



Structural investigation of $\text{Sr}_2\text{LiReO}_6$. Evidence for a continuous tetragonal–cubic phase transition

René B. Macquart, Qingdi Zhou, Brendan J. Kennedy *

School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

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ABSTRACT

The presence of a continuous and reversible $Fm\bar{3}m$ – $I4/m$ phase transition in a polycrystalline sample of the ordered double perovskite $\text{Sr}_2\text{LiReO}_6$ is described. The transition that occurs near 300°C is a consequence of in-phase tilting of the BO_6 octahedra. The temperature dependence of both the lattice parameters and the spontaneous strains are consistent with a second order phase transition as would be expected for a soft mode transition.

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1. Introduction

The observation of large magnetoresistance and high Curie temperatures in double-perovskite oxides containing heavier $4d$ and $5d$ transition metals has served as the impetus for numerous studies over the past decade [1,2]. The rhenate double perovskites A_2BReO_6 were first described by Sleight et al. [3,4] almost 50 years ago, and re-investigation of these using modern physical methods has been particularly fruitful. Very recently Bharathy and zur Loye [5] reported the crystal growth and structural characterisation of some rhenate double perovskites where the B -type cation was an alkali metal (Li or Na). In particular they reported that whereas single crystals of $\text{Sr}_2\text{LiReO}_6$ were cubic, powder samples of the same composition were tetragonal and the measurements reported in this paper suggested that once formed these two structures apparently did not interconvert [5]. This observation is unexpected. The ideal double perovskite structure is cubic in space group $Fm\bar{3}m$ where ordering of the two B -site cations results in a doubling of the unit cell from that seen in the archetypal ABO_3 perovskite [6]. When the A -site cation is smaller then optimal cooperative tilting of the BO_6 octahedra occurs lowering the symmetry. The tetragonal $I4/m$ double perovskite is derived from the cubic $Fm\bar{3}m$ structure by in-phase tilting of the octahedra about one axis [6]—this is labelled $a^0a^0c^-$ in Glazer's [7] notation. These tilts are associated with a R -point instability and a soft-mode induced transition between the two structures may be anticipated. Since such transitions were first reported for SrTiO_3

[8] numerous examples have been reported including in the related double perovskites Sr_2BWO_6 ($B = \text{Ni}, \text{Co}$) [9,10] and Sr_2BMoO_6 ($B = \text{Fe}$) [11]. A group theoretical analysis of the possible structures in double perovskites shows that a $Fm\bar{3}m$ – $I4/m$ transition is allowed to be continuous [6]. The report by Bharathy and zur Loye [5] that these two structures can be obtained for $\text{Sr}_2\text{LiReO}_6$ at room temperature and that these do not show a continuous temperature dependent phase transition is clearly anomalous and worthy of further investigation.

The current communication presents studies of the $Fm\bar{3}m$ – $I4/m$ transition in polycrystalline samples of $\text{Sr}_2\text{LiReO}_6$. Using variable temperature powder diffraction we find this transition is continuous and occurs near 290°C .

2. Experimental

2.1. Synthesis

A polycrystalline sample of $\text{Sr}_2\text{LiReO}_6$ was prepared by heating a finely ground mixture of stoichiometric quantities of SrCO_3 , Li_2CO_3 and Re metal (all Aldrich Chemicals) for 4 h at 600°C , 4 h at 800°C and finally 2 h at 800°C with intermediate re-grinding. The starting carbonates were dried overnight prior to use.

2.2. X-ray diffraction

Powder X-ray diffraction patterns were collected on a PANalytical X'Pert PRO X-ray diffractometer using $\text{CuK}\alpha$ radiation and a PIXcel solid-state detector in scanning mode with an active length of 3.4° . Temperature control was achieved using an Anton PARR

* Corresponding author. Fax: +61 2 9351 3329.

E-mail address: B.Kennedy@chem.usyd.edu.au (B.J. Kennedy).

Table 1
Selected crystallographic data for Sr₂LiReO₆.

Temperature (°C)	30	500
Crystal system	Tetragonal	Cubic
Space group	<i>I4/m</i>	<i>Fm</i> $\bar{3}$ <i>m</i>
<i>a</i> (Å)	5.55033(4)	7.94014(5)
<i>c</i> (Å)	7.92269(7)	–
Volume (Å ³)	244.068(3)	500.590(6)
No. of reflections	118	44
No. of parameters	17	14
O(1) _x	0.308(1)	0.2288(6)
O(1) _y	0.228(1)	–
O(2) _z	0.268(1)	–
R _p (%)	7.11	7.56
R _{wp} (%)	9.06	9.77
R _{exp} (%)	6.73	6.79
R _{Bragg} (%)	5.78	7.56

XRK 900 Reactor Chamber fitted with a TCU 750 temperature control unit. The sample was allowed to equilibrate for 5 min after reaching each measurement temperature. Each pattern was recorded in continuous scan mode using a counting time of 10.87 s per 0.0171°(2θ) step and took around 8 min to collect. The structure was refined by the Rietveld method implemented in the program Rietica [12] using data in the range 15° ≤ 2θ ≤ 90°. The peak profiles were fitted using a pseudo-Voigt function coupled with an asymmetry function. Crystallographic data and details of the Rietveld refinement are given in Table 1. Differential scanning calorimetry (DSC) curves were recorded using a Mettler-Toledo DSC 823e with liquid nitrogen cooling assembly between temperatures –140 and 500 °C.

3. Results and discussion

That the polycrystalline sample of Sr₂LiReO₆ was tetragonal at room temperature, as described by Bharathy and zur Loye [5], was immediately obvious from inspection of the powder X-ray diffraction pattern, Fig. 1. The narrowness of the diffraction peaks demonstrates the sample to be highly crystalline and there is no evidence from this diffraction pattern for any crystalline impurities. Refinement in the tetragonal *I4/m* system yielded lattice parameters of *a* = 5.55033(4) and *c* = 7.92269(7) Å in good agreement with those reported by Bharathy and zur Loye [5] (*a* = 5.5467(2) and *c* = 7.9197(4) Å). The average Re–O (1.846 Å) and Li–O (2.124 Å) bond distances derived from the refinement are chemically reasonable, the Re–O distance being comparable to the values reported for the various A₂BReO₆ oxides studied using single crystal X-ray methods [5]. The structure remained tetragonal to 90 K, the lowest temperature available in this study.

Heating the polycrystalline sample of Sr₂LiReO₆ leads to a progressive reduction in the observed splitting of the diagnostic reflections. The patterns collected at or above 290 °C showed no splitting or asymmetry indicative of tetragonal symmetry and were well fitted using a model in *Fm* $\bar{3}$ *m*. The refined Re–O (1.817(5) Å) and Li–O (2.154 Å) distances obtained from data collected at 500 °C remained chemically sensible. This observation is in contrast with the observation by Bharathy and zur Loye [5] that there was no indication, from DTA analysis, for a temperature induced structural phase transition. Our own DSC measurements revealed a very weak feature near 300 °C that we believe is associated with the phase transition. It is our experience that diffraction measurements are superior to DTA in the analysis of continuous phase transitions, although thermal methods are a valuable tool in the study of first order events.

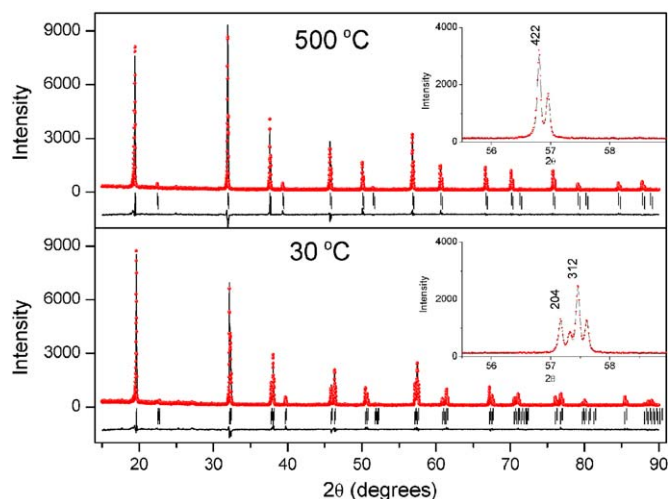


Fig. 1. Rietveld refinement fit for Sr₂LiReO₆ at 30 and 500 °C. The circles represent the observed data and the solid lines the calculated and difference profiles. The lower tick marks show the positions of the space group allowed reflections for both the α₁ and α₂ wavelengths. The inserts highlight the loss of the tetragonal splitting upon heating.

