**La1+*x*Ba1-*x*Ga3O7+0.5*x* Oxide Ion Conductor: Cationic Size Effect on the Interstitial Oxide Ion Conductivity in Gallate Melilites**

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**Abstract**

Substitution of La3+ for Ba2+ in LaBaGa3O7 melilite yields new interstitial-oxide-ion conducting La1+*x*Ba1-*x*Ga3O7+0.5*x* solid solution, which only extends up to *x* = 0.35, giving a maximum interstitial oxygen content allowed in La1+*x*Ba1-*x*Ga3O7+0.5*x* as about half of those allowed in La1+*x*(Sr/Ca)1-*x*Ga3O7+0.5*x*. La1.35Ba0.65Ga3O7.175 ceramic displays bulk conductivities ~ 1.9 × 10-3 S/cm at 600 °C, which is lower than those of La1.35(Sr/Ca)0.65Ga3O7.175, showing the reduced mobility for the oxygen interstitials in La1+*x*Ba1-*x*Ga3O7+0.5*x* than in La1+*x*(Sr/Ca)1-*x*Ga3O7+0.5*x*. Rietveld analysis of neutron powder diffraction data reveals that the oxygen interstitials in La1.35Ba0.65Ga3O7.175 are located within the pentagonal tunnels at the Ga level between two La/Ba cations along the *c*-axis and stabilized via incorporating into the bonding environment of a three-linked GaO4 among the five GaO4 tetrahedra forming the pentagonal tunnels, similar to the Sr and Ca counterparts. Both static lattice atomistic simulation and density functional theory calculation show that LaBaGa3O7 has the largest formation energy for oxygen interstitial defects among La1+*xM*1-*x*Ga3O7+0.5*x* (*M* = Ba, Sr, Ca), consistent with the large Ba2+ cations favouring interstitial oxygen defects in melilite less than the small cations Sr2+ and Ca2+. The cationic-size control of the ability to accommodate the oxygen interstitials and maintain high mobility for the oxygen interstitials in La1+*xM*1-*x*Ga3O7+0.5x (*M* = Ba, Sr, Ca) gallate melilites is understood in term of local structural relaxation to accommodate and transport the oxygen interstitials. The accommodation and migration of the interstitials in the melilite structure requires the tunnel-cations being able to adapt with the synergic size expansion for the interstitial-containing tunnel and contraction for the tunnels neighbouring the interstitial-containing tunnel and continuous tunnel-size expansion and contraction. However the large oxygen bonding separation requirement of the large Ba2+ along the tunnel not only suppresses the ability to accommodate the interstitials in the tunnels neighbouring the Ba2+-containing tunnel but also reduces the mobility of the oxygen interstitials among the pentagonal tunnels.

**Keywords**: Melilite; Interstitial oxide ion conductor; Size effect; Defect chemistry; Atomistic simulation; Density functional theory calculation.

**Introduction**

Recently ABGa3O7-based gallate melilites received considerable interest in their oxide ion conducting properties due to the ability to accommodate mobile oxygen interstitial defects in the two-dimensional (2D) layered tetrahedral network.[1-5](#_ENREF_1) The ABGa3O7 gallate melilite structure consists of alternating 8-coordinate large A/B cationic layers and (3,4)-linked GaO4 tetrahedral layers forming pentagonal tunnels, which are perpendicular to the tetrahedral layers and contain the A/B cations. The donor-substitution of La3+ for *M*2+ in La1+*xM*1-*x*Ga3O7+0.5*x* (*M* = Sr, Ca) induces excess oxygen atoms, which enter into the pentagonal tunnels between two La/*M* cations and are incorporated into the bonding environment of the tetrahedra defining the pentagonal tunnels.[1](#_ENREF_1), [2](#_ENREF_2) The terminal oxygen atoms in 3-linked GaO4 ensure deformation and rotation flexibility of the 2D tetrahedral network, which is the key factor for accommodation and motion of oxygen interstitials among the pentagonal tunnels. [1](#_ENREF_1), [4](#_ENREF_4), [5](#_ENREF_5)

La1+*xM*1-*x*Ga3O7+0.5*x* (*M*= Sr, Ca) are the most interesting melilite materials owing to their highest interstitial oxide ion conductivity among the gallate melilite family. In both solid solutions, the maximum interstitial oxygen contents were found to be comparable (~ *x* = 0.64),[2](#_ENREF_2), [3](#_ENREF_3) where the interstitial oxide ion ordering occurred leading to a pseudo-orthorhombic phase as well as a reduced anionic conductivity.[2](#_ENREF_2), [3](#_ENREF_3) At the same concentration of oxygen interstitials (*x* = 0.5), the Ca-compound (La1.5Ca0.5Ga3O7.25) showed higher ionic conductivity than the Sr-compound (La1.5Sr0.5Ga3O7.25), which was ascribed to the structural modulation owing to the greater interlayer mismatch induced by the smaller cation Ca2+.[6](#_ENREF_6) In La1+*x*Sr1−*x*Ga3O7+0.5*x* the La was replaced by other lanthanide elements (Ln = Ce, Pr, Nd, Sm, Eu, Gd, Dy, Yb, Y) and it was found that large La3+ cation favors the stabilization of the oxygen interstitials[7](#_ENREF_7), [8](#_ENREF_8): Liu *et al*[8](#_ENREF_8) observed that the maximum solid solution limit for the other Ln cations only extended to *x* = 0.2 on the Pr-composition; whereas no oxygen-excess phase was obtained for the Ln = Yb and Y materials. This suggests that the A/B-cationic size plays an important role in the stabilization and migration of oxygen interstitials in the gallate melilites. Similar size effect was also observed in CeSrGa3O7+δ melilite[7](#_ENREF_7) where the interstitial oxide anions are induced by the oxidation of Ce3+ to Ce4+, differing with the donor-substitution of Ln3+ for the *M*2+ in La1+*xM*1-*x*Ga3O7+0.5*x*. The size reduction owing to the Ce3+ oxidation to the smaller Ce4+ in CeSrGa3O7+δ results in a different accommodation of the oxygen interstitials, which enter into bonding environment of 4-linked GaO4 tetrahedra and are preferably close to Ce4+ centers, thus significantly constraining the mobility of oxygen interstitial defects.[7](#_ENREF_7)

The gallate melilite network has shown strong flexibility in accommodating various A/B cations with different sizes.[9](#_ENREF_9) This is well evidenced by the stoichiometric La*M*Ga3O7-type melilites, where *M* can be Ba2+, a much larger divalent cation than Ca2+ and Sr2+.[10](#_ENREF_10) So far, there is little attention on the formation of oxygen-hyperstoichiometric LaBaGa3O7-based melilites and their oxide ion conductivity. Herein we investigate the solid solution formation, structure and electrical properties of oxygen-excess La1+*x*Ba1-*x*Ga3O7+0.5*x* melilites, and compare the content and mobility of oxygen interstitial defects in this solid solution with LaSrGa3O7 and LaCaGa3O7-based oxide ion conductors. This comparison emphasizes the A/B-cationic size effect on controlling the accommodation and mobility of interstitial oxide ion in the ABGa3O7-based gallate melilites, which is discussed in term of the local structural relaxation for accommodating and transporting the interstitial oxygen defects.

