CHAPTER 6

A STUDY ON THE SOLID STATE REACTION SYNTHESIS
OF Sr<sub>2</sub>GdRuO<sub>6</sub> (Sr-2116)

6.1 INTRODUCTION

The crystal structure of Sr<sub>2</sub>GdRuO<sub>6</sub> often called Sr-2116, because of its stoichiometry, belongs to the class of double perovskites of the general formula A<sub>2</sub>B<sub>B'</sub>O<sub>6</sub> with an alkaline earth A = Ca, Sr, Ba, a rare earth element B = Y, La, Nd, Eu, Gd-Lu and a transition metal B', in this case B' = Ru. As determined by neutron (Battle et al 1983, 1991) and X ray diffraction (Doi and Hinatsu 1999), these structures are composed of distorted perovskites with monoclinic space group P2<sub>1</sub>/n, and can be visualized as corner-sharing tilted oxygen octahedra alternately centered by B and B', while the bigger A ions are located in the twelve-fold coordinated site between the oxygen octahedra. The crystal structure of Sr<sub>2</sub>LnRuO<sub>6</sub> (Ln = Eu-Lu) is illustrated in Figure 6.1 (Doi and Hinatsu 1999).

Sr<sub>2</sub>GdRuO<sub>6</sub> offers the rare opportunity to study the magnetic behaviour of a 4d<sup>3</sup> electron system. The investigation of the magnetic properties of Sr-2116 revealed that the Ru moments order antiferromagnetically but most likely in a canted arrangement at about 35 K (Papageorgiou et al 2002). This canting of the Ru moments creates an internal field, which polarizes the Gd moments, leading to a rapid increase of the magnetization at 30 K. At about ~18 K, Gd-Gd antiferromagnetic interactions start to dominate the polarizing effect.
Figure 6.1 Crystal Structure of Sr$_2$LnRuO$_6$ (Ln = Eu-Lu) (Doi and Hinatsu 1999)
and the magnetization decreases. The actual antiferromagnetic ordering of Gd takes place at 3 K (Papageorgiou et al 2002).

A particular interest for the investigation of \( \text{Sr}_2\text{GdRuO}_6 \) arises from the fact that this compound plays an important role in the preparation of \( \text{RuSr}_2\text{GdCu}_2\text{O}_8 \) (Ru-1212) and \( \text{RuSr}_2\text{Gd}_{1.3}\text{Ce}_{0.7}\text{Cu}_2\text{O}_{10} \) (Ru-1222) superconductors. Using Sr-2116 as one of the precursors along with \( \frac{1}{2}\text{CeO}_2 \), \( \frac{1}{4}\text{Gd}_2\text{O}_3 \) and CuO high purity Ru-1212 and Ru-1222 can be synthesized. This preparation route is essential to avoid the appearance of perovskite impurities in Ru-1212 and Ru-1222 samples (Bauernfeind et al 1996, Bauernfeind 1998, Braun et al 2002) and has been widely adopted (Bernhard et al 1999, Tallon et al 1999, Mclaughlin et al 1999, Furukawa et al 2000, Hai et al 2001). It appears that the presence of pentavalent ruthenium in \( \text{Sr}_2\text{GdRuO}_6 \) effectively inhibits the formation of impurities (with tetravalent ruthenium) under oxidizing conditions. Braun et al (2002) proposed that the reaction path of Sr-2116 and CuO most likely follows the straight line in the phase diagram involving pseudo-binary equilibria and thus giving no room for the appearance of other phases.

It is beneficial for an improved synthesis method and for the understanding of magnetic properties to investigate the solid-state reaction occurring in the Sr-2116 formation based on thermal kinetics. Generally, Sr-2116 was prepared from stoichiometric mixtures of binary oxides and SrCO\(_3\) by calcination at 950°C in air, pressed into pellets and then sintered at 1250°C for 16 h in air (Papageorgiou et al 2002). Similarly, high purity Sr-2116 was synthesized in a water vapor atmosphere using SrCO\(_3\) as a raw material (Mingde et al 2002). The present study is aimed at investigating the reaction kinetics of Sr-2116 by the differential thermogravimetry analysis (DTA) and
X-ray diffractometry (XRD) methods during solid state reaction synthesizes using binary oxides as raw materials.

6.2 EXPERIMENTAL

High purity analytical grade powders of RuO$_2$, Gd$_2$O$_3$, SrCO$_3$ were used in this study. SrO was synthesized through decomposition of SrCO$_3$ calcined at 950°C in air for 24 h. Under ambient conditions, SrO as well as RuO$_2$ easily absorb water, so it was dried at 400°C for 4 h before weighing. The stoichiometric mixture of SrO, RuO$_2$ and Gd$_2$O$_3$ taken according to the composition of Sr-2116 was dryly blended in a zirconia jar for 12 h, and then pressed into pellets. The pellets were sintered in air: a) at 400°C for 4 h; b) at 850°C, 950°C, 1000°C, 1050°C, 1100°C, 1150°C and 1200°C for 1 h at each temperature. c) at 1250°C for 36 h; d) at 1070°C for various time periods of 10, 20, 30, 40, 50, 60, 80, 100 and 120 minutes.

X-ray powder diffraction was performed with a Seifert XRD 3000P diffractometer using Cu$K_a$ radiation at a scanning rate of 0.6° 2θ/min. The monoclinic lattice parameters at room temperature for Sr-2116 are $a = 5.792(4)$ Å, $b = 5.829(4)$ Å, $c = 8.200(1)$ Å and $\beta = 90.2(4)$°.

For the DTA experiments, the mixtures prepared by the above procedure were loaded in an alumina crucible, and heated in a Netzsch STA 409C analyser at a heating rate of 2.5, 5 and 10 °C/min. to obtain DTA curves.

6.3 RESULTS AND DISCUSSION

The sample calcined at 400°C for 4 h consists of SrO, Gd$_2$O$_3$ and RuO$_2$ as detected by XRD and shown in Figure 6.2a. However, the Sr$_4$Ru$_2$O$_9$
phase appears after sintering at 850°C for 1h, and the diffraction peak for a set of (300) planes is clearly observed as shown in Figure 6.2b. This solid-state reaction can be expressed as follows:

$$4\text{SrO} + 2\text{RuO}_2 + \frac{1}{2} \text{O}_2 = \text{Sr}_4\text{Ru}_2\text{O}_9$$  \hfill (6.1)

Simultaneously, a trace of \(\text{Sr}_2\text{RuO}_4\) is also visualized in the same sample, and its (110) diffraction peak slightly emerges in the spectrum. This solid-state reaction is

$$2\text{SrO} + \text{RuO}_2 = \text{Sr}_2\text{RuO}_4$$  \hfill (6.2)

Therefore, \(\text{Sr}_4\text{Ru}_2\text{O}_9\) is the first phase formed in the sample during the solid state reaction synthesis. With the increase of sintering temperature, the \(\text{Sr}-2116\) phase is generated as shown in Figure 6.2c. The characteristic (020) peak can be distinctly seen in the sample sintered at 950°C. In this procedure, the solid-state reaction is given as:

$$\text{Sr}_4\text{Ru}_2\text{O}_9 + \text{Gd}_2\text{O}_3 = 2\text{Sr}_2\text{GdRuO}_6$$  \hfill (6.3)

At 1000°C, the amount of \(\text{Sr}_2\text{RuO}_4\) increases while that of \(\text{Sr}_4\text{Ru}_2\text{O}_9\) gradually decreases until the latter disappears at 1050°C. In this reaction, \(\text{Sr}_4\text{Ru}_2\text{O}_9\) transforms into \(\text{Sr}_2\text{RuO}_4\) after losing one oxygen atom, and the production of \(\text{Sr}-2116\) is then mainly controlled by

$$\text{Sr}_2\text{RuO}_4 + \frac{1}{2} \text{Gd}_2\text{O}_3 + \frac{1}{2} \text{O}_2 = \text{Sr}_2\text{GdRuO}_6$$  \hfill (6.4)

As mentioned above, \(\text{Sr}_4\text{Ru}_2\text{O}_9\) is not stable at higher temperatures in air, and \(\text{Sr}-2116\) is formed through the reaction of Eq.(6.4). The phase pure \(\text{Sr}-2116\) is obtained after sintering at 1250°C for 36 h.
Figure 6.2  The XRD spectrum for samples sintered at a) 400°C for 4 h; b) 850°C for 1 h; c) 950°C for 1 h; d) 1000°C for 1 h; e) 1050°C for 1 h and f) 1250°C for 36 h

- O $\text{RuO}_2$;  • $\text{Gd}_2\text{O}_3$;  □ $\text{SrO}$;  ■ $\text{Sr}_4\text{Ru}_2\text{O}_9$;  
- ♦ $\text{Sr}-2116$;  A $\text{Sr}_2\text{Ru}_2\text{O}_7$
Sr$_2$RuO$_4$ is a noncuprate layered perovskite material, which exhibits superconductivity below $T_c\sim 1.5$ K (Maeno et al 1994) with a structure of K$_2$NiF$_4$ type (Chmaissem et al 1998). Sr$_4$Ru$_2$O$_9$ is related to the 2H hexagonal perovskite structure, and the stacking sequence along the c-axis corresponds to an ordering between three consecutive Sr$_3$O$_6$ layers and one Sr$_3$O$_9$ layer. Chains parallel to c are formed by double octahedra separated by empty trigonal prisms (Dussarrat et al 1995, Dussarrat 1998). The two available oxidation states of Ru allow two oxygen stoichiometries yielding two different structures (Rijssenbeek et al 2002). Although structurally very different, the stoichiometries of Sr$_2$RuO$_4$ and Sr$_4$Ru$_2$O$_9$ differ only in their oxygen content. Our experimental result reveals that the Ru$^{5+}$ state is stable near 850°C when synthesised in air. So Sr$_2$Ru$_2$O$_9$ is easily formed. However, above 1050°C in air, the Ru$^{4+}$ state dominates, Sr$_4$Ru$_2$O$_9$ loses an oxygen atom and transforms into Sr$_2$RuO$_4$. Similar transformations have been observed in other compounds with similar structures. For example, Sr$_3$CaRu$_2$O$_9$, initially synthesized in air, was quantitatively converted into Sr$_{1.5}$Ca$_{0.5}$RuO$_4$ by a treatment in 1 bar flowing argon for 24 h at 1200°C (Rijssenbeek et al 2002). Re-oxidation returned the original 3D structure after 24 h heat treatment at 1000 °C in 1 bar flowing oxygen. This transformation was reproducible for multiple times. (Rijssenbeek et al 2002).

Figure 6.3 shows the changes in X-ray intensity ratio $I_{\text{Sr-2116}}/(I_{\text{Sr-2116}}+I_{\text{Gd2O3}})$ with synthesis temperature. In this solid state reaction, the content of Gd$_2$O$_3$ appears to be changing independently. However, it depends on the amount of Sr$_3$Ru$_2$O$_9$ or Sr$_2$RuO$_4$ which is formed in the reaction process. Therefore, more than two variables are needed to determine the transformed volume fraction of Sr-2116. Only if a mixture of either pure Sr$_3$Ru$_2$O$_9$ or pure Sr$_2$RuO$_4$ and Gd$_2$O$_3$ is used in the solid state reaction, $I_{\text{Sr-2116}}/(I_{\text{Sr-2116}}+I_{\text{Gd2O3}})$ can
be used as a unique variable to describe the transformed volume fraction of Sr-2116. With prolonged isothermal sintering time at 1070°C, the ratio $I_{\text{Sr-2116}}/(I_{\text{Sr-2116}}+I_{\text{Gd_2O_3}})$ increases as shown in Figure 6.4. The curves shown in Figure 6.3 and Figure 6.4 reflect the basic characteristics of the solid-state reactions which occur during the formation of Sr-2116, but further investigation is needed to explore the kinetic mechanism.

Figure 6.5 shows the DTA curves obtained at the heating rates of 2.5, 5, 10°C/min. The summits of the peaks at different positions represent the temperatures of maximum reaction rate at three different heating rates. A shift in the peak temperature to higher value with increasing heating rate has been observed. The first set of endothermic peaks between 700 and 950°C have the large full width at half maximum of nearly 70-90°. According to the XRD results on the powders sintered in the temