may be transferred between the interstitial voids. Here, the discovery of reduced local symmetry (symmetry breaking) in small domains of Li$_2$SrSiO$_4$ is reported by employing Eu$^{3+}$ as a spectroscopic probe, for which X-ray, neutron, and electron diffraction have confirmed the average long-range structure with the space group $P\overline{3}1\overline{2}1$. However, luminescence shows a lower local symmetry, as confirmed by the extended X-ray absorption fine structure. By considering the reduced symmetry of the local structure, this work opens the door to a new class of understanding of the properties of materials.

Energy represents a better life for generations to come. For that lithium compounds have never attracted so much attention in the past until recently, driven by the requirements of energy-storage and energy-saving applications, such as Li-ion batteries (LBs) and light-emitting diodes (LEDs). Aiming at these applications, lithium-containing silicates with the general formula ABC$_2$X$_4$, such as Li$_2$SrSiO$_4$,[1–11] Li$_2$EuSiO$_4$,[12] Li$_2$BaSiO$_4$,[13] Li$_2$CaSiO$_4$,[14] Li$_2$MgSiO$_4$,[15] Li$_2$ZnSiO$_4$,[15] Li$_2$FeSiO$_4$,[16] Li$_2$CoSiO$_4$,[17] and Li$_2$MnSiO$_4$[17,18] have been extensively investigated. Among them, Li$_2$SrSiO$_4$ is a desirable host for LED phosphors, including the yellow emission of Eu$^{2+}$,[5–7] the blue emission of Ce$^{3+}$,[8] the white co-emission of Ce$^{3+}$ and Eu$^{2+}$,[9–11] and the multiband emission of Ce$^{3+}$ and Pr$^{3+}$ for plant growth,[3] in Li$_2$SrSiO$_4$ and a promising optical coating for the cathodes of LBs.[1]

In 1998, Haferkorn first determined the crystal structure of Li$_2$EuSiO$_4$ and considered it isostructural with Li$_2$SrSiO$_4$.[12] Later, several scholars carried out structure refinement of Li$_2$SrSiO$_4$ by taking Li$_2$EuSiO$_4$ as a starting model, confirming that Li$_2$SrSiO$_4$ crystallizes into the trigonal space group $P\overline{3}1\overline{2}1$. However, luminescence shows a lower local symmetry, as confirmed by the extended X-ray absorption fine structure. By considering the reduced symmetry of the local structure, this work opens the door to a new class of understanding of the properties of materials.

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significantly from those expected based on the ionic radii and bond valence sums, and the $\text{[SiO}_4\text{]}$ polyhedron presents an extremely distorted structure with a much larger eccentric distance and sphericity than expected. In 2010, Fukuda also revised this structure, based on synchrotron data, with space group $P\bar{3}121$. Nevertheless, the structural model of space group $P\bar{3}121$ (noted as the $P\bar{3}121$ model hereafter) possesses one Sr$^{2+}$ site and thus cannot interpret the luminescence properties of Eu$^{3+}$ and Ce$^{3+}$ in Li$_2$SrSiO$_4$ in a straightforward way.

Structures are always fundamental to understanding material properties. However, the performance and mechanisms of materials are generally elucidated based on a static structure in regards to a standard structural model. However, in some situations, dynamic processes are not ignorable, such as the charging and recharging processes in batteries and the popular carburizing, boronizing, and natural aging treatments used to enhance the mechanical strength of steels, due to the transfer of small atoms, such as B, C, and N, and defects from one site to another. Li$^+$ is the smallest and lightest alkali metal ion and can easily be incorporated into the interstitial sites in crystal lattices. The mobility and static displacement of small atoms may result in characteristic local symmetry breaking due to tiny distortions in the structure that do not propagate over long-ranges.

Symmetry is a beautiful and harmonic natural concept, but much of the changes in the world have been caused by symmetry breaking, including the origin of species. On one hand, the development of modern physics is filled with such violation of parity laws in weak interactions, CP violation in the decay of neutral K-mesons, spontaneous symmetry breaking in subatomic physics related to the Higgs mechanism, and spatial-parity-symmetry breaking of quantum phase transitions. Symmetry breaking does not imply that no symmetry is present; rather, the initial symmetry is lowered to a subgroup. Phase transitions and spontaneous symmetry breaking are widespread topics in condensed matter physics, and studies on spatial symmetry have greatly improved our understanding of materials. Yet, finding an observable quantity that is hidden under the superfine structure is still a big challenge in experiments.

According to Lee (the Nobel Laureate in Physics in 1957), “the root of all symmetry principles lies in the assumption that it is impossible to observe certain basic quantities.” In contrast, any discovery of symmetry breaking suggests the existence of a specific measurement. According to symmetry breaking, forbidden transitions of electrons may occur due to a perturbation in the Hamiltonian. Therefore, fluorescence spectra originating from parity violation promisingly provides a probe for hyperfine interactions. In 1984, Zhang calculated the values of the Stark energy levels for $^1F_3$ splitting and the $^2D_{5/2}-^2F_3$ transitions of the $P$ configuration in 32 point groups, with consideration of the odd crystal field in Judd–Ofelt theory, and reported that the relationship between luminescence spectra and crystal structures could be used to investigate the local environments in crystal structures by doping trace amounts of Eu$^{3+}$ (or Sm$^{3+}$) into compounds as a probe. Later, this method was developed by improving the calculations for the electronic states and designing charts via the work of Binnemans, Görler-Walrand, and Tanner to aid in the assignment of point symmetry. In addition to Eu$^{3+}$, other rare-earth ions, such as Dy$^{3+}$ and Sm$^{3+}$, have also been used as structural probes to study local site symmetry, but comparatively, Eu$^{3+}$ is the best probe due to the large splitting of the $^2F_5/2$ and $^2F_7/2$ levels of Eu$^{3+}$ in the visible wavelength region, which results in easily identified emission peaks. Moreover, the development of optical laser spectroscopy technologies have promisingly provided ultrafast-response, high-intensity, and high-resolution tools for experimental studies.

Society longs to find the beauty of a structure. Therefore, in this work, we report the discovery of symmetry breaking in small domains of Li$_2$SrSiO$_4$. Two Sr$^{2+}$ sites in the Li$_2$SrSiO$_4$ structure with $P\bar{3}121$ symmetry are broken into $C$ subgroups, as distinguished by employing Eu$^{3+}$ as a spectroscopic probe. The difference between the two sites is 0.2 nm for the Eu$^{3+}^5D_0^0-^7F_0$ transition, which is out of the discernable range of X-ray, electron and neutron diffraction, and nuclear magnetic resonance measurements but is sensitive to Eu$^{3+}$ fluorescence spectra. This work demonstrates a facile, but powerful, optical tool to probe hyperfine structures and opens a door to identify new material properties and mechanisms by considering their reduced symmetry. Justifiably, symmetry breaking will not only exist in Li$_2$SrSiO$_4$ but also in other lithium compounds. Thereby, this discovery represents a landmark in exploring hyperfine structures with subgroups, which will improve our comprehension of modern physics and existing philosophy.

The XRD patterns of Ce$^{3+}$, Eu$^{3+}$, and Eu$^{3+}$-doped Li$_2$SrSiO$_4$ shown in Figure S1 in the Supporting Information, match well with those of Li$_2$EuSiO$_4$ (JCPDS 07-0120). Based on their ionic radii and charge balance, Eu$^{3+}$ (103 pm) and Eu$^{2+}$ (109 pm) should replace Sr$^{2+}$ (112 pm) in the blue-emitting Li$_2$SrSiO$_4$:Ce$^{3+}$ and yellow-emitting Li$_2$SrSiO$_4$:Eu$^{2+}$ phosphors. Eu$^{3+}$ should also occupy the Sr$^{2+}$ site in Li$_2$SrSiO$_4$ despite its smaller radius (95 pm), as is known, e.g., from Eu$^{3+}$-doped Zn$_2$SiO$_4$ or Sr$_5$Nb$_2$O$_{12}$ pervoskites. Although a minority of the sites may be occupied, the luminescence of Eu$^{3+}$ may be used as a spectroscopic probe for the symmetry of the initial coordination of Sr$^{2+}$ in Li$_2$SrSiO$_4$.

The asymmetrical shapes of the spectra in Figure S2a,b in the Supporting Information suggest that the emission peaks of Li$_2$SrSiO$_4$:Ce$^{3+}$ and Li$_2$SrSiO$_4$:Eu$^{2+}$ comprise more than one peak each, as can be observed in previous reports. These spectra can be fit with two Gaussian functions (Figure S2a, b). In the Supporting Information, for Ce$^{3+}$, the doublet peaks can be attributed to transitions from the lowest 5d excited state to the ground substates of $^2F_{7/2}$ and $^2F_{5/2}$ (degenerate). However, this conclusion is not possible for Eu$^{3+}$ because there is no spin-orbit splitting for the $^5S_{5/2}$ ground state of Eu$^{3+}$. Nevertheless, emission peaks originating from different environments around Eu$^{2+}$ cannot be excluded. However, there is only one Sr site in the P$\bar{3}121$ model of Li$_2$SrSiO$_4$. To clarify the recognition of the spectral assignment, site occupation, and energy transfer of Ce$^{3+}$ and Eu$^{3+}$ in Li$_2$SrSiO$_4$, an accurate crystal structure should be confirmed first. An exact crystal structure is helpful for understanding the intrinsic properties of a material and further inspiring new applications.
Figure 1. Low-temperature emission and excitation spectra of Li2SrSiO4:Eu3+. a) Full-spectrum emission under 393 nm excitation at 10 K, measured with a Fluorolog-3-Tau spectrometer; b) the 5D0-7F0 transitions for the 5D0-7F1 (586 nm) and 5D0-7F2 (611 nm) emission; c) the 5D0-7F1 emission excited at 526.5 nm and the 7F0-5D1 excitation by monitoring at 589.3 nm; d) the 5D0-7F1 emission by exciting the 5D2 level at 464.3, 464.7, and 466.0 nm, respectively. (b–d) were measured with an OPO at 20 K.

Figure 1a presents the full-level 5D0-7FJ (J = 0, 1, 2, 3, and 4) emission spectra of Li2SrSiO4:Eu3+ with a nominal composition of Li2Sr0.995Eu0.005SiO4. The electric dipole transition of 5D0-7F2 is parity-forbidden, but it can potentially occur in a noninversion site by mixing with the opposite component. If allowed, its intensity would be far stronger than the intensity of the magnetic 5D0-7F1 transition. Therefore, the strong 5D0-7F1 emission in Figure 1a should come from Eu3+ that occupies an inversion or approximate inversion site. However, the Wyckoff positions 3d[12] (or 3i[19]) of Sr in the P3121 model have noninversion symmetry.

Figure 1b presents the 5D0-7F0 transition as measured with an optical parametric oscillator (OPO) at 20 K. One peak at 579.2 nm can be observed by monitoring the 5D0-7F1 emission at 611 nm, while two peaks at 579.2 and 579.4 nm can be observed by monitoring the 5D0-7F1 emission at 586 nm. Theoretically, the number of peaks for the Eu3+ 5D0-7FJ transition will be no more than 2J + 1, where J is the total angular momentum. Thus, the number of peaks for the 5D0-7F0 transition at each site, which is strictly forbidden by parity and spin rules due to ΔJ = 0 for the transition from J = 0 to J = 0, should be no more than 1. Two peaks for the 5D0-7F0 transition can be observed in Figure 1b, indicating the existence of two different environments of Eu3+ in Li2SrSiO4.

In addition to detection the number of sites, site symmetry could be probed by the 5D0-7F1 transition, for which the splitting strongly depends on the symmetry. In the P3121 model, the Sr2+ at the Wyckoff 3a[12] (or 3i[19]) position has C2 symmetry. Thus, the 5D0-7F1 emission should have 3 peaks if only one Sr2+ site with C2 symmetry exists in Li2SrSiO4.[39–42] However, six peaks, for both the 5D0-7F1 emission and the 7F1-5D0 excitation, are observed in Figure 1c. These peaks may be attributed to two different centers (S1 and S2), each with triplet emission. More than 3 peaks for the 5D0-7F1 emission are observed upon exciting the 5D2 level at 464.3, 464.7, and 446.0 nm, as shown in Figure 1d, where the relative luminescence intensities of the two centers change with changing excitation wavelength, indicating multiple paths of energy relaxation from the 5D2 to 5D1 levels. From the above results, we can conclude that two different environments for Eu3+ exist in the crystal lattice of Li2SrSiO4.

The luminescence spectra suggest more than one local environment for Eu3+. To analyze this apparent disparity, the long-range structure of Li2SrSiO4 was studied with X-ray diffraction (XRD), synchrotron X-ray diffraction (SXRD), and neutron diffraction (ND). By decreasing the symmetry of the P3121 model, a hypothetical model with the translationengleiche subgroup C2 was derived and tentatively refined. No significant differences between the refined structures in the C121 and P3121 space groups were found, either in the XRD or in the ND data (Figure 2a–d).

Systematically absent Bragg reflections of P3121, such as the 001 and 002 diffractions, are allowed in C121 but were not
observed in the XRD (Figure 2a,b), SXRD (Figure S3a,b, Supporting Information), and ND patterns (Figure 2c,d). Details regarding the comparison of the \( \text{C}_2 \) and \( \text{P}_3 \text{1}_2 \text{1} \) models are included in Figures S4 and S5 in the Supporting Information.

To check for possible phase transitions at low temperature, X-ray diffraction data were collected at \( 12 \text{ K} \leq T \leq 295 \text{ K} \) and analyzed by Rietveld refinement. However, no new reflection peaks occurred, and no splitting or broadening of the reflection

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**Figure 2.** The Rietveld refinement of the crystal structure of \( \text{Li}_2\text{SrSiO}_4 \) with initial models in space groups a,c) \( \text{C}_2 \) and b,d) \( \text{P}_3 \text{1}_2 \text{1} \) based on a,b) X-ray diffraction and c,d) neutron diffraction; c,d) the second row of Bragg markers belongs to the secondary phase (1.4(1) wt%) of \( \text{SrCO}_3 \) identified in the neutron diffraction data; e,f) the selected area electron diffraction patterns ([03\( \overline{1} \)]) and [350] zone axes) of \( \text{Li}_2\text{SrSiO}_4 \).
peaks was observed. Except for a slight lattice parameter decrease with decreasing temperature (Table S1, Supporting Information), which can be attributed to regular thermal expansion effects, no significant changes in the crystal structure were detected. Therefore, we can conclude that no phase transition occurs down to 12 K and that the crystal structure is best described by the model of space group $P3_121$ for all investigated temperatures. Details for the methodology of the XRD, SXRD, and ND Rietveld refinement are given in Figures S3–S5 and Table S2 in the Supporting Information.

Figure 2e presents the selected area electron diffraction (SAED) pattern of the [03̅1] zone axis, which can be perfectly simulated with both the $C2$ and the $P3_121$ models (Figure S6, Supporting Information). For space group $P3_121$, kinematic theory only allows for 00l reflections with $l = 3n$, but these reflections may increase in intensity via dynamic electron diffraction. Nevertheless, the 003 peak intensity is much stronger than that of the other peaks in the [350] pattern (Figure 2f). In other words, Figures 2c,f shows that there is no superstructure with an enlarged unit cell, which could be another explanation for the multiple independent sites without lowering the point symmetry.

Solid-state nuclear magnetic resonance (NMR) is sensitive to the local chemical environments of Li and Si atoms. In the $C2$ model, there are three sites of Li and two sites of Si, whereas there is only one site of Li and Si in the $P3_121$ model (Table S2, Supporting Information). However, only one type of chemical environment for Li and Si can be clearly discriminated in Figure 3, in accordance with the $P3_121$ model. The chemical shifts of the $^7$Li and $^{29}$Si resonances are 0.5842 and −68 ppm, respectively, and the twin peaks at −98.3730 ppm and −94.2838 ppm are the first two and the second two spinning sidebands of $^7$Li. Since different sites can have the same chemical shift, the Li- and Si-NMR results are inconclusive. Therefore, the NMR data are consistent with the higher symmetry, but they cannot exclude the lower symmetry.

Next, the local structure was examined with extended X-ray absorption fine structure spectroscopy (EXAFS) to obtain information on the local coordination numbers, interatomic distances and possibly structural disorder. The Sr K-edge EXAFS spectrum and its transformation in K-space are shown in Figures 4a,b, respectively. Starting from the $C2$ and $P3_121$ models that were hypothesized above and their 2 and 1 Sr-atom sites, respectively, all 8 Sr–O bonds of the first coordination sphere of Sr cannot be fit at one time due to the large variations in the bond lengths. Instead, fitting was performed by classifying the 8 Sr–O bonds into two groups: a shorter group and a longer group. As shown in Figure 4c,d, the experimental curve with a main peak at 2.1 Å (no phase correction) can be more perfectly fit by the two sites of the $C2$ model than by the $P3_121$ model. In Figure 4c,d, the strongest peak at ≈2.1 Å in R-space can be considered to correspond to the Sr–O bonds, and the second peak at 3.0 Å possibly corresponds to the main Sr–Si bond. The difference between the distances of the Fourier transform (FT) peaks in R-space and the real bond lengths is ≈0.5 Å for the first FT-EXAFS shell of most metal–oxygen bonds. The real length of the Sr–O bonds can be obtained by fitting the experimental FT-EXAFS curve. Table S3 in the Supporting Information gives the fitting results. As shown in Table S3 in the Supporting Information, the average lengths of the 8 Sr–O bonds in the $P3_121$ model are close to those in the $C2$ model, including both of the shorter Sr–O1 bonds (2.53 ± 0.02 Å for $C2$; 2.54 ± 0.02 Å for $P3_121$) and the longer Sr–O2 bonds (2.67 ± 0.02 Å for $C2$; 2.70 ± 0.02 Å for $P3_121$); the disorder factors of these bonds are within a reasonable range. When fit with the $C2$ model, the coordination number for the shorter and longer groups are both 4.0, and the total sum, 8.0, is consistent with the above results from XRD and SXRD; when fit with the $P3_121$ model, however, the coordination number for the shorter and longer groups are both 3.7, and the total sum, 7.4, is far below the coordination number, 8.0, resolved from the XRD and SXRD results. Therefore, the fit from $C2$ symmetry gives a more reasonable coordination number of $N = 8.0$, which is consistent with the crystal structure. Based on the coordination numbers (Table S3, Supporting Information), the analyses of the EXFAS spectra indicates a structure with two different environments of Sr in Li$_2$SrSiO$_4$ (as is theoretically possible for the $C2$ model).

XRD, SXRD, ND, and SAED data indicate that the long-range average structure of Li$_2$SrSiO$_4$ does not deviate significantly from that of the $P3_121$ model, whereas the cryogenic spectra of Eu$^{3+}$ demonstrate that more than one Eu$^{3+}$ site has to be taken into account. The diffraction data give an average structure model that projects the structure into a single unit cell, which requires a periodicity over an area larger than the coherence length of the radiation used. If local distortions are not long-range ordered, they do not influence the space group assignment.

![Figure 3](image-url)
The multiple $^5D_0 - ^7F_j$ transitions of Eu$^{3+}$, either allowed or forbidden, are determined by the local symmetry. The cryogenic spectra of Eu$^{3+}$ suggest that more than one Eu$^{3+}$ site has to be considered. To explore the reason for the electronic structure, the charge deformation density of Li$_2$SrSiO$_4$ was obtained from first-principles calculation as shown in Figure 5, in which the blue color (negative value) indicates the loss of electrons and the red color (positive value) denotes gaining electrons. Although they are rather similar to each other, three distinct areas of electron density (labeled as hf-1, hf-2, and hf-3 for the hyperfine structures) can be distinguished in Figure 5a for the C$_2$ model, whereas these patterns merge (labeled as gb-1, gb-2, and gb-3 for the gobbets) in Figure 5b for P$_3$121. It seems that the spectroscopic probe of Eu$^{3+}$ also interacts with the shape of the electron density, a further aspect of the local structure in addition to its symmetry. The ab initio geometry optimization shows that the final enthalpies for C$_2$ ($-9251.08$ eV) and P$_3$121 ($-9250.79$ eV) are very close to each other. Because the lower symmetry C$_2$ model has a lower energy, local symmetry breaking seems to be possible due to the small energy barrier.

Finally, we discuss the origin of symmetry breaking in Li$_2$SrSiO$_4$. Its crystal structure consists of [LiO$_4$] and [SiO$_4$] tetrahedrons. The periodic arrangement of three [SiO$_4$] and six [LiO$_4$] tetrahedrons forms a channel. Thus, the crystal structure of Li$_2$SrSiO$_4$ may be described by incorporating Sr atoms into the framework channels. There is one type of channel in P$_3$121 (Figure 6a) but two in the hypothetical C$_2$ model (Figure 6b). For instance, previous research has shown that with 20% of the Sr substituted with Ba, the structure of Li$_2$[Sr$_{0.8}$Ba$_{0.2}$]SiO$_4$ changes from trigonal to hexagonal, indicating that Li$_2$SrSiO$_4$ has a nonrigid structure. The tiny differences between the channels may lead to symmetry breaking from P$_3$121 into C$_2$ (i.e., the symmetry breaking from one channel into two channels) since the superposition of local deviations results in P$_3$121 symmetry, described in Figure 6a,b. Figure 6c shows that by sharing Li–O bonds, the Sr atoms are
located in different channels. Additionally, in either the C2 or the P3\(_{2}1\) model, all the Sr atoms are coordinated by 8 neighboring atoms, as shown in Figure 6d. For the comparison of the initial coordination of Sr with O and the Sr–O bond lengths in the C2 and P3\(_{2}1\) models, based on XRD data, the bond lengths of Sr1–O range from 2.553 to 2.691 Å, and Sr2–O range from 2.567 to 2.757 Å in the C2 model, wherein the variation amplitudes of the Sr1–O and Sr2–O bonds are 0.138 and 0.190 Å, respectively. However, the variation range of the Sr–O bond length in the P3\(_{2}1\) model is as small as 0.077 Å, changing from 2.576 to 2.653 Å. Because the effects of the surface, interface, crystal defects, etc., are always unavoidable, they cause a wide variation in the Sr–O bond lengths, which breaks the local symmetry of the Sr site in the P3\(_{2}1\) model, resulting in the appearance of two Sr sites in the C2 model.

By neglecting the minor differences in the local environments of the same types of atoms, including Li, Sr, Si, and O, the C2 structural model of Li\(_2\)SrSiO\(_4\) can be approximated as the P3\(_{2}1\) model, which follows the same principle for ignoring higher order terms in the Taylor series expansion in mathematics. However, the results achieved in this work by employing Eu\(^{3+}\) as a spectroscopic probe suggest that the difference between Sr1 and Sr2 in Li\(_2\)SrSiO\(_4\) is non-negligible, as discussed above, regarding perturbations to the Hamiltonian of the system energy. This work not only distinguishes the hyperfine structures of Li\(_2\)SrSiO\(_4\) but also presents a facile optical tool for detecting local structures and, more importantly, helps to explain crystal structures at the subgroup symmetry level. These discoveries will produce far-reaching implications for understanding the properties and mechanisms of materials.