**Methods**

**Synthesis.** Phase relations of La1+*x*Ba1-*x*Ga3O7+0.5*x* were investigated by solid state reaction using La2O3 (99.999%, Alfa Aesar), BaCO3 (99.997%, Alfa Aesar), and Ga2O3 (99.999%, Alfa Aesar) as starting materials, which were weighed according to the correct stoichiometries and mixed in ethanol. The mixtures were calcined at 1200 °C for 12 h. After regrinding, the powders were uniaxially pressed into pellets, placed on platinum foil in covered alumina crucibles and fired at 1400 °C for 12 h. A ~ 6 g batch of La1.35Ba0.65Ga3O7.175 sample for neutron powder diffraction was made via by adding ~ 1.7% mol extra Ga2O3 into the mixture to compensate the loss of Ga2O3 during the high temperature firing and depress the competing Ba-doped LaGaO3 perovskite phase and pelletizing in a cold isostatic pressing facility under 30000 psi pressure the powder calcined at 1200 °C for 12 h, followed by a final firing at 1350 °C for 12 h. For conductivity comparison with La1.35Ba0.65Ga3O7.175, La1.35Sr0.65Ga3O7.175 and La1.35Ca0.65Ga3O7.175 pellets were synthesized at 1400 °C for 12 h using starting materials of La2O3, SrCO3 (99.995%, Aladdin), CaCO3 (99%, Aladdin) and Ga2O3 with slightly excess of Ga2O3 (~ 1.7 mol%) in the initial compositions. The densities of La1.35Ba0.65Ga3O7.175, La1.35Sr0.65Ga3O7.175 and La1.35Ca0.65Ga3O7.175 pellets reached ~ 95.4%, ~ 95.8% and 96.4% of X-ray theoretical densities, respectively.

**Characterization.** The phase purity was checked by powder X-ray diffraction data (XRD) with a Panalytical X’pert Pro X-ray diffractometer (Co K*α1* radiation *λ* = 1.78901Å and Cu K*α* radiation). The XRD data for Rietveld refinement were collected over a 2*θ* range of 10-120°. Silicon was added as an internal standard during the XRD experiments in order to refine the cell parameter change with the composition. Time-of-flight (TOF) neutron powder diffraction (NPD) data of La1.35Ba0.65Ga3O7.175 sample was collected at ambient temperature on the HRPD diffractometer at ISIS. Rietveld refinement[11](#_ENREF_11) was carried out using the Topas-Academic.[12](#_ENREF_12) Bond valence sums (BVSs) were calculated by Brown and Altermatt’s method.[13](#_ENREF_13) AC impedance spectroscopy (IS) measurements in air were performed with a Solartron 1260 frequency response analyzer over the 10-1-107 Hz frequency range. Prior to the IS measurements, the platinum paste was coated on the opposite faces of the pellets and fired at 600 °C for 30 min for removing the organic component to form electrodes. The impedance data was analysed using ZView program.[14](#_ENREF_14)

**Defect formation energy calculation.** The energies of interstitial defect formation in gallate melilites were investigated through the atomistic static lattice simulation and density functional theory (DFT) calculation. The former was performed using the General Utility Lattice Program (GULP)[15](#_ENREF_15), [16](#_ENREF_16) based on the interatomic potential approach[17](#_ENREF_17), while the later using the CASTEP program implemented in Materials Studio software package employing the Ultra-Soft pseudo-potential method.[18](#_ENREF_18)

For the atomistic static lattice simulations, the Buckingham potential function[19](#_ENREF_19) was used to model interaction between ions with the shell model[19](#_ENREF_19) to describe the electronic polarizability for the structure modelling of gallate melilites. The interatomic potential parameters used for the atomistic simulation are listed in Table 1. The parameters for La3+-O2-, Ga3+-O2-, Sr2+-O2- and O2--O2- were obtained from the previous MD simulation by Tealdi et al.[4](#_ENREF_4) Initial parameters of Ba2+-O2- from Fisher et al.[20](#_ENREF_20) were slightly modified on the *ρ* parameter for better reproduction of the crystal structure of LaBaGa3O7. The Ca2+-O2- parameters were obtained through the relax fitting procedure. The formation energies for oxygen interstitial defects were calculated based on the appropriate combination of dopant and interstitial defect energies and lattice energies of the binary oxides.

**Table 1**. Buckingham interatomic potential and shell model parameters for the gallate melilites.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Interaction | A (eV) | ρ (Å) | C (eV Å6) | Y (e) | *k* (eV Å-2) |
| La3+-O2- | 4579.23 | 0.30437 | 0 | 0 | / |
| Ga3+-O2- | 1625.72 | 0.3019 | 5.79 | 0 | / |
| Sr2+-O2- | 1400 | 0.35 | 0 | 1.33 | 21.53 |
| Ba2+-O2- | 2096.8 | 0.3385 | 8 | 1.848 | 29.1 |
| Ca2+-O2- | 8573.82 | 0.308 | 560.48 | 0 | / |
| O2--O2- | 22764.3 | 0.149 | 27.89 | -2.869 | 74.92 |

In the DFT calculation, the formation energy of the interstitial oxygen defect in La*M*Ga3O7 can be simply determined using the following relationship, similar to the method employed in Na/K-doped SrSiO3 case[21](#_ENREF_21):

La4*M*4Ga12O28(s) + La2O3(s) → La6*M*2Ga12O29(s) + 2*M*O(s)  (1)

*i.e.*

△Hf = [*E*(La6*M*2Ga12O29(s) + 2*E*(*M*O(s))] –[*E*(La4*M*4Ga12O28(s)) + *E*(La2O3(s))] (2)

where *M* = Ca, Sr or Ba and *E*(X) is the calculated total energy of the species of interest after its geometry optimisation. For the parent La4*M*4Ga12O28 and interstitial-containing La6*M*2Ga12O29 compositions, the optimisations were performed on a 1×1×2 super cell with P1 space group based on the parent tetragonal La*M*Ga3O7 cell (P21m, *Z* = 2). In La6*M*2Ga12O29 corresponding to La1.5M0.5Ga3O7.25 composition, two *M* atoms are replaced by La resulting in one interstitial oxygen atom in the super cell. A 5×5×4 Monkhorst-Pack *k*-point grid was used for both La4*M*4Ga12O28 and La6*M*2Ga12O29. For La2O3, a trigonal structure (*Pm*1, *Z* = 1) were selected for energy calculation with a 12×12×8 Monkhorst-Pack *k*-point grid. The cubic structure (*Fmm*, *Z* = 4) and a 10×10×10 Monkhorst-Pack *k*-point grid was used for *M*O. The interaction between ions and electrons were described by the Perdew-Burke-Ernzerhof (PBE) in generalized gradient approximation (GGA).[22](#_ENREF_22) Valence electrons of Ga 3d104s24p1, O 2s22p4, La 5s25p65d16s2, Ca 3s23p64s2, Sr 4s24p65s2 and Ba 5s25p66s2 were considered in this study. The plane-wave energy cutoff was set to 500 eV for all of these geometry optimizations.