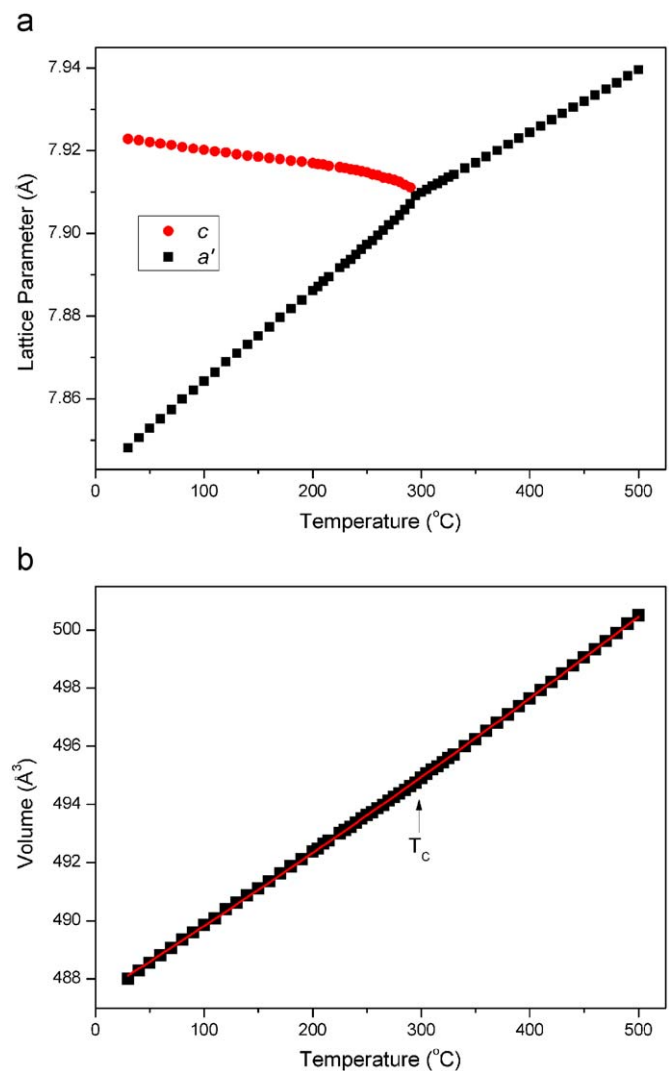


Fig. 2. (a) Temperature dependence of the lattice parameters for Sr₂LiReO₆. The values for the *a* parameter have been multiplied by $\sqrt{2}$ in the tetragonal phase to obtain an equivalent cell in the tetragonal and cubic structures. (b) Temperature dependence of the, appropriately scaled, unit cell volume of Sr₂LiReO₆.

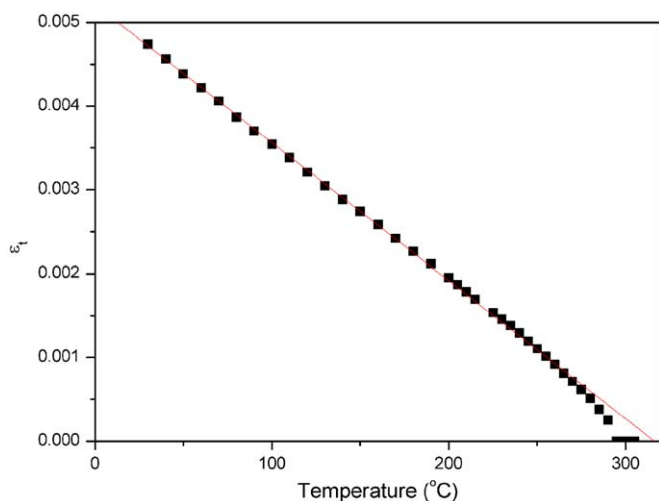


Fig. 3. Temperature dependence of the tetragonal strain calculated as $\varepsilon_t = (c - a\sqrt{2})/(c + a\sqrt{2})$. The solid line is a linear fit to the data.

The temperature dependence of the lattice parameters for $\text{Sr}_2\text{LiReO}_6$, obtained from the Rietveld analysis, is illustrated in Fig. 2. This behaviour is indicative of a continuous phase transition from $I4/m$ to $Fm\bar{3}m$ upon heating. A continuous $I4/m - Fm\bar{3}m$ phase transition associated with the removal of the tilting of the BO_6 octahedron has been observed in other ordered double perovskites including Sr_2NiWO_6 and Sr_2CoWO_6 [9,10]. As is also evident from Fig. 2 there is no obvious discontinuity on the unit cell volume at the transition. Bharathy and zur Loye [5] reported the volume of the single crystal cubic phase, $494.37(16)\text{Å}^3$, to be measurably different to the equivalent value of the tetragonal phase $488.136(6)$ or $488.578(22)\text{Å}^3$ in Ref. [5].

The spontaneous strain in the tetragonal structure, defined as $\varepsilon_t = (c - a\sqrt{2})/(c + a\sqrt{2})$, showed, Fig. 3, a linear reduction with increasing temperature as expected for a second order $I4/m - Fm\bar{3}m$ phase transition [13]. A deviation from linear behaviour is observed just below the transition. Such deviations have been noted previously [14] and in the present case it is probable that the resolution of our diffractometer is such that the splitting/broadening of the main perovskite peaks disappears at a temperature below the actual transition temperature [15]. The temperature dependence of both the lattice parameters and spontaneous strains are consistent with a second order phase transition as would be expected for a soft mode transition. Further, upon re-cooling the sample from 500 to below 295°C resulted in the re-appearance of the tetragonal cell. Duplicate

measurements on a second sample, prepared using the same method, yielded essentially identical results.

In conclusion we have demonstrated that polycrystalline samples of $\text{Sr}_2\text{LiReO}_6$ undergo a continuous and reversible $Fm\bar{3}m - I4/m$ transition. The fact that single crystals of the same material apparently do not undergo such a transition is surprising but not without precedent [16]. It is possible that this is a consequence of small variations in the stoichiometry. Partial occupancy of the B-site by the larger Sr^{2+} [17] cation, for example would increase the cell volume and the perovskite tolerance factor. This would have the effect of further stabilising the cubic structure. We note that attempts to refine anti-site disorder of the Li and Re cations were unsuccessful.

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