In summary, the phenomenon of a local structure with reduced symmetry, i.e., symmetry breaking, was discovered in Li\(_2\)SrSiO\(_4\) by employing Eu\(^{3+}\) as a spectroscopic probe. The X-ray, synchrotron X-ray, and neutron diffraction results show that the long-range average structure of Li\(_2\)SrSiO\(_4\) is consistent with the symmetry of space group P3\(_{2}1\). However, the cryogenic spectra of Eu\(^{3+}\) suggest a lower local symmetry with the C2 space group. A comparison of the electron diffraction and NMR data suggest the presence of the P3\(_{2}1\) model but cannot exclude the possibility of the C2 model. Nevertheless, the Sr K-edge EXAFS confirms that the local environment deviates from that of the P3\(_{2}1\) model but is similar to that of the C2 model. All of these evidences indicate that Li\(_2\)SrSiO\(_4\) exists in a medium possessing characteristic symmetry in space group P3\(_{2}1\), for its long-range structure and a lower symmetry local structure in space group C2. One site of Sr exists in P3\(_{2}1\),
while two sites of Sr exist in the hypothetical C2 model. All the Sr atoms are eightfold coordinated irrespective of the symmetry model. Two sites of Sr could rationally explain the photoluminescent properties of Eu$^{3+}$ and Eu$^{2+}$ in Li$_2$SrSiO$_4$. The resolution of the Eu$^{3+}$ 5D$_0$→7F$_0$ emission for distinguishing the two sites of Sr$^{2+}$ is 0.2 nm. Therefore, the powerful ability of a Eu$^{3+}$ spectroscopic probe for detecting local hyperfine structures has been demonstrated; moreover, this work opens the door to elucidating the properties of lithium compounds by considering the reduced symmetry of the local structures. These results will produce far-reaching implications for characterizing material structures and properties.

**Experimental Section**

Samples were synthesized via a two-step solid-state reaction. Initially, Li$_2$SrSiO$_4$ was synthesized from SrCO$_3$ (AR), Li$_2$CO$_3$ (AR), and SiO$_2$ (99%). The residual SrCO$_3$ in the final compound that had not been fully reacted was identified from ND in Figure 2c,d. Later, the samples were synthesized from SrO (AR), Li$_2$O (AR), SiO$_2$ (99%), Eu$_2$O$_3$ (99.99%), and CeO$_2$ (99.99%) sources via the following process. First, stoichiometric amounts of the raw materials with a 3% excess of Li were thoroughly ground, and the mixture was heated at 500 °C for 2 h in air. Then, the mixture was ground again and sintered at 850 °C for 8 h. The blue-emitting Li$_2$SrSiO$_4$:Ce$^{3+}$ and yellow-emitting Li$_2$SrSiO$_4$:Eu$^{2+}$ phosphors were reacted under a 90% N$_2$ + 10% H$_2$ reductive atmosphere, and the red-emitting Li$_2$SrSiO$_4$:Eu$^{3+}$ phosphor was obtained in air. Conventional XRD was measured using a Rigaku D/Max-II A diffractometer with an X-ray wavelength of 1.5418 Å. SXRD was recorded on a high-energy X-ray diffraction beamline SPS2B1 of a Spring-8 in Japan with an X-ray wavelength of 0.6888 Å. The neutron diffraction was collected on a D20 diffractometer at the Institute Laue-Langevin in Grenoble, France. The programs of GSAS[53] and FullProf Suite[53] were used to perform XRD, SXRD, and ND Rietveld refinement. Low-temperature PL spectra at 10 K were collected with a Fluorolog-3-Tau (Jobin Yvon) spectrometer. High-resolution (~0.02 nm) PL spectra were recorded using an OPO equipped with a tunable laser system with a pulse duration of 7 ns at a 20 Hz repetition rate over an excitation wavelength range of 410–2200 nm. The electron diffraction pattern was recorded on a JEOL-2010 transmission electron microscope operating at 200 kV with a camera length of 80 cm. The solid-state MAS NMR spectra of $^7$Li and $^{29}$Si were collected on a Bruker Avance-III, 400 MHz NMR instrument. The Sr K-edge EXAFS was collected at the 01C1 beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The EXAFS data were fit using the FEFF8lite program. The ab initio geometry optimization and first-principles calculations of the charge deformation density were performed using the CASTEP module of Materials Studio 7.0.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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Note: The fourth affiliation was updated on August 21, 2019 after initial online publication.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

crystal structures, Eu$^{3+}$ spectroscopy probes, lithium compounds, luminescence, symmetry breaking

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