

Electron density distribution and crystal structure of lithium strontium silicate, $\text{Li}_2\text{SrSiO}_4$

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Crystal structure of $\text{Li}_2\text{SrSiO}_4$ was reinvestigated by laboratory X-ray powder diffraction. The title compound was trigonal with space group $P3_121$, $Z=3$, unit-cell dimensions $a=0.502\ 281(4)$ nm and $c=1.245\ 520(8)$ nm, and $V=0.272\ 129(3)$ nm³. The initial structural model was derived by the direct methods and further refined by the Rietveld method. The maximum-entropy method-based pattern fitting (MPF) method was used to confirm the validity of the structural model, in which conventional structure bias caused by assuming intensity partitioning was minimized. The final reliability indices calculated from MPF were $R_{\text{wp}}=8.04\%$, $S=1.22$, $R_{\text{p}}=6.01\%$, $R_{\text{B}}=1.50\%$, and $R_{\text{F}}=0.66\%$. Atomic arrangements of the final structural model were in excellent agreement with the three-dimensional electron-density distributions determined by MPF. © 2010 International Centre for Diffraction Data. [DOI: 10.1154/1.3308570]

Key words: lithium strontium silicate, X-ray powder diffraction, Rietveld method, maximum-entropy method, electron-density distributions

I. INTRODUCTION

Eu^{2+} -activated lithium strontium silicate ($\text{Li}_2\text{SrSiO}_4$) exhibits an intense emission peak from yellow to orange-red under a broad excitation band of 400 to 470 nm, and hence attempts have been made to develop white light-emitting diodes (LEDs) through the integration of blue LED chips (Saradhi and Varadaraju, 2006; Zhang *et al.*, 2008; He *et al.*, 2008; Kulshreshtha *et al.*, 2009a, 2009b). The $\text{Li}_2\text{SrSiO}_4:\text{Eu}^{2+}$ -coated LED showed improved red emission compared to the commercial YAG: Ce^{3+} -coated LED.

Haferkorn and Meyer (1998) determined the crystal structure of $\text{Li}_2\text{EuSiO}_4$ [space group $P3_121$, $Z=3$, and unit-cell dimensions $a=0.502\ 70(5)$ and $c=1.2470(2)$ nm] by single crystal X-ray diffraction. They also reported the unit-cell dimensions of $\text{Li}_2\text{SrSiO}_4$ [$a=0.502\ 59(4)$ and $c=1.2471(1)$ nm] to conclude that these two compounds are isotypic. Recently, Saradhi and Varadaraju (2006) determined the crystal structure of $\text{Li}_2\text{SrSiO}_4$ from laboratory X-ray powder diffraction (XRPD) data by taking $\text{Li}_2\text{EuSiO}_4$ as the initial structural model. The reliability indices of the Rietveld refinement were satisfactory. However, the final structural model can still be improved because the interatomic distances do not agree well with those expected from the ionic radii or bond valence sums. In order to clarify the highly efficient luminescence mechanism and further improve the performance of $\text{Li}_2\text{SrSiO}_4:\text{Eu}^{2+}$ phosphor, a more detailed structural study of the host material will be useful.

A combined use of the Rietveld method (Rietveld, 1967), the maximum-entropy method (MEM) (Takata *et al.*, 2001) and the MEM-based pattern fitting (MPF) method (Izumi *et al.*, 2001), has enabled us to determine three-dimensional (3D) electron-density distributions (EDDs), which efficiently disclose structural details such as positional disordering of atoms and/or orientational disordering of atomic groups (Izumi, 2004). The Rietveld method and MEM have a drawback in determining the EDD from XRPD data because the observed structure factors, F_o (Rietveld), are biased toward the structural model assuming intensity partitioning. On the other hand, the MPF method can minimize the structural bias. Thus, the MEM and MPF analyses are alternately repeated (REMEDY cycle) until the reliability indices reach minima. Crystal structures are represented not by structural parameters but by 3D EDD in MPF.

In the present structural study of $\text{Li}_2\text{SrSiO}_4$, we successfully derived the coordinates of all atoms, including those of Li, using the direct methods and further refined them using the Rietveld method. The validity of the final structural model was confirmed by the 3D EDD determined by MPF.

