SYNTHESIS AND CONDUCTIVITIES OF THE APATITE-TYPE PHASES, La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26.5}$, La$_9$BaSi$_{6-x}$Ge$_x$O$_{26.5}$, AND RELATED TITANIUM DOPED SYSTEMS

J. E. H. Sansom, P. A. Sermon and P. R. Slater
Chemistry Division, SBMS, University of Surrey
Guildford, Surrey, GU2 7XH, UK

ABSTRACT

Apatite-type phases, e.g. (La/Sr)$_{10-x}$Si$_6$O$_{26+y}$, are attracting significant interest as an important new class of oxide ion conductor. The highest conductivities have been observed for the germanium based analogues, (La/Sr)$_{10-x}$Ge$_x$O$_{26+y}$, although these systems are complicated by germanium volatility problems. In this paper results are presented on mixed silicon/germanium systems, La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ and La$_9$BaSi$_{6-x}$Ge$_x$O$_{26.5}$ (0 $\leq$ x $\leq$ 6). We discuss how factors such as conductivity and germanium volatility vary with silicon to germanium ratio. In the former system, the highest conductivity was observed for x = 4, i.e. $\sigma_{200^\circ C}$ (La$_{9.33}$Si$_2$Ge$^4$O$_{26}$) = 0.06 S cm$^{-1}$, while for the latter, the highest conductivity was observed for x = 0, i.e. $\sigma_{200^\circ C}$ (La$_9$BaSi$_6$O$_{26.5}$) = 0.05 S cm$^{-1}$. Data on related titanium doped systems are also reported, and this substitution is shown to have a detrimental effect on the conductivity.

INTRODUCTION

Oxide ion conducting materials are attracting considerable interest, due to their applications in a range of technological applications, such as solid oxide fuel cell (SOFC) electrolytes. Most studies have focused on fluorite (e.g. doped ZrO$_2$, CeO$_2$) or perovskite (e.g. La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.03}$) related structures (see for example the review by Goodenough [1]). In these materials, the key defect consists of oxide ion vacancies, and conduction progresses via these vacant sites. More recently, interest has been developing in apatite-type phases, e.g. (La/Sr)$_{10-x}$(Si/Ge)$_x$O$_{26+y}$, following initial reports of high oxide ion conductivity in these phases by Nakayama et al. [2-28]. Apatite-type oxides have the general formula A$_{10-x}$M$_6$O$_{26+y}$, where A and M can be a range of cations, e.g. A = alkaline earths, rare earths; M = Si, Ge or P. The structure comprises isolated MO$_4$ tetrahedra, with the A cations located on 7 coordinate and 9 coordinate cavity sites. Of relevance to the oxide ion conductivity, are the oxide ion channels that run through the structure (figure 1).

Since these systems are quite complex structurally it is important to be able to rationalise the relationship between structure and properties, and this has been a key aim of the research in our group. Early work showed that fully stoichiometric systems, e.g. La$_9$Sr$_2$Si$_6$O$_{26}$, had much lower conductivities and higher activation energies than systems that contained either cation vacancies, e.g. La$_{9.33}$Si$_6$O$_{26}$, or oxygen excess, e.g.
La$_9$Sr$_2$Si$_6$O$_{26}$ [8]. Neutron diffraction experiments on the compounds La$_{9.33}$Si$_6$O$_{26}$ and La$_8$Sr$_2$Si$_6$O$_{26}$ showed that these materials have significant complexities in their structures, particularly within the channel oxygen sites, with the former sample showing significant disorder within the channels, in the form of oxygen Frenkel defects [8]. The importance of interstitial oxygens was further supported by computer modelling studies on La$_{9.33}$Si$_6$O$_{26}$ and La$_8$Sr$_2$Si$_6$O$_{26}$, which suggested that oxide ion conduction proceeded via an interstitial mechanism in La$_{9.33}$Si$_6$O$_{26}$, while for La$_8$Sr$_2$Si$_6$O$_{26}$ the mechanism involved vacancy migration [12,13]. The modelling studies predicted the presence of an energetically favourable oxygen interstitial position located at the periphery of the channels. Furthermore, a complicated interstitial migration mechanism, which was strongly dependent on the ability of the silicate substructure to relax towards the La sites, that contain the cation vacancies, was also predicted. Further support for the presence of interstitial oxide ions has come from recent structural studies of oxygen excess systems, La$_{9.33+x}$(Si/Ge)$_6$O$_{26+3x/2}$, and Mössbauer studies of Fe doped samples [14,18,19].

Most of the initial work in this area focused on the silicate-based systems discussed above. More recently, there has been growing interest in Ge based analogues. The initial report on these Ge based systems noted conductivities significantly higher than those of the silicates at temperatures > 600°C [20]. However, a wide range of conductivity data has since been reported [21-24], which may be related to the number of complexities within this system. In addition there have also been reports that the conducting phase is cation deficient La$_2$GeO$_5$ [25]. A key problem with these Ge based systems is that of GeO$_2$ volatility [22]. This leads to an increase in the La/Ge ratio, with La$_2$GeO$_5$ impurities being observed on extended GeO$_2$ loss. This probably accounts for the wide range of conductivities reported for these systems, with the presence of a high grain boundary component in such samples.

Key research, which has aided the understanding of the structural characteristics of the Ge based systems has been performed by Berastegui et al. and Leon-Reina et al. [14,23,24]. These studies have shown that the conducting phase was indeed apatite-type, and identified that, depending on the composition, the structure was either hexagonal or triclinic.

In this paper we expand on this work, by reporting studies of mixed silicon/germanium apatite systems, to examine how the conductivity varies with germanium content. We summarise our previously reported results for La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ (0 ≤ x ≤ 6) [28], and report new data for the series La$_8$BaSi$_{6-x}$Ge$_x$O$_{26.5}$ (0 ≤ x ≤ 6). We also report new studies
on the effect of titanium doping in these two systems, showing that this cation can be substituted onto the Si/Ge site.

**EXPERIMENTAL**

High purity La₂O₃, SiO₂, GeO₂, TiO₂, and BaCO₃, were used to prepare a range of samples. The dried starting materials were ground together in stoichiometric proportions and heated to high temperature for typically 28 hours, with an intermediate regrind (the synthesis temperatures employed are listed below). For samples containing Ge, the initial synthesis temperatures were kept low in order to limit Ge loss.

La₉.₃₃Si₆-xGeₓO₂₆ (x=0, 1350°C; x=1-5, 1100°C followed by 1250°C; x=6, 1150°C)
La₉.₃₃Si₄-xGeₓTi₂O₂₆ (x=0, 1300°C; x=2, 4, 1100°C)
La₉BaSi₆-xGeₓO₂₆.₅ (x=0, 1350°C; x=1-6, 1200-1250°C)
La₉BaSi₄-xGeₓTi₂O₂₆.₅ (x=0, 1300°C; x=2, 4, 1100°C)

The samples were then reground, pressed as pellets (1.3 cm diameter, 6000 kg cm⁻²) and sintered at 1550-1600°C for 2 hours. Densities of all pellets were in the region 86-94% theoretical. Phase purity was examined both before and after sintering using powder X-ray diffraction (Seifert 3003TT X-ray diffractometer). Conductivities of the single phase samples were determined using ac impedance measurements (Hewlett Packard 4192A Impedance analyser). Sintered pellets were coated with Pt paste to act as electrical contact for the measurements. Conductivities were measured in air for all samples. Extra measurements were taken under N₂ for the titanium doped samples in order to elucidate whether there was an electronic contribution to the conductivity. Total conductivities are reported due to problems resolving bulk and grain boundary components, which is a general problem, particularly for Ge containing apatite systems [7,8,22,28].

**RESULTS AND DISCUSSION**

La₉.₃₃Si₆-xGeₓO₂₆ (0 < x < 6) and La₉.₃₃Si₄-xGeₓTi₂O₂₆ (0 < x < 4)

Using the synthesis conditions employed, X-ray diffraction indicated the successful synthesis of single phase La₉.₃₃Si₆-xGeₓO₂₆ for x=0, 4-6. Refinement of the cell parameters indicated a hexagonal apatite cell, with cell parameters increasing with increasing Ge content [28]. For the samples with x=1-3, close inspection of the X-ray diffraction patterns revealed the presence of small shoulders on the peaks, suggesting the presence of two apatite phases with different Si/Ge ratio. In the case of the Ti doped samples, La₉.₃₃Si₄-xGeₓTi₂O₂₆ (0 ≤ x ≤ 4), all samples showed evidence for small impurities as prepared.

After the powders had been pressed as pellets and sintered at 1550-1600°C, the samples were again analysed using X-ray diffraction. After this heat treatment, the La₉.₃₃Si₆-xGeₓO₂₆ series was shown to be single phase hexagonal apatite for 0≤ x ≤ 4, with cell volume increasing with increasing Ge content (table 1, figure 2). From this data, however, it is clear that there are deviations from Vegard’s law for higher Ge contents. This can be related to Ge volatility, which then leads to an increase in Si:Ge ratio and consequently a smaller cell. For samples with higher Ge content (x>4), a complex pattern
was observed, with peak broadening/extra satellite peaks. This pattern was typical of that recently refined by Leon-Reina et al. as a triclinic apatite system [14,24].

For the Ti doped systems, \( \text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26} \) \( (0 \leq x \leq 4) \), X-ray diffraction of the sintered pellets showed that the phase with no Ge \( (x=0) \) was still not quite single phase. The X-ray pattern did show peak shifts to lower angles consistent with the successful incorporation of the larger Ti onto the Si site, and further work is planned to modify the synthesis conditions so as to achieve a single phase sample of this material. The Ge containing samples were, however, shown to be phase pure, with a hexagonal apatite cell even for the sample with the highest Ge content \( (x=4) \). Therefore Ti doping appears to help favour the hexagonal apatite lattice over the triclinic lattice. The cell volumes for these samples were higher than the comparable phases without Ti doping (table 1, figure 2), consistent with the larger size of \( \text{Ti}^{4+} \), compared to \( \text{Si}^{4+} \), \( \text{Ge}^{4+} \), and therefore confirming successful Ti substitution. Attempts were made to increase the Ti content further in such systems, e.g. \( \text{La}_{9.33}\text{Ge}_3\text{Ti}_3\text{O}_{26} \), but this led to the presence of significant impurities, suggesting that the Ti solubility limit had been exceeded.

Table 1. Cell parameters (hexagonal cell) for \( \text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26} \) \( (0 \leq x \leq 4) \) and \( \text{La}_{9.33}\text{Si}_{4-x}\text{Ge}_x\text{Ti}_2\text{O}_{26} \) \( (2 \leq x \leq 4) \).

| Sample composition | (nominal composition) | a (Å)       | c (Å)       |
|--------------------|-----------------------|-------------|-------------|
| \( \text{La}_{9.33}\text{Si}_5\text{O}_{26} \) |                       | 9.721(3)    | 7.187(3)    |
| \( \text{La}_{9.33}\text{Si}_3\text{Ge}_2\text{O}_{26} \) |                       | 9.760(2)    | 7.222(2)    |
| \( \text{La}_{9.33}\text{Si}_4\text{Ge}_2\text{O}_{26} \) |                       | 9.790(4)    | 7.247(4)    |
| \( \text{La}_{9.33}\text{Si}_3\text{Ge}_3\text{O}_{26} \) |                       | 9.811(4)    | 7.265(4)    |
| \( \text{La}_{9.33}\text{Si}_2\text{Ge}_3\text{O}_{26} \) |                       | 9.820(4)    | 7.281(4)    |
| \( \text{La}_{9.33}\text{Si}_3\text{Ge}_4\text{O}_{26} \) |                       | 9.828(4)    | 7.289(4)    |
| \( \text{La}_{9.33}\text{Si}_2\text{Ge}_2\text{Ti}_2\text{O}_{26} \) |                       | 9.859(4)    | 7.285(4)    |
| \( \text{La}_{9.33}\text{Ge}_4\text{Ti}_2\text{O}_{26} \) |                       | 9.914(5)    | 7.312(4)    |

Figure 2. The variation of cell volume with Ge content \( (x) \) for (a) \( \text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26} \) and (b) \( \text{La}_{9.33}\text{Si}_{4-x}\text{Ge}_x\text{Ti}_2\text{O}_{26} \). The straight lines represent the expected cell volume if the system obeys Vegard's law.
For the Ti doped samples, there was a decrease in the conductivity compared to the equivalent samples without Ti doping. A possible explanation for this decrease could be the trapping of interstitial oxide ions by Ti increasing its coordination sphere from 4 to 6, and this feature needs further study. In order to determine whether the conductivity in this novel Ti doped series was mainly due to oxide ions, or whether there was significant electronic conductivity, conductivity measurements were repeated under N₂. In all cases the results showed no significant change in conductivity, suggesting that the conductivity is essentially ionic in nature.

Table 2. Conductivity data for La₉.₃₃Si₆₋ₓGeₓO₂₆ (0 ≤ x ≤ 6) and La₉.₃₃Si₄₋ₓGeₓTi₂O₂₆ (0 ≤ x ≤ 4).

| Sample (nominal composition) | Conductivity at 800°C (Scm⁻¹) | Ea (eV) |
|------------------------------|-------------------------------|--------|
| La₉.₃₃Si₆O₂₆                 | 2.02 × 10⁻³                   | 0.74   |
| La₉.₃₃Si₉Ge₂O₂₆             | 0.01                          | 0.87   |
| La₉.₃₃Si₄Ge₂O₂₆             | 0.03                          | 1.10   |
| La₉.₃₃Si₁₃Ge₂O₂₆            | 0.04                          | 1.10   |
| La₉.₃₃Si₂₅Ge₂O₂₆            | 0.06                          | 1.16   |
| La₉.₃₃Si₃₃Ge₂O₂₆            | 0.06                          | 1.11   |
| La₉.₃₃Si₅₅Ge₂O₂₆            | 0.05                          | 1.13   |
| La₉.₃₃Si₆₅Ge₂O₂₆            | 0.05                          | 1.30   |
| La₉.₃₃Ge₂O₂₆                | 0.01                          | 1.28   |
| La₉.₃₃Si₂Ge₂Ti₂O₂₆          | 1.40 × 10⁻³                   | 1.14   |
| La₉.₃₃Ge₄Ti₂O₂₆             | 9.10 × 10⁻³                   | 1.02   |

Since the sample, La₉.₃₃Si₂Ge₄O₂₆, showed very promising conductivity characteristics, further work was performed to examine the long term high temperature stability of this phase, and in particular to determine whether germanium volatility was still a problem for this mixed Si/Ge system. A portion of this material was sintered for 120 hours at 1500°C. In addition, the pellet used for conductivity measurements was also heated for 96 hours at 1500°C. In the case of the pellet, there was evidence for a small mass loss (≤1%), but there was no evidence for any impurity phases in the diffraction pattern. In addition the conductivity was similar to that previously obtained (σ₉₀₀°C = 0.05 S cm⁻¹, Eₐ = 1.12 eV). Sintering a portion of the powder for 120 hours at 1500°C resulted in a mass loss of >1%. In this case, the X-ray diffraction pattern of the sintered powder showed evidence for the formation of a small amount of La₂GeO₅ impurity. The conductivity of a pellet pressed and sintered of this powder showed a significantly lower conductivity, σ₉₀₀°C = 5.09 × 10⁻⁴ S cm⁻¹. The lower conductivity is probably related to the presence of poorly conducting La₂GeO₅ impurity. These results show that germanium loss is still a problem in the mixed silicon/germanium systems, although it does not appear to be as severe in this mixed Si/Ge sample as that reported previously for the Ge endmember, La₉.₃₃Ge₆O₂₆ [22].

La₉BaSi₆₋ₓGeₓO₂₆.₅ (0 ≤ x ≤ 6) and La₉BaSi₄₋ₓGeₓTi₂O₂₆.₅ (0 ≤ x ≤ 4)

As observed for the La₉.₃₃Si₆₋ₓGeₓO₂₆ series, the as-synthesised La₉BaSi₆₋ₓGeₓO₂₆.₅ series of samples were shown to be only single phase for the compositions, x=0, 4-6. Samples with 1 ≤ x ≤ 3 showed evidence for shoulders on the peaks, indicative of two apatite
phases of different Si:Ge ratios. After sintering as pellets at 1600°C for 2 hours, however, all samples became single phase. Refinement of cell parameters showed that all La$_9$BaSi$_{6-x}$Ge$_x$O$_{26.5}$ samples had a hexagonal apatite cell (table 3, figure 3). Thus Ba doping appears to help stabilise the hexagonal lattice in the high Ge content systems.

Table 3. Cell parameters (hexagonal cell) for La$_9$BaSi$_{6-x}$Ge$_x$O$_{26.5}$ (0 ≤ x ≤ 6) and La$_9$BaSi$_{4-x}$Ge$_x$Ti$_2$O$_{26.5}$ (0 ≤ x ≤ 4)

| Sample composition | (nominal composition) | a (Å)    | c (Å)    |
|--------------------|-----------------------|----------|----------|
| La$_9$BaSi$_6$O$_{26.5}$ | 9.743(4)             | 7.268(4) |
| La$_9$BaSi$_5$GeO$_{26.5}$ | 9.78(2)              | 7.30(2)  |
| La$_9$BaSi$_4$Ge$_2$O$_{26.5}$ | 9.815(5)         | 7.316(3) |
| La$_9$BaSi$_3$Ge$_3$O$_{26.5}$ | 9.840(3)            | 7.333(3) |
| La$_9$BaSi$_2$Ge$_4$O$_{26.5}$ | 9.874(3)            | 7.349(3) |
| La$_9$BaSiGe$_5$O$_{26.5}$ | 9.907(5)             | 7.359(5) |
| La$_9$BaGe$_6$O$_{26.5}$ | 9.927(9)             | 7.364(9) |
| La$_9$BaSiGeTi$_2$O$_{26.5}$ | 9.823(5)            | 7.297(5) |
| La$_9$BaSi$_2$Ge$_2$Ti$_2$O$_{26.5}$ | 9.899(3)        | 7.328(3) |
| La$_9$BaGe$_4$Ti$_2$O$_{26.5}$ | 9.970(3)            | 7.353(3) |

For the Ti doped samples, La$_9$BaSi$_{4-x}$Ge$_x$Ti$_2$O$_{26.5}$ (0 ≤ x ≤ 4), the phase La$_9$BaSi$_4$Ti$_2$O$_{26.5}$ was single phase as prepared, while the Ge containing systems required the high temperature sintering (1550°C for 2 hours) to achieve phase purity. All samples were shown to have a hexagonal cell, with cell parameters higher than the comparable sample without Ti doping (table 3, figure 3), consistent with the larger size of Ti$^{4+}$, compared to Si$^{4+}$, Ge$^{4+}$.

For both series of samples, the cell parameters appear to follow Vegard’s law, although for the La$_9$BaSi$_{6-x}$Ge$_x$O$_{26.5}$ series, the x=0, 6 samples lie slightly off the line. This needs to be investigated in more detail through structural studies.

![Figure 3. Variation in cell volume with Ge content (x) for (a) La$_9$BaSi$_{6-x}$Ge$_x$O$_{26.5}$ (0 ≤ x ≤ 6) and (b) La$_9$BaSi$_{4-x}$Ge$_x$Ti$_2$O$_{26.5}$ (0 ≤ x ≤ 4). The straight lines represent the expected cell volume if the system obeys Vegard’s law.](image-url)
The conductivities recorded for La$_9$Ba$_{6-x}$Ge$_x$O$_{26.5}$ ($0 \leq x \leq 6$) were high for all samples, ranging between 0.02 S cm$^{-1}$ and 0.05 S cm$^{-1}$ at 800°C (table 4). In this particular series, it appears that the silicate end member La$_9$BaSi$_6$O$_{26.5}$ is the optimum composition. This system shows the highest conductivity, 0.05 S cm$^{-1}$, and the lowest activation energy, 0.58/0.51 eV. In contrast, the activation energies for all the systems containing germanium are higher in value, ranging between 0.85 eV and 1.06 eV. The low activation energy for La$_9$BaSi$_6$O$_{26.5}$ means that at lower temperatures this material shows even higher conductivity than any of the germanium containing phases.

On Ti doping, the data shows a significant reduction in conductivity, which is particularly evident in comparing the samples, La$_9$BaSi$_4$Ti$_2$O$_{26.5}$ and La$_9$BaSi$_6$O$_{26.5}$. In this case there is a decrease in the conductivity at 800°C by nearly three orders of magnitude, along with a substantial increase in the activation energy (table 4). As noted earlier, this could be related to the trapping of interstitial oxide ions by Ti increasing its coordination sphere from 4 to 6. Measurements of the conductivities in N$_2$ showed negligible change compared to the data recorded in air, which suggests that the conductivity is ionic. A comparison of the data for La$_9$Ba$_{3.33}$Ge$_4$Ti$_2$O$_{26}$ and La$_9$Ba$_{3.33}$Ge$_4$Ti$_2$O$_{26}$ shows that the former has a higher conductivity. This is interesting, as previous studies of apatite systems have generally observed the highest conductivities for samples containing oxygen excess [8,9,16]. This needs further investigation, in particular through detailed structural studies.

### Table 4. Conductivity data for La$_9$Ba$_{6-x}$Ge$_x$O$_{26.5}$ ($0 \leq x \leq 6$) and La$_9$Ba$_{4-x}$Ge$_x$Ti$_2$O$_{26.5}$ ($0 \leq x \leq 4$).

| Sample (nominal composition) | Conductivity at 800°C (S cm$^{-1}$) | Ea (eV) (low temperature/ high temperature) |
|-----------------------------|------------------------------------|--------------------------------------------|
| La$_9$BaSi$_6$O$_{26.5}$    | 0.05                               | 0.58/0.51                                  |
| La$_9$BaSi$_5$Ge$_{0.5}$O$_{26.5}$ | 0.03                         | 0.85                                       |
| La$_9$BaSi$_4$Ge$_2$O$_{26.5}$ | 0.02                           | 1.01/0.88                                  |
| La$_9$BaSi$_3$Ge$_3$O$_{26.5}$ | 0.02                           | 1.02                                       |
| La$_9$Ba$_{3.33}$Ge$_4$Ti$_2$O$_{26}$ | 0.03                        | 1.06                                       |
| La$_9$BaSi$_{3.33}$Ge$_4$Ti$_2$O$_{26}$ | 0.02                      | 1.15/0.97                                  |
| La$_9$BaGe$_4$O$_{26.5}$    | 0.03                               | 1.06                                       |
| La$_9$Ba$_{3.33}$Si$_4$Ti$_2$O$_{26}$ | 5.99 x 10$^{-5}$       | 1.49                                       |
| La$_9$Ba$_{3.33}$Si$_4$Ge$_2$Ti$_2$O$_{26}$ | 1.80 x 10$^{-4}$       | 1.38                                       |
| La$_9$BaGe$_4$Ti$_2$O$_{26.5}$ | 1.15 x 10$^{-3}$           | 1.27                                       |

### CONCLUSIONS

In conclusion, a range of mixed Si/Ge and mixed Si/Ge/Ti systems have been prepared and their conductivities measured. For the series, La$_9$Ba$_{6-x}$Ge$_x$O$_{26}$ ($0 \leq x \leq 6$), all phases show high conductivities, although the activation energy is shown to increase with increasing Ge content. Samples with intermediate Ge content appear to show the highest conductivities at high temperature, e.g. $\sigma_{800\, ^\circ\text{C}}$ (La$_9$Ba$_{3.33}$Si$_4$Ge$_2$O$_{26}$) = 0.06 S cm$^{-1}$. For systems containing oxygen excess, La$_9$BaSi$_{6-x}$Ge$_x$O$_{26.5}$ ($0 \leq x \leq 6$), the pure silicate system appears to be the optimum composition, $\sigma_{800\, ^\circ\text{C}}$ (La$_9$BaSi$_6$O$_{26.5}$) = 0.05 S cm$^{-1}$. 

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On Ti doping in both systems, a significant decrease in conductivity is observed particularly for the Ti doped LaBaSi6-xGe6O26.5 series. This may be related to a readiness of Ti to expand its coordination sphere, and so trap the interstitial oxide ions, which are vital for the conductivity in these apatite systems.

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