**Results and discussion**

**La1+*x*Ba1-*x*Ga3O7+0.5*x* solid solution.** XRD data of La1+*x*Ba1-*x*Ga3O7+0.5*x* (in Figure 1a) shows that a single melilite phase was achieved within the La-rich compositions until *x* = 0.35 and Ba-doped LaGaO3 and LaBa2Ga11O20 impurity phases appeared when *x* ≥ 0.375. The refined cell parameters (Figure 1 b-d) for the melilite phases in La1+*x*Ba1-*x*Ga3O7+0.5*x* (*x* = 0-0.35) samples obey Vegard’s law and remain essentially constant when *x* is great than 0.35, confirming that the solid solution limit of La1+*x*Ba1-*x*Ga3O7+0.5*x* is close to *x =* 0.35. The cell contraction of La1+*x*Ba1-*x*Ga3O7+0.5*x* melilite phases within the solid solution limit is consistent with the La3+ substitution for the bigger Ba2+ cations.[10](#_ENREF_10)



**(b)**

**(a)**

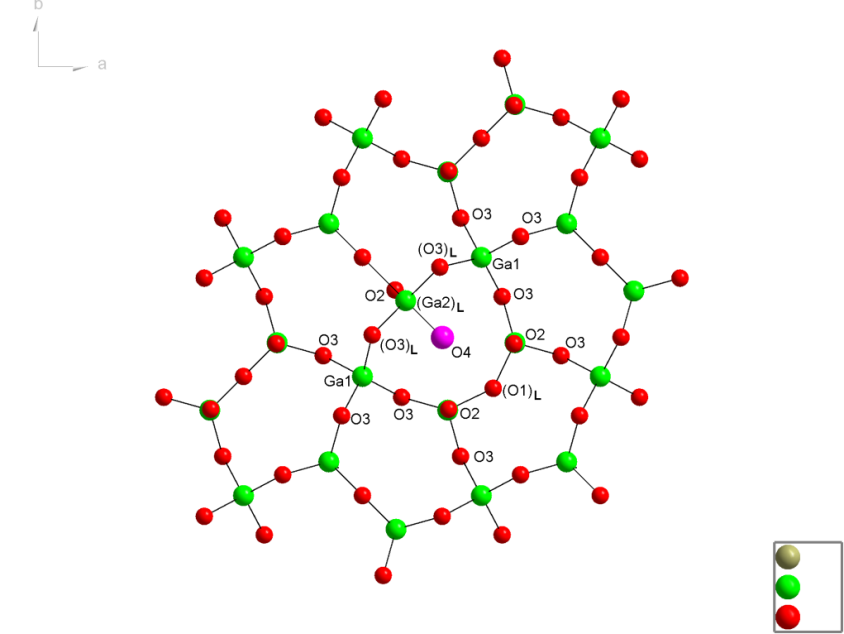
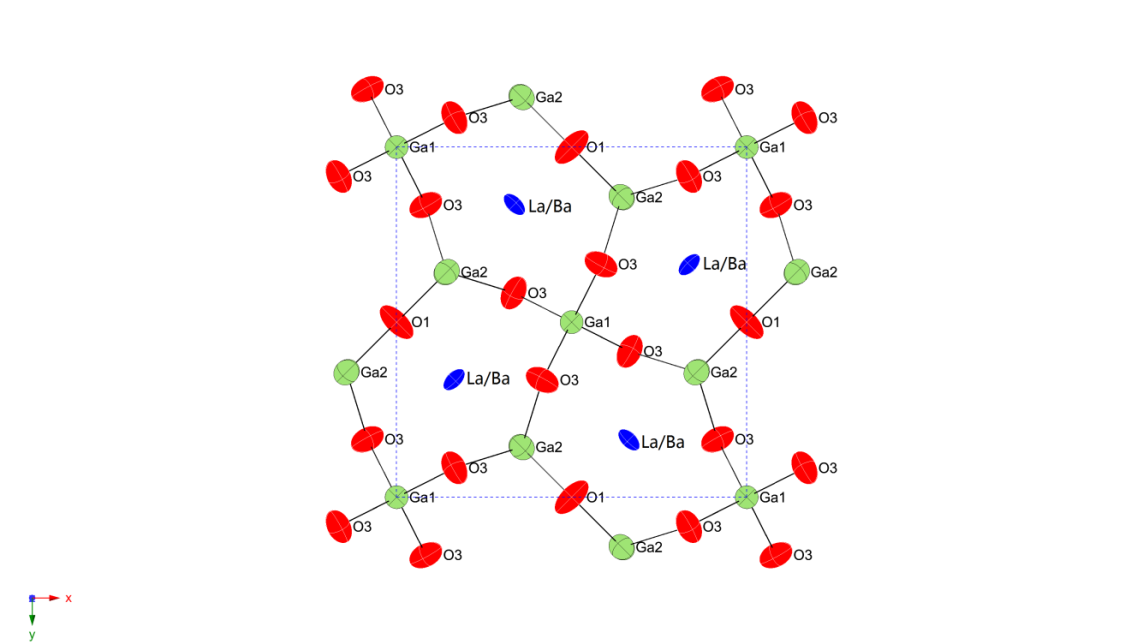
 

**(d)**

**(c)**

**Figure 1.** (a) XRD patterns of La1+*x*Ba1-*x*Ga3O7+0.5*x* (Co K*α1* radiation). ♦ and ♥ symbols mark the reflections of Ba-doped LaGaO3 and LaBa2Ga11O20 impurities, respectively. The *hkl* indices for the melilite phase are labelled. (b-d) Cell parameters of the melilite phases in La1+*x*Ba1-*x*Ga3O7+0.5*x* samples.

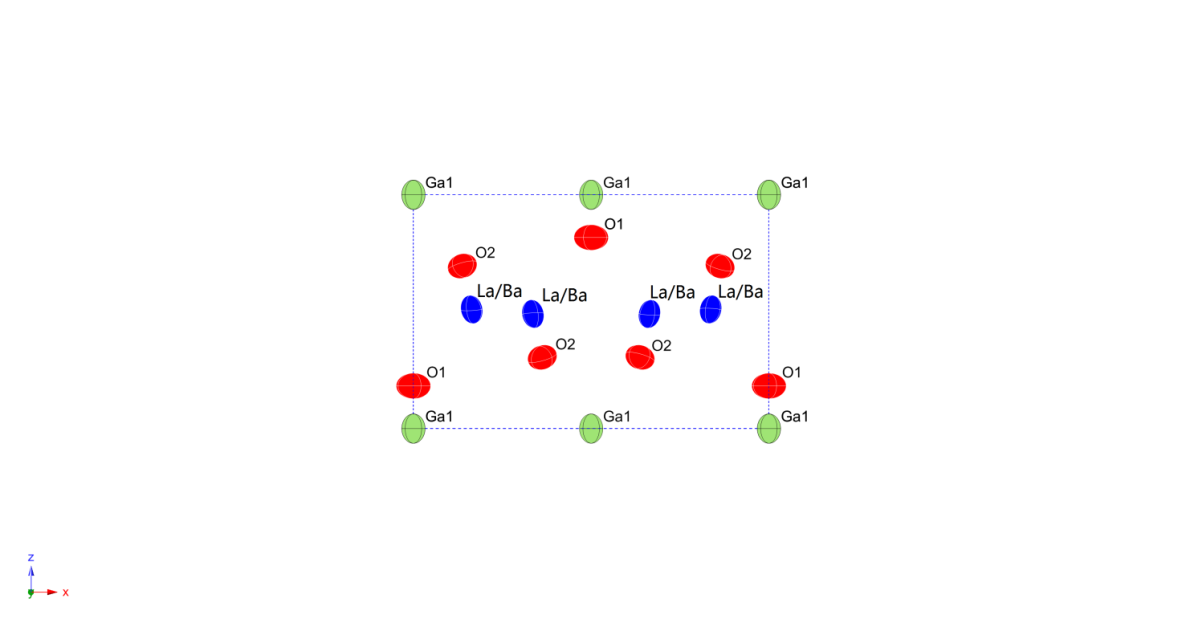
**Structure of La1.35Ba0.65Ga3O7.175**. Preliminary Rietveld analysis of the NPD data of La1.35Ba0.65Ga3O7.175 was carried out based on the structural model of LaBaGa3O79 containing one La/Ba site, two Ga sites (Ga1, Ga2), three framework oxygen sites (O1, O2 and O3). This converged to *Rwp* ≈ 6.6% and *RB* ≈ 2.8%. Following this refinement, difference Fourier maps were generated to locate the additional nuclear density arising from the interstitial oxygen content. The strongest residual nuclear density peak was found at a 4*e* position (∼0.34, ∼0.16, ∼0), which labelled as O4 (Figure S1), similar with the case of La1.54Sr0.46Ga3O7.27.1 The refinement with inclusion of this O4 site improved the fit to *Rwp* ≈ 6.1% and *RB* ≈ 2.5% and gave an oxygen occupancy of 0.083(2) on the O4 site with the atomic displacement factor Biso fixed at 1 Å2 owing to the small concentration of oxygen interstitials, giving an extra oxygen content of 0.166(2) per formula, close to that described in the nominal composition. Freely refining the occupancy and Biso for O4 site resulted in unacceptably larger occupancy 0.111(1) and Biso ~ 5.24 Å2. While with the Biso of O4 fixed within 0.5-2 Å2, the occupancy, *Rwp* and *RB* values changed from 0.078(1), 6.10% and 2.50% to 0.089(2), 6.09% and 2.48%, respectively, indicating that the O4 occupancy and R-factors are not sensitive to the initial Biso value within 0.5-2 Å2 and validating the acceptability of the refined occupancies of O4 under Biso = 1 Å2. Thus the refinement confirmed the incorporation of interstitial oxygen atoms in La1.35Ba0.65Ga3O7.175 into the pentagonal tunnels at nearly the same level with Ga3+ cationic plane along the *c*-axis, similar with the La1+*x*(Sr/Ca)1-*x*Ga3O7+0.5*x* cases,[1](#_ENREF_1), [2](#_ENREF_2) but differing from CeSrGa3O7+δ where the interstitial oxide ions lie on the framework oxygen level along the *c*-axis.7

**(b)**

**(a)**

**(c)**



**Figure 2**. Ellipsoid plots of the framework atoms from the refined average structure for La1.35Ba0.65Ga3O7.175: (a) view along the *c-*axis. (b) view along the *b*-axis, O3 and Ga2 atoms are omitted for clarity. Thermal ellipsoids are drawn at the 80% probability level. The ADPs for the interstitial site O4 were not refined owing to its low occupancy thus O4 are not plotted here. (c) Local environment around the O4 interstitial defect from the site-split model viewed along the *c-*axis for illustrating the synergic size-expansion for the interstitial-containing tunnel and size-contraction for the neighbouring pentagonal tunnels owing to the relaxation of tetrahedral framework for accommodating the interstitial oxygen defect.

Refinement of anisotropic displacement parameters (ADPs) for the framework atoms improved the NPD data fit (*Rwp* ~ 5.9%, Table S1). The ellipsoid sizes and shapes for the framework atoms (Figure 2 a and b) suggest positional disorder, to which both the mixed occupation at the same crystallographic site of the tunnel cations La3+ and Ba2+ with apparent size contrast (1.42 Å for Ba2+ versus 1.16 Å for La3+)[10](#_ENREF_10) and the incorporation of oxygen interstitial defects into the pentagonal tunnels contribute. To describe the local relaxation for accommodating the oxygen interstitials, a site-split model was then refined for La1.35Ba0.65Ga3O7.175, similar to La1.54Sr0.46Ga3O7.27 case.[1](#_ENREF_1) This site-split model involves La/Ba, Ga2, O1 and O3 sites partly split off from their original sites to new sites (as indicated by the ellipsoid shapes shown in Figure 2 a and b), respectively denoted as (La/Ba)L, (Ga2)L, (O1)L and (O3)L according to the occupancy of interstitial oxygen site O4. The reﬁned site-split model avoids the short contacts of O4 interstitials with framework O1 and O3 atoms via being partially displaced toward the neighbouring tunnels (Figure 2c) and increase the BVS of O4 to a satisfactory value of 2.05 from 1.26 in the average structure via shortening the contacts (La/Ba)L and (Ga2)L with O4 to 2.31 Å and 1.80 Å from 2.63 Å and 2.34 Å in the average structure (Table S2), respectively. The (Ga2)L centres have distorted 5-coordinate bi-pyramid geometry owing to the interstitial oxygen atom O4, thus confirming the stabilization of oxygen interstitials via bonding to the framework tetrahedra as revealed in La1+*x*(Sr/Ca)1-*x*Ga3O7+0.5*x*.[1](#_ENREF_1), [2](#_ENREF_2) The reﬁnement of the site-split model converged to *Rwp* ≈ 4.1% and RB ≈ 1.5%. The Rietveld plot of the NPD data for La1.35Ba0.65Ga3O7.175 is shown in Figure 3. The ﬁnal reﬁned structural parameters and selected interatomic distances for the split-site model of La1.35Ba0.65Ga3O7.175 are provided in Table 2 and Table S3, respectively.



**Figure 3.** Rietveld plot of NPD data for La1.35Ba0.65Ga3O7.175. The inset enlarges the plot in the low d-spacing range below 1 Å.

**Table 2**. Final reﬁned structural parameters for the site-split model of La1.35Ba0.65Ga3O7.175.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Atom | Site | *x* | *y* | *z* | Occupancy | Biso(Å2) |
| La/Ba | 4*e* | 0.3365(1) | 0.1635(1) | 0.4954(1) | 0.619/0.298 | 1.42(1) |
| (La/Ba)L\* | 4*e* | 0.335(1) | 0.165(1) | 0.423(1) | 0.056/0.027 | 1.42(1) |
| Ga1 | 2*a* | 0 | 0 | 0 | 1 | 1.60(3) |
| Ga2 | 4*e* | 0.142(1) | 0.358(1) | 0.0300(1) | 0.917 | 1.61(1) |
| (Ga2)L\* | 4*e* | 0.157(6) | 0.343(2) | 0.044(1) | 0.083 | 1.61(1) |
| O1 | 2*c* | 0.5 | 0 | 0.1881(3) | 0.834 | 1.47(4) |
| (O1)L\* | 4*e* | 0.4502(6) | 0.0498(6) | 0.136(2) | 0.083 | 1.47(4) |
| O2 | 4*e* | 0.1374(1) | 0.3626(1) | 0.3062(1) | 1 | 1.67(2) |
| O3 | 8*f* | 0.0873(2) | 0.1648(1) | 0.8026(1) | 0.917 | 2.08(1) |
| (O3)L\* | 8*f* | 0.0412(1) | 0.175(1) | 0.740(1) | 0.083 | 2.08(1) |
| O4 | 4*e* | 0.3363(8) | 0.1637(8) | 0.010(1) | 0.083(2) | 1*a* |

\*Occupancies were constrained according to the occupancy of the oxygen interstitial O4 site and the isotropic displacement parameters for the bulk and local sites were constrained to be identical. *a*. The Biso value of interstitial oxygen site O4 was fixed as 1 during the refinement owing to its low occupancy.

**Conductivity.** The conductivity for the La1.35Ba0.65Ga3O7.175 composition near the solid solution limit of La1+*x*Ba1-*x*Ga3O7+0.5*x* was examined by impedance measurements. Figure 4a show complex impedance plot of La1.35Ba0.65Ga3O7.175 pellet at 350 °C, which comprises partially-overlapping bulk and grain boundary responses in high frequency region, which can be modelled with an equivalent circuit consisting of a serial combination of two circuits consisting of three parallel *Ri* , *Ci*, and (CPE)i elements (*i* is b for bulk or gb for grain boundary, and CPE is a constant phase element).[14](#_ENREF_14) In addition, a small tail of Warburg-type electrode response with an associated large capacitance > 10-7 F/cm in low frequency region (< 10 Hz) was observed, due to the oxide ionic conduction.[23](#_ENREF_23) Above 500 °C, the electrode responses gradually collapsed to a semi-circular arc and dominate the impedance data. The impedance data of the La1.35Sr0.65Ga3O7.175 and La1.35Ca0.65Ga3O7.175 compositions were also examined for comparison with La1.35Ba0.65Ga3O7.175, and the typical complex plot at 350 °C of La1.35Sr0.65Ga3O7.175 is given in Figure 4b. La1.35Ba0.65Ga3O7.175, La1.35Sr0.65Ga3O7.175 and La1.35Ca0.65Ga3O7.175 pellets display similar ionic-conducting impedance behaviour but clearly the La1.35Ba0.65Ga3O7.175 possesses lower conductivity than those of La1.35Sr0.65Ga3O7.175 and La1.35Ca0.65Ga3O7.175 (Figure 4c) with the same concentration of oxygen interstitials, indicating lower mobility of oxygen interstitial defects in La1.35Ba0.65Ga3O7.175 than La1.35Sr0.65Ga3O7.175 and La1.35Ca0.65Ga3O7.175. The mobility μ were calculated according to the equation σ = *n* × *q* × μ, where *n* and *q* are concentration and charge of interstitial oxygen defects, respectively. Here the interstitial oxygen defect concentration *n* in La1.35M0.65Ga3O7.175 (M = Ba, Sr, Ca) was calculated using the number of the molecule (Z) and volume of unit cell (*V*) by *n* = Z×0.175/*V* and the calculated mobility values (10-7 cm2 V-1 s-1) at 400 °C for La1.35Ba0.65Ga3O7.175, La1.35Sr0.65Ga3O7.175 and La1.35Ca0.65Ga3O7.175 are 1.95, 5.78and 12.33, respectively.







**Figure 4**. Typical complex impedance plots of (a) La1.35Ba0.65Ga3O7.175 pellet and (b) La1.35Sr0.65Ga3O7.175 at 350 °C. Rb and Rgb denote bulk and grain boundary resistivities, respectively; the numbers denote the logarithms of the selected frequencies marked by the filled squares. In (a) the experimental and calculated data are shown as open squares and red solid line respectively and the deconvoluted bulk and grain boundary response arcs are shown in blue solid line. (c) Arrhenius plot of bulk conductivity of La1.35Ba0.65Ga3O7.175 (LBG), La1.35Sr0.65Ga3O7.175 (LSG), and La1.35Ca0.65Ga3O7.175 (LCG) pellets.

**Cationic-size control of accommodation and mobility of oxygen interstitials**. The maximum oxygen interstitials allowed in La1+*x*Ba1-*x*Ga3O7+0.5*x* is about half of that in La1+*x*Sr1-*x*Ga3O7+0.5*x* or La1+*x*Ca1-*x*Ga3O7+0.5*x*, suggesting that the ability of gallate melilites to accommodate oxygen interstitials is highly dependent on the sizes of cations in the pentagonal tunnels: the large Ba2+ cations are less favourable for stabilizing the oxygen interstitials than the smaller Sr2+ and Ca2+ cations in La1+*xM*1-*x*Ga3O7+0.5*x* (*M* = Ba, Sr, Ca) melilites. As the variation on the cationic sizes directly affects the long-range columbic interactions and short-range electrostatic repulsions among the atoms that determine the lattice energy, the static lattice atomistic simulations were performed based on the interatomic potential method to obtain the formation energies of oxygen interstitial defects in La1+*xM*1-*x*Ga3O7+0.5*x* melilites. Such energies allow to quantitatively measure the ease of accommodation of the oxygen interstitial defects and correlate it with the *M*2+ size in La1+*xM*1-*x*Ga3O7+0.5*x*.

The static lattice atomistic simulations were performed on the parent La*M*Ga3O7 initially with the tetragonal cell in P21m containing disordered La/*M* over the pentagonal tunnels, which well reproduced the experimental structures (Table S4-6), e.g. the differences between the experimental and calculated cell parameters are less than 0.07 Å and the differences between the experimental and calculated bond lengths are less than 0.13 Å. In the tetragonal La*M*Ga3O7 melilites, the tunnel cations La3+ and *M*2+ share the same crystallographic site in a disordered manner. In order to simplify the static lattice atomistic simulations, at next stage, the P21m structures were transformed into 1×1×1 cells in *P*1 and simply an ordered structural model containing two pure La arrays and two *M* arrays (which is shown in Figure 5a but in a 1×1×2 supercell) in the tunnels was employed for the defect energy calculations. The formation energies for the oxygen interstitials in the La-containing and *M*-containing tunnels were calculated, and the differences of the formation energies are less than 0.19 eV for all of La*M*Ga3O7 (*M* = Ba, Sr, Ca) melilites, indicating that the local disorder distribution of La and *M* in the tunnels has a minor effect on the incorporation of oxygen interstitial defects into the tunnels in La*M*Ga3O7 from the energy point view. As shown in Table 3, LaBaGa3O7-based melilite has the largest formation energy for the oxygen interstitials among La*M*Ga3O7 materials. This indicates that large Ba2+ cations in the tunnels are the least energy-favourable for the interstitial oxygen accommodation, consistent with the experimental observation of that La1+*x*Ba1-*x*Ga3O7+0.5*x* has the narrowest solid solution limit among La1+*x*M1-*x*Ga3O7+0.5*x*.

**Table 3.** Formation energies of oxygen interstitial defects in La*M*Ga3O7 (*M* = Ba, Sr, Ca) from the static-lattice simulation.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *M* | Defect equation | Solid solution limit | r*M*2+(Å)\* | Energy (eV) | |
| La tunnel | *M* tunnel | |
| Ba |  | *x* = 0.35 | 1.42 | 2.71 | 2.74 | |
| Sr |  | *x* = 0.64[3](#_ENREF_3) | 1.26 | 1.69 | 1.50 | |
| Ca |  | *x* = 0.64[2](#_ENREF_2) | 1.12 | 2.08 | 2.23 | |

\*. The 8-coordinate radii are quoted here from Shannon database.[10](#_ENREF_10) The radius of La3+ is 1.16 Å.



**Figure 5**. Structural models of La1+*xM*1-*x*Ga3O7+0.5*x* melilite in a 1×1×2 super cell considered in the theoretical calculations: (a) La*M*Ga3O7 with pure La or M array in each tunnel, (b) La*M*Ga3O7 with mixed La/M array in each tunnel, (c) La1.5*M*0.5Ga3O7.25 with an interstitial oxygen placed between one La and one Sr cations, (d) La1.5*M*0.5Ga3O7.25 with an interstitial oxygen placed between two M cations, (e) La1.5*M*0.5Ga3O7.25 with an interstitial oxygen placed between two La cations. Model (a) was used for the static lattice simulation while models (b-e) were used for the DFT calculations.

As we know, the static-lattice simulations employ the empirical interatomic potential parameters, which were verified here based on only the reproduction of structural properties owing to absence of many other physical properties. Thus the reliability of these defect-formation energies remains questionable, particularly given the defect-formation energies in Table 3 do not vary systematically with the M cationic size. In order to confirm these defect-formation energies of the oxygen interstitial defects in La*M*Ga3O7 materials from the static-lattice simulation, the DFT calculations of total energies of reactants and products in reaction (1) described in the method section were performed to quantify the defect-formation energies of the oxygen interstitial defects according to the equation (2). For the parent structure, two models were taken into consideration: (1) a tunnel-cation ordered model in which each tunnel is filled with either pure La or pure M atoms (Figure 5a, referred to as model-p1); (2) a model in which each tunnel is filled with mixed La and M atoms (Figure 5b, referred to as model-p2). Three structural models of La1.5*M*0.5Ga3O7.25 were considered here: (1) a model with the interstitial defect placed between one La and one Sr cations (Figure 5c, referred to as model-d1); (2) a model with interstitial defect placed between two M cations (Figure 5d, referred to as model-d2); (3) a model with the interstitial defect placed between two La cations (Figure 5e, referred to as model-d3). The calculated formation energies of oxygen interstitial defects from 5 different appropriate combinations of models taking the tunnel-cation order-disorder into consideration for both the parent and defect-containing compositions are listed in Table 4. The DFT calculations gave interstitial defect formation energies 2.62-2.52 eV and 1.88-1.66 eV in La1+*x*Ba1-*x*Ga3O7+0.5*x* and La1+*x*Sr1-*x*Ga3O7+0.5*x*, respectively, which agree well with those from the static-lattice simulations. However the DFT calculation gave interstitial defect formation energies (0.81-0.92 eV) in La1+*x*Ca1-*x*Ga3O7+0.5*x* considerably lower than those (2.08-2.23 eV) from the static-lattice simulation. The DFT calculations also suggest that the local order-disorder of La and M distribution in the tunnels has a minor effect on the incorporation of oxygen interstitial defects into the tunnels for all of La*M*Ga3O7, consistent with the static lattice simulations. Therefore the DFT calculation essentially confirms the static-lattice simulation results except for the defect formation energy in La1+*x*Ca1-*x*Ga3O7+0.5*x*.

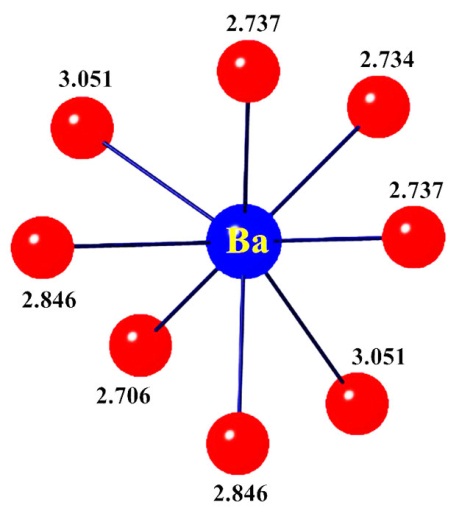
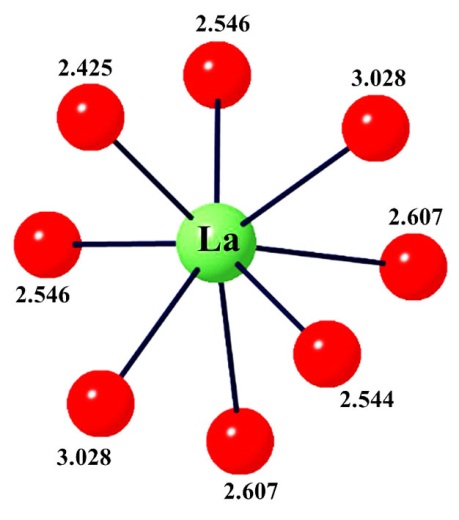
**Table 4**. Formation energies (△Hf) of oxygen interstitial defects in La1.5*M*0.5Ga3O7.25 (*M* = Ba, Sr, Ca) from the DFT calculations.

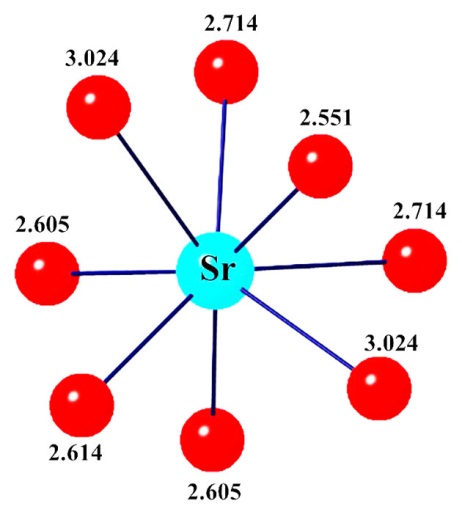
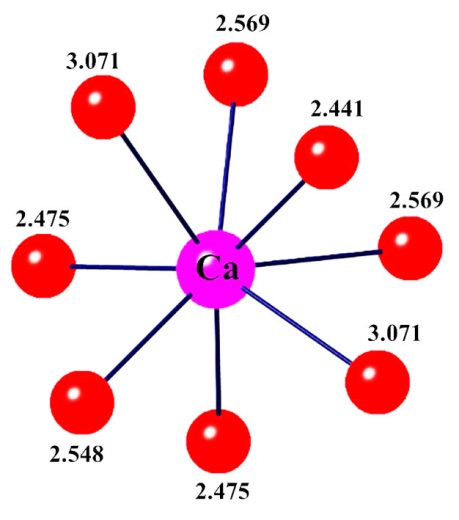
|  |  |  |
| --- | --- | --- |
| **M** | **Reactions** | **△Hf (eV)** |
| Ba | model-p1 + La2O3 → model-d1 + 2BaO | 2.62 |
| model-p1 + La2O3 → model-d2 + 2BaO | 2.61 |
| model-p1 + La2O3 → model-d3 + 2BaO | 2.55 |
| model-p2 + La2O3 → model-d1 + 2BaO | 2.59 |
| model-p2 + La2O3 → model-d3 + 2BaO | 2.52 |
|  |  |  |
| Sr | model-p1 + La2O3 → model-d1 + 2SrO | 1.88 |
| model-p1 + La2O3 → model-d2 + 2SrO | 1.85 |
| model-p1 + La2O3 → model-d3 + 2SrO | 1.77 |
| model-p2 + La2O3 → model-d1 + 2SrO | 1.77 |
| model-p2 + La2O3 → model-d3 + 2SrO | 1.66 |
|  |  |  |
| Ca | model-p1 + La2O3 → model-d1 + 2CaO | 0.81 |
| model-p1 + La2O3 → model-d2 + 2CaO | 0.87 |
| model-p1 + La2O3 → model-d3 + 2CaO | 0.81 |
| model-p2 + La2O3 → model-d1 + 2CaO | 0.93 |
| model-p2 + La2O3 → model-d3 + 2CaO | 0.92 |

The interstitial defect formation energies (△Hf) obtained from the DFT calculation indeed systematically vary with the *M*2+ cationic size: △Hf(Ba) > △Hf(Sr) > △Hf(Ca) (Table 4), suggesting the ability of accommodating interstitial defects with an order of Ca > Sr > Ba in La1+*xM*1-*x*Ga3O7+0.5*x* although La1+*x*Sr1-*x*Ga3O7+0.5*x* and La1+*x*Ca1-*x*Ga3O7+0.5*x* compositions display the same experimental solid solution limits. These interstitial defect formation energies appear as being inversely proportional to the conductivity of La1.35*M*0.65Ga3O7.175 with the same interstitial defect concentration, i.e. the mobility of oxygen interstitial defects (μ(Ba) < μ(Sr) < μ(Ca)). This indicates the tunnel-cation-size effect acts on the formation energy and mobility (i.e. energy barrier along the migration pathway) for the oxygen interstitial defect in a similar way, which is discussed below.

The weaker ability to accommodate the oxygen interstitials and lower mobility of oxygen interstitials in La1+*x*Ba1-*x*Ga3O7+0.5*x* than La1+*x*Sr1-*x*Ga3O7+0.5*x* and La1+*x*Ca1-*x*Ga3O7+0.5*x* indicate that the large size of Ba2+ is unfavourable for interstitial conductivity in the gallate melilites. The tunnel-cationic-size effect on the accommodation and mobility of oxygen interstitials in La1+*xM*1-*x*Ga3O7+0.5*x* melilite may be understood based on the stabilization and migration mechanism of oxygen interstitials. The oxygen interstitials incorporate into the pentagonal tunnels and bond into the coordination geometry of one 3-linked GaO4 of the five GaO4tetrahedra defining the tunnels; owing to the blocking from the A/B cations along the tunnel direction, the migration of oxygen interstitials take places among the pentagonal tunnels within the tetrahedral layers. In order to accommodate oxygen interstitials, the framework oxygen atoms around the interstitial-containing tunnel have synergic relaxation toward the neighbouring tunnels to avoid the short contacts with the oxygen interstitial (Figure 2c). This results in simultaneous size expansion for the interstitial-containing tunnel and contraction for the tunnels neighbouring the interstitial-containing tunnel (Figure 2c). Therefore for both accommodating the interstitials and sustaining their high mobility in the gallate melilites, both A and B cations are expected to have suitable sizes to adapt to the continuous tunnel-size expansion and contraction for lowering the energy barrier for the migration of oxygen interstitials among the pentagonal tunnels within the tetrahedral layers.

The large Ba2+ cations in the pentagonal tunnels of the gallate melilite are expected to have larger BaO8 polydedra than LaO8, SrO8 and CaO8 polyhedra. As the La3+ and Ba2+ cations share the same crystallographic sites in the crystal structure of LaBaGa3O7, the La/Ba-O bond lengths calculated from the refined structural parameters are average distances (accounting for the apparent over-bonding of Ba2+ and under-bonding of La3+ based on their BVSs in Table S3) thus can not reflect the size contrast between LaO8 and BaO8 polyhedra. Owing to the size contrast between La3+ and *M*2+ cations in La1+*xM*1-*x*Ga3O7+0.5*x*, the local oxygen-coordination geometry for the La3+ and *M*2+ cations are expected to be different on the cation-oxygen lengths. Here geometry-optimised structures based on the DFT calculations were used to describe the local coordination environments of La3+ and *M*2+ in La1+*xM*1-*x*Ga3O7+0.5*x*. The geometry optimizations of both parent La*M*Ga3O7 and interstitial-containing La1.5*M*0.5Ga3O7.25 compositions well evidence the O8-polyhedral size contrast relevant to the tunnel cationic size. The typical distances of tunnel cations with oxide anions in O8-polyhedra for the parent La*M*Ga3O7 are illustrated in Figure 6: the Ba-O distances vary within ~ 2.71-3.05 Å with an average Ba-O bond length ~ 2.84 Å, which is larger than those for La-O (~ 2.43-3.03 Å, ~ 2.65 Å), Sr-O (~ 2.55-3.02 Å, ~ 2.73 Å) and Ca-O (~ 2.44-3.07 Å, ~ 2.66 Å). The details on the typical distances of tunnel cations with oxide anions in interstitial-containing La1.5*M*0.5Ga3O7.25 in model-d1 (Figure 5c) are supplied in Table S7. Compared with La/Sr/Ca-containing tunnels, the Ba2+-containing tunnel has larger size, which itself should be favourable for accommodating the interstitials. However, the chemical bonding requirement of the large Ba-O separation within the tunnels is detrimental to the interstitial incorporation into the tunnels neighbouring the Ba-containing tunnel, as this could result in energy-unfavourable shrinkage of BaO8 polyhedron. Therefore compared with Ca2+ and Sr2+, the large Ba2+ is less favourable for both the accommodation and mobility of oxygen interstitials in the gallate melilite. The inverse relation between the mobility of oxygen interstitials and the *M*2+ cationic size in La1+*xM*1-*x*Ga3O7+0.5*x* (*M* = Ba, Sr, Ca) emphasizes that the smallest Ca2+ cation is the most beneficial to the interstitial oxygen mobility. The small tunnel cations results in misfit of tetrahedral layer with the interlayer cations, which may be accommodated by the displacive and occupational modulations and leads to long-range distortion for the tetrahedral framework, enabling the flexible deformation thus further facilitating the interstitial motion.[5](#_ENREF_5) Although the smaller-size tunnel cations Ca2+ and Sr2+ yield higher oxygen interstitial content and oxide ion conductivity than the Ba2+, further reducing the tunnel cationic size on the trivalent elements Ln3+ has shown detrimental effect on maintaining the oxygen interstitials in the melilite structure.[8](#_ENREF_8) This could be ascribed to both the small tunnel size and short bonding requirement arising from the small A/B cations hindering the incorporation of interstitials into the pentagonal tunnels since it could induce the energy-unfavourable polyhedral expansion for the small A/B cations in the tunnels. Therefore there should be an intermediate size range for the A/B cations that are favourable for the accommodation of oxygen interstitials in the gallate melilites, *i.e.* too small or too large tunnel A/B cations should be avoided in order to accommodate the oxygen interstitials with the high mobility retained in the melilite gallates.

**Figure 6**. Representative BaO8, LaO8, SrO8 and CaO8 polyhedra from the DFT-based geometry optimization of La*M*Ga3O7 melilites in model-p1 illustrated in Figure 5a. The red spheres denote oxide ions, and the numbers denote the bond lengths (Å) between cations and oxide ions. The calculated LaO8 polyhedra in the Ba, Sr, Ca-compounds have similar geometries thus only the one form Ba-compound is shown here.

**Conclusions**

Interstitial-oxygen conducting La1+*x*Ba1-*x*Ga3O7+0.5*x* solid solution was synthesised, showing a maximum interstitial oxygen concentration (*x* ≤ 0.35) of about half of those found in La1+*x*(Ca/Sr)1-*x*Ga3O7+0.5*x*. The static lattice atomistic simulation shows that the large Ba2+ cations are the least energy-favourable to create interstitial oxygen defects than the small cations Sr2+ and Ca2+ in La1+*xM*1-*x*Ga3O7+0.5*x* (*M* = Ba, Sr, Ca) melilites. Rietveld analysis of NPD data for La1.35Ba0.65Ga3O7.175 confirms the incorporation of the oxygen interstitials into the pentagonal tunnels and the local structural relaxation for stabilizing the interstitials in La1+*x*Ba1-*x*Ga3O7+0.5*x*, similar to the Sr and Ca counterparts. The conductivity comparison for La1+*xM*1-*x*Ga3O7+0.5*x* at the same content of oxygen interstitials (*x* = 0.35) indicates that the oxygen interstitials in La1+*x*Ba1-*x*Ga3O7+0.5*x* are less mobile than those in La1+*x*(Sr/Ca)1-*x*Ga3O7+0.5*x*. The cationic-size control of the interstitial oxide ion conductivity in La1+*xM*1-*x*Ga3O7+0.5*x* gallate melilites is interpreted using the local structural relaxation of synergic tunnel-size expansion/contraction required for accommodating and transporting the oxygen interstitials. The large oxygen bonding separation requirement of the large Ba2+ along the tunnel not only suppresses the ability to accommodate the interstitials in the tunnels neighbouring the Ba2+-containing tunnel but also reduces the mobility of the oxygen interstitials among the pentagonal tunnels within the tetrahedral layers.

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**Supporting information:** The calculated difference Fourier map at z = 0 section for La1.35Ba0.65Ga3O7.175; The reﬁned structural parameters for the average structural model of La1.35Ba0.65Ga3O7.175, Interatomic distances of La1.35Ba0.65Ga3O7.175 for the average structure model and site-split model;Calculated and experimental structural parameters for La*M*Ga3O7 (*M* = Ba, Sr, Ca); Crystallographic information in CIF format for the site-split model of La1.35Ba0.65Ga3O7.175; The distances of tunnel cations with oxide anions from the DFT-based geometry optimisation for the interstitial-containing La1.5*M*0.5Ga3O7.25 in model-d1.

**References**

1. Kuang, X.; Green, M. A.; Niu, H.; Zajdel, P.; Dickinson, C.; Claridge, J. B.; Jantsky, L.; Rosseinsky, M. J., Interstitial Oxide Ion Conductivity in the Layered Tetrahedral Network Melilite Structure. *Nat. Mater.* **2008,** *7*, 498-504.

2. Li, M. R.; Kuang, X.; Chong, S. Y.; Xu, Z.; Thomas, C. I.; Niu, H.; Claridge, J. B.; Rosseinsky, M. J., Interstitial Oxide Ion Order and Conductivity in La1.64Ca0.36Ga3O7.32 Melilite. *Angew. Chem. Int. Ed.* **2010,** *49*, 2362-2366.

3. Thomas, C. I.; Kuang, X.; Deng, Z.; Niu, H.; Claridge, J. B.; Rosseinsky, M. J., Phase Stability Control of Interstitial Oxide Ion Conductivity in the La1+xSr1−xGa3O7+x/2 Melilite Family. *Chem. Mater.* **2010,** *22*, 2510-2516.

4. Tealdi, C.; Mustarelli, P.; Islam, M. S., Layered LaSrGa3O7-Based Oxide-Ion Conductors: Cooperative Transport Mechanisms and Flexible Structures. *Adv. Funct. Mater.* **2010,** *20*, 3874-3880.

5. Wei, F.; Baikie, T.; An, T.; Schreyer, M.; Kloc, C.; White, T. J., Five-Dimensional Incommensurate Structure of the Melilite Electrolyte [CaNd]2[Ga]2[Ga2O7]2. *J. Am. Chem. Soc.* **2011,** *133*, 15200-15211.

6. Wei, F.; Gasparyan, H.; Keenan, P. J.; Gutmann, M.; Fang, Y.; Baikie, T.; Claridge, J. B.; Slater, P. R.; Kloc, C. L.; White, T. J., Anisotropic oxide ion conduction in melilite intermediate temperature electrolytes. *J. Mater. Chem. A* **2015,** *3*, 3091-3096.

7. Xu, J.; Kuang, X.; Véron, E.; Allix, M.; Suchomel, M. R.; Porcher, F.; Liang, C.; Pan, F.; Wu, M., Localization of Oxygen Interstitials in CeSrGa3O7+δ Melilite. *Inorg. Chem.* **2014,** *53*, 11589-11597.

8. Liu, B.; Ding, D.; Liu, Z.; Chen, F.; Xia, C., Synthesis and electrical conductivity of various melilite-type electrolytes Ln1+xSr1−xGa3O7+x/2. *Solid State Ionics* **2011,** *191*, 68-72.

9. Skakle, J. M. S.; Herd, R., Crystal chemistry of (RE,A)2M3O7 compounds (RE=Y, lanthanide; A=Ba, Sr, Ca; M=Al, Ga). *Powder Diffr.* **1999,** *14*, 195-202.

10. Shannon, R., Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallographica Section A* **1976,** *32*, 751-767.

11. Rietveld, H. M., A Profile Refinement Method for Nuclear and Magnetic Structures. *J. Appl. Crystallogr.* **1969,** *2*, 65-71.

12. Coelho, A. A. *Topas Academic V4*, Coelho Software: Brisbane, Australia, 2005.

13. Brown, I. D.; Altermatt, D., Bond-Valence Parameters Obtained from a Systematic Analysis of the Inorganic Crystal-Structure Database. *Acta Crystallogr., Sect. B: Struct. Sci.* **1985,** *41*, 244-247.

14. Johnson, D., ZView: A Software Program for IES Analysis, Version 2.8,. *Scibner Associates, Inc., Southern Pines, NC,* **2002**.

15. Gale, J. D., GULP: A Computer Program for the Symmetry-Adapted Simulation of Solids. *J. Chem. Soc., Faraday Trans.* **1997,** *93*, 629-637.

16. Gale, J. D.; Rohl, A. L., The General Utility Lattice Program (GULP). *Mol. Simul.* **2003,** *29*, 291-341.

17. Islam, M. S., Ionic Transport in ABO3 Perovskite Oxides: A Computer Modelling Tour. *J. Mater. Chem.* **2000,** *10*, 1027-1038.

18. Vanderbilt, D., Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Physical Review B* **1990,** *41*, 7892-7895.

19. Dick, B.; Overhauser, A., Theory of the Dielectric Constants of Alkali Halide Crystals. *Physical Review* **1958,** *112*, 90-103.

20. Fisher, C.; Islam, M., Defect, protons and conductivity in brownmillerite-structured Ba2In2O5. *Solid State Ionics* **1999,** *118*, 355-363.

21. Bayliss, R. D.; Cook, S. N.; Scanlon, D. O.; Fearn, S.; Cabana, J.; Greaves, C.; Kilner, J. A.; Skinner, S. J., Understanding the defect chemistry of alkali metal strontium silicate solid solutions: insights from experiment and theory. *J. Mater. Chem. A* **2014,** *2*, 17919-17924.

22. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996,** *77*, 3865-3868.

23. Irvine, J. T. S.; Sinclair, D. C.; West, A. R., Electroceramics: Characterization by Impedance Spectroscopy. *Adv. Mater.* **1990,** *2*, 132-138.

**Synopsis**

The cationic-size effect on the interstitial oxide ion conductivity in La1+*xM*1-*x*Ga3O7+0.5*x* (*M* = Ba, Sr, Ca) melilites is investigated through the static lattice atomistic simulation and density functional theory calculation and elucidated based on the local structural relaxation of synergic tunnel-size expansion/contraction required for accommodating and transporting the oxygen interstitials.



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