II. EXPERIMENTAL

A sample of $\text{Li}_2\text{SrSiO}_4$ was prepared from stoichiometric amounts of reagent-grade chemicals Li_2CO_3 , SrCO_3 , and SiO_2 . Well-mixed chemicals were pressed into pellets (20 mm diameter and 5 mm thick), heated at 873 K for 3 h, and followed by quenching in air. The densely sintered pellets were finely ground to obtain a powder specimen.

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TABLE I. Crystal data for $\text{Li}_2\text{SrSiO}_4$.

Chemical composition	$\text{Li}_2\text{SrSiO}_4$
Space group	$P3_121$
a/nm	0.502 281(4)
c/nm	1.245 520(8)
V/nm^3	0.272 129(3)
Z	3
$D_x/\text{Mg m}^{-3}$	3.54

A diffractometer (X'Pert PRO Alpha-1, PANalytical B.V., Almelo, The Netherlands), equipped with an incident-beam Ge(111) Johansson monochromator to obtain $\text{Cu } K\alpha_1$ radiation and a high-speed detector, was used in the Bragg-Brentano geometry. The X-ray generator was operated at 45 kV and 40 mA. A variable divergence slit was used to keep a constant illuminated length of 5 mm on the specimen surface. Other experimental conditions were continuous scan, experimental 2θ range from 18.0154° to 148.9314° (an accuracy in 2θ of $\pm 0.0001^\circ$), 7835 total data points, and 5.5 h total experimental time. The structure data were standardized according to rules formulated by Parthé and Gelato (1984) using the computer program STRUCTURE TIDY (Gelato and Parthé, 1987). The crystal-structure models, equidensity isosurfaces of EDD, and two-dimensional (2D) EDD map were visualized with the computer program VESTA (Momma and Izumi, 2008). Distortion parameters for the coordination polyhedra were found using the computer program IVTON (Balic-Zunic and Vickovic, 1996).

III. RESULTS AND DISCUSSION

A. Structure refinement

Peak positions of the experimental diffraction pattern were first determined by finding minima in the second derivatives using the computer program PowderX (Dong, 1999). The 2θ values of 40 observed peak positions were then used as input data to the automatic indexing computer program TREOR90 (Werner *et al.*, 1985). One hexagonal unit cell was found with satisfactory figures of merit: $M40/F40 = 285/415$ (0.001 787, 54) (de Wolff, 1968; Smith and Snyder, 1979). The derived unit-cell parameters of $a = 0.502 422(5)$ and $c = 1.245 93(1)$ nm could index all reflections in the observed diffraction pattern.

The observed diffraction peaks were examined to confirm the presence or absence of reflections. Systematic absences $l \neq 3n$ for hkl reflections were found, suggesting that

TABLE II. Structural parameters for $\text{Li}_2\text{SrSiO}_4$.

Site	Wyckoff position	x	y	z	$100B$ (nm^2)
Li	6c	0.070(2)	0.405(2)	0.4223(6)	1.4(1)
Sr	3a	0.4182(1)	0	1/3	0.76(6)
Si	3b	0.2772(3)	0	5/6	0.60(6)
O1	6c	0.0361(9)	0.4843(5)	0.0607(2)	0.80(7)
O2	6c	0.3048(6)	0.2386(6)	0.1694(5)	0.75(8)

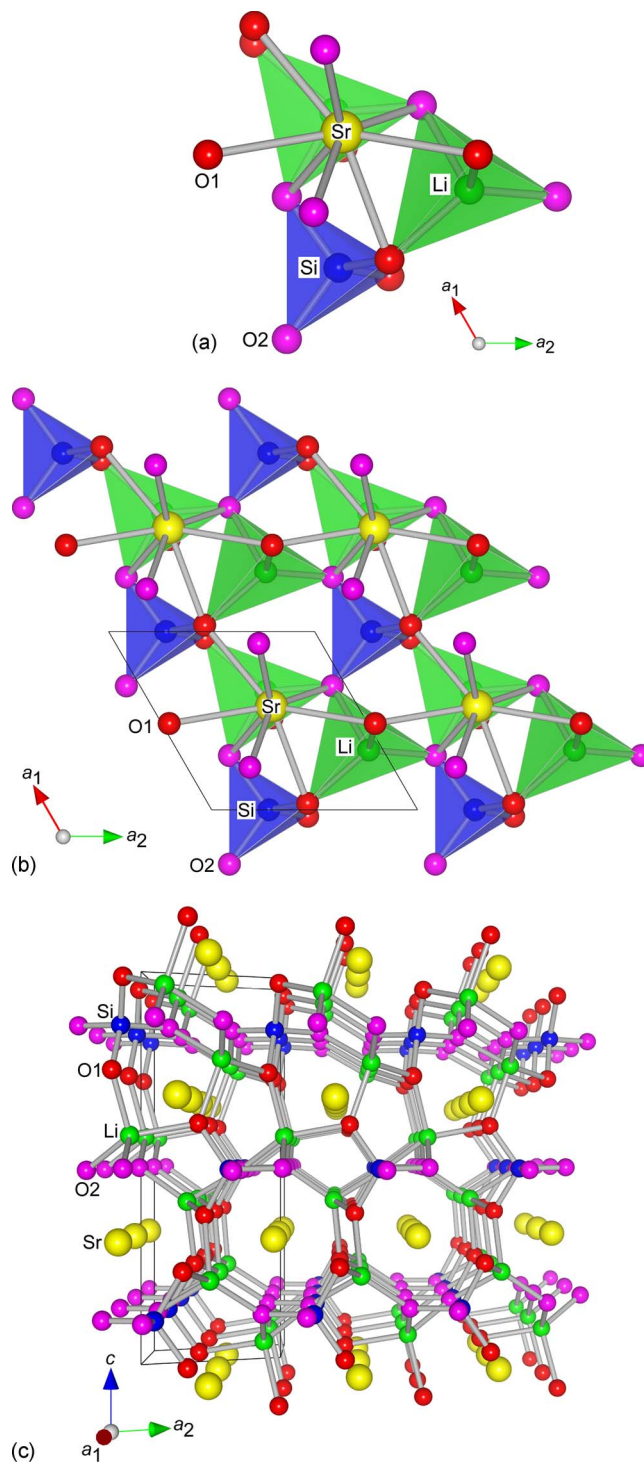


Figure 1. (Color online) Crystal structure of $\text{Li}_2\text{SrSiO}_4$. (a) A basic structural unit $[\text{Li}_2\text{SrSiO}_{13}]^{18-}$ viewed along the c axis. (b) Individual units are linked together with formation of a two-dimensional layer parallel to (001). (c) The layers are stacked in the [001] direction to form a three-dimensional structure (perspective view). Atom numbering corresponds to that given in Table II.

possible space groups are $P3_1$, $P3_2$, $P3_121$, $P3_221$, $P3_112$, $P3_212$, $P6_3$, $P6_3/m$, and $P6_322$. All these space groups were tested and confirmed using the EXPO2004 package (Altomare *et al.*, 1999). A unit-cell content with $[6\text{Li } 3\text{Sr } 3\text{Si } 12\text{O}]$ was used as input data for the search of a crystal-structure model. A promising structural model with the minimum reliability

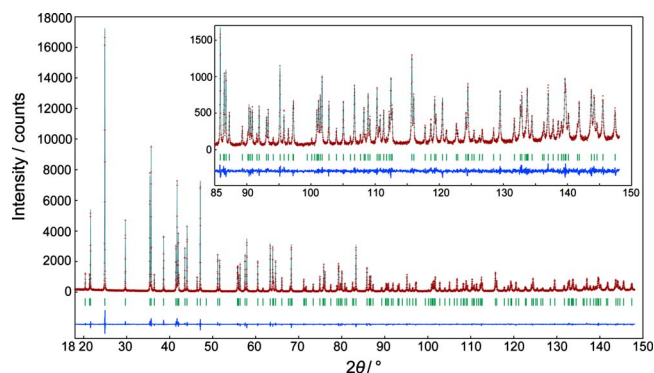


Figure 2. (Color online) Comparison of the observed diffraction pattern of $\text{Li}_2\text{SrSiO}_4$ (symbol: +) with the corresponding calculated pattern (upper solid line). The difference curve is shown in the lower part of the diagram. Vertical bars indicate the positions of possible Bragg reflections.

index R_F (Young, 1993) of 4.50% was successfully obtained with the space group $P3_121$ in a default run of the program. There were five independent sites (i.e., one Li site located at the Wyckoff position $6c$, one Sr site at $3a$, one Si site at $3b$, and two O sites at $6c$) in the unit cell.

Structural parameters of all atoms were refined by the Rietveld method using the computer program RIETAN-FP (Izumi and Momma, 2007) with the profile intensity data in the 2θ range of 18.0154° to 148.0792° (7784 total data points). A Legendre polynomial with 12 adjustable parameters was fitted to background intensities. The split Pearson VII function (Toraya, 1990) was used to fit the peak profiles. Isotropic displacement (B) parameters were assigned to all atoms. Reliability indices of the Rietveld refinement were

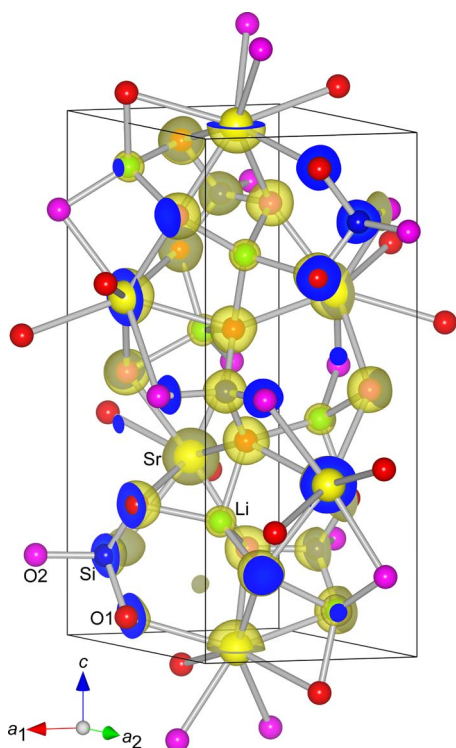


Figure 3. (Color online) Three-dimensional electron-density distributions determined by MPF with the structural model. Isosurfaces expressed in smooth shading style for an equidensity level of 0.002 nm^{-3} .

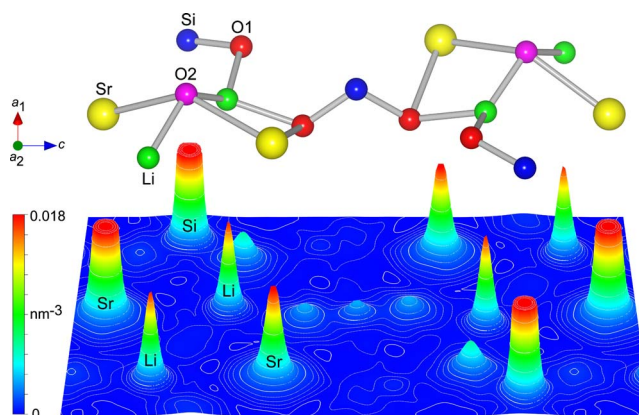


Figure 4. (Color online) A bird's eye view of electron densities up to 3.3% of the maximum (0.552 nm^{-3}) on the plane parallel to (110) at the height of Li sites (lower part) with the corresponding atomic arrangements (upper part). Atom numbering corresponds to that given in Table II.

$R_{wp}=8.06\%$, $S(=R_{wp}/R_e)=1.22$, $R_p=6.01\%$, $R_B=1.75\%$, and $R_F=0.88\%$ (Young, 1993). Crystal data are given in Table I and the final atomic positional and B parameters are given in Table II. Figure 1 shows the final structural model, which is isomorphous with that of $\text{Li}_2\text{EuSiO}_4$.

The EDDs with $80 \times 80 \times 198$ pixels in the unit cell, the spatial resolution of which is approximately 0.0063 nm , were obtained from the MPF method using the computer programs RIETAN-FP and PRIMA (Izumi and Dilanian, 2002). After one REMEDY cycle, R_{wp} , S , R_p , R_B , and R_F further decreased to 8.04%, 1.22, 6.01%, 1.50%, and 0.66%, respectively. Subtle EDD changes as revealed by MPF significantly improve the

TABLE III. Selected bond lengths (nm) and angles (deg) in $\text{Li}_2\text{SrSiO}_4$.

Li–O1	0.1980(8)
Li–O1	0.2007(7)
Li–O2	0.1914(9)
Li–O2	0.2028(8)
$\langle \text{Li–O} \rangle$	0.1982
O1–Li–O1	96.1(4)
O1–Li–O2	116.6(4)
O1–Li–O2	102.4(3)
O1–Li–O2	132.6(4)
O1–Li–O2	104.9(4)
O2–Li–O2	100.5(3)
$\langle \text{O–Li–O} \rangle$	108.9
Si–O1	$0.1634(3) \times 2$
Si–O2	$0.1637(3) \times 2$
$\langle \text{Si–O} \rangle$	0.1635
O1–Si–O1	108.9(2)
O1–Si–O2	$106.2(2) \times 2$
O1–Si–O2	$113.7(2) \times 2$
O2–Si–O2	108.2(2)
$\langle \text{O–Si–O} \rangle$	109.5
Sr–O1	$0.2642(4) \times 2$
Sr–O1	$0.2671(4) \times 2$
Sr–O2	$0.2572(5) \times 2$
Sr–O2	$0.2638(5) \times 2$
$\langle \text{Sr–O} \rangle$	0.2631

TABLE IV. Polyhedral distortion parameters. Δ =eccentricity; r_s =radius of sphere fitted to ligands; V_s =sphere volume; σ =sphericity; V_p =volume of coordination polyhedron; v =volume distortion; and σ , for coordination number four, is 1 by definition.

Polyhedron	Distortion parameters					
	Δ (nm ⁻¹)	r_s (nm ⁻¹)	V_s (nm ⁻³)	σ	V_p (nm ⁻³)	v
LiO ₄	0.038	0.198	0.0323	1	0.0038	0.050
SiO ₄	0.002	0.164	0.0183	1	0.0022	0.005
SrO ₈	0.009	0.263	0.0761	0.986	0.0305	0.075

R_B and R_F indices. The decreases in R indices demonstrate that the crystal structure can be seen more clearly from EDD instead from the conventional structural parameters reported in Table II. Observed, calculated, and difference XRPD patterns for the final MPF are plotted in Figure 2. The individual equidensity isosurfaces of EDD are in reasonably good agreement with the corresponding atom arrangements (Figure 3), indicating that the crystal is free from structural disordering. The 2D EDD map at the height of Li sites shows that the positions of Li atoms are successfully disclosed by the EDD (Figure 4). We found the peak positions of EDD from the 3D pixel data and compared them with the coordinates of all atoms that were determined by the Rietveld method. The positional deviations of all atoms in the unit cell were found to be necessarily less than 0.004 nm, which is within the resolution limit of the 3D EDD. We therefore concluded that the present structural model would reasonably and satisfactorily represent the crystal structure of Li₂SrSiO₄.

B. Structure description

Selected interatomic distances and bond angles, together with their standard deviations, are listed in Table III. The average Li–O bond length in the LiO₄ tetrahedra is 0.1982 nm, which is comparable to those of the LiO₄ tetrahedra in Li₂EuSiO₄ (0.1982 nm), Li₂BaSiO₄ (0.1979 nm), and Li₂CaSiO₄ (0.1969 nm) (Haferkorn and Meyer, 1998; Kim *et al.*, 2009; Gard and West, 1973). The average Si–O bond length (0.1635 nm) agrees well with the interatomic distance of 0.164 nm calculated from the ionic radii of Si⁴⁺ and O²⁻ in the fourfold coordination $\{r[\text{Si}^{4+}(4)]=0.026 \text{ nm}$ and $r[\text{O}^{2-}(4)]=0.138 \text{ nm}\}$ (Shannon, 1976). The average value of the O–Si–O angles is 109.5°. These interatomic distance and bond angle are in good agreement with those found in other silicates (Baur, 1971). When the volume distortion parameters v (Table IV) are compared between the two types of tetrahedra LiO₄ and SiO₄, the extent of the distortion is much larger for the former than for the latter.

The SrO₈ polyhedron showed the bond lengths ranging from 0.2572 to 0.2671 nm. Ionic radii of Sr²⁺ in the eightfold coordination $\{r[\text{Sr}^{2+}(8)]=0.126 \text{ nm}$ and $r[\text{O}^{2-}(8)]=0.142 \text{ nm}\}$ predict the interatomic distance of 0.268 nm for Sr–O. This predicted value is in good agreement with the corresponding average interatomic distance of 0.2631 nm. Ratio of volumes of the circumscribed sphere and the polyhedron (V_s/V_p) for the SrO₈ is 2.493. Because the V_s/V_p value of the Archimedean square antiprism is 2.4369 and that of square antiprism with maximum volume is 2.3906 (Mak-

ovicky and Balic-Zunic, 1998), the present SrO₈ can be described as a distorted Archimedean square antiprism.

Valence bond sums calculated on the basis of bond-strength analysis (Li: 1.00, Sr: 2.01, Si: 3.88) are in good agreement with the expected formal oxidation states of Li⁺, Sr²⁺, and Si⁴⁺ ions (Brown and Altermatt, 1985; Brese and O’Keeffe, 1991). The average bond lengths of Li–O, Si–O, and Sr–O are in agreement with those expected from the bond valence sums (Li–O: 0.1979 nm, Si–O: 0.1624 nm, Sr–O: 0.2631 nm).

The crystal structure of lithium strontium silicate consists of the three types of polyhedra, LiO₄, SiO₄, and SrO₈. Two LiO₄ tetrahedra and one SiO₄ tetrahedron are connected via corners to form a [Li₂SiO₉]⁻¹² ring. This ring and SrO₈ polyhedron are joined by sharing faces and edges to build up a basic structural unit [Li₂SrSiO₁₃]⁻¹⁸, as shown in Figure 1(a). Individual units are further linked through oxygen atoms to form layers parallel to (001) [Figure 1(b)]. These layers are stacked in the [001] direction with three layers per unit cell to form a three-dimensional structure [Figure 1(c)]. This compound is isomorphous with Li₂EuSiO₄ (Haferkorn and Meyer, 1998).

IV. CONCLUSION

We successfully refined the crystal structure of lithium strontium silicate Li₂SrSiO₄, having a trigonal unit cell with space group $P3_121$. The basic units of the crystal structure were [Li₂SrSiO₁₃]⁻¹⁸, each comprising three types of polyhedra LiO₄, SrO₈, and SiO₄. These basic units were connected by sharing corners and edges to form layers parallel to (001). These layers were stacked in the [001] direction with three layers per unit cell to form a three-dimensional structure. The validity of the structural model was confirmed by the EDD determined by MPF.

- Altomare, A., Burla, M. C., Camalli, M., Carrozzini, B., Casciarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G., and Rizzi, R. (1999). “EXPO: A program for full powder pattern decomposition and crystal structure solution,” *J. Appl. Crystallogr.* **32**, 339–340.
- Balic-Zunic, T. and Vickovic, I. (1996). “IVTON: Program for the calculation of geometrical aspects of crystal structures and some crystal chemical applications,” *J. Appl. Crystallogr.* **29**, 305–306.
- Baur, W. H. (1971). “Prediction of bond length variations in silicon-oxygen bonds,” *Am. Mineral.* **56**, 1573–1599.
- Brese, N. E. and O’Keeffe, M. (1991). “Bond-valence parameters for solids,” *Acta Crystallogr., Sect. B: Struct. Sci.* **47**, 192–197.
- Brown, I. D. and Altermatt, D. (1985). “Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database,” *Acta Crystallogr., Sect. B: Struct. Sci.* **41**, 244–247.

- de Wolff, P. M. (1968). "A simplified criterion for the reliability of a powder pattern indexing," *J. Appl. Crystallogr.* **1**, 108–113.
- Dong, C. (1999). "PowderX: Windows-95-based program for powder X-ray diffraction data processing," *J. Appl. Crystallogr.* **32**, 838.
- Gard, J. A. and West, A. R. (1973). "Preparation and crystal structure of $\text{Li}_2\text{CaSiO}_4$ and isostructural $\text{Li}_2\text{CaGeO}_4$," *J. Solid State Chem.* **7**, 422–427.
- Gelato, L. M. and Parthé, E. (1987). "STRUCTURE TIDY: A computer program to standardize crystal structure data," *J. Appl. Crystallogr.* **20**, 139–143.
- Haferkorn, B. and Meyer, G. (1998). " $\text{Li}_2\text{EuSiO}_4$, an europium(II) lithosilicate. $\text{Eu}[(\text{Li}_2\text{Si})\text{O}_4]$," *Z. Anorg. Allg. Chem.* **624**, 1079–1081.
- He, H., Fu, R., Wang, H., Song, X., Pan, Z., Zhao, X., Zhang, X., and Cao, Y. (2008). " $\text{Li}_2\text{SrSiO}_4:\text{Eu}^{2+}$ phosphor prepared by the Pechini method and its application in white light emitting diode," *J. Mater. Res.* **23**, 3288–3294.
- Izumi, F. (2004). "Beyond the ability of Rietveld analysis: MEM-based pattern fitting," *Solid State Ionics* **172**, 1–6.
- Izumi, F. and Dilanian, R. A. (2002). "Structure refinement based on the maximum-entropy method from powder diffraction data," in *Recent Research Developments in Physics*, edited by S. G. Pandalai (Transworld Research Network, Trivandrum), Vol. 3, Pt. II, pp. 699–726.
- Izumi, F., Kumazawa, S., Ikeda, T., Hu, W.-Z., Yamamoto, A., and Oikawa, K. (2001). "MEM-based structure-refinement system REMEDY and its applications," *Mater. Sci. Forum* **378–381**, 59–64.
- Izumi, F. and Momma, K. (2007). "Three-dimensional visualization in powder diffraction," *Solid State Phenom.* **130**, 15–20.
- Kim, J., Ahn, D., Kulshreshtha, C., Sohn, K.-S., and Shin, N. (2009). "Lithium barium silicate, $\text{Li}_2\text{BaSiO}_4$, from synchrotron powder data," *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **65**, i14–i16.
- Kulshreshtha, C., Sharma, A. K., and Sohn, K.-S. (2009a). "Effect of local structures on the luminescence of $\text{Li}_2(\text{Sr}, \text{Ca}, \text{Ba})\text{SiO}_4:\text{Eu}^{2+}$," *J. Electrochem. Soc.* **156**, J52–J56.
- Kulshreshtha, C., Shin, N., and Sohn, K.-S. (2009b). "Decay behavior of $\text{Li}_2(\text{Sr}, \text{Ba}, \text{Ca})\text{SiO}_4:\text{Eu}^{2+}$ phosphors," *Electrochem. Solid-State Lett.* **12**, J55–J57.
- Makovicky, E. and Balic-Zunic, T. (1998). "New measure of distortion for coordination polyhedra," *Acta Crystallogr., Sect. B: Struct. Sci.* **54**, 766–773.
- Momma, K. and Izumi, F. (2008). "VESTA: A three-dimensional visualization system for electronic and structural analysis," *J. Appl. Crystallogr.* **41**, 653–658.
- Parthé, E. and Gelato, L. M. (1984). "The standardization of inorganic crystal-structure data," *Acta Crystallogr., Sect. A: Found. Crystallogr.* **40**, 169–183.
- Rietveld, H. M. (1967). "Line profiles of neutron powder-diffraction peaks for structure refinement," *Acta Crystallogr.* **22**, 151–152.
- Saradhi, M. P. and Varadaraju, U. V. (2006). "Photoluminescence studies on Eu^{2+} -activated $\text{Li}_2\text{SrSiO}_4$ —A potential orange-yellow phosphor for solid-state lighting," *Chem. Mater.* **18**, 5267–5272.
- Shannon, R. D. (1976). "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **32**, 751–767.
- Smith, G. S. and Snyder, R. L. (1979). " F_N : A criterion for rating powder diffraction patterns and evaluating the reliability of powder-pattern indexing," *J. Appl. Crystallogr.* **12**, 60–65.
- Takata, M., Nishibori, E., and Sakata, M. (2001). "Charge density studies utilizing powder diffraction and MEM. Exploring of high T_c superconductors, C60 superconductors and manganites," *Z. Kristallogr.* **216**, 71–86.
- Toraya, H. (1990). "Array-type universal profile function for powder pattern fitting," *J. Appl. Crystallogr.* **23**, 485–491.
- Werner, P. E., Eriksson, L., and Westdahl, M. (1985). "TREOR: A semi-exhaustive trial-and-error powder indexing program for all symmetries," *J. Appl. Crystallogr.* **18**, 367–370.
- Young, R. A. (1993). *The Rietveld Method*, edited by R. A. Young (Oxford University Press, Oxford), pp. 1–38.
- Zhang, X., He, H., Li, Z., Yu, T., and Zou, Z. (2008). "Photoluminescence studies on Eu^{2+} and Ce^{3+} -doped $\text{Li}_2\text{SrSiO}_4$," *J. Lumin.* **128**, 1876–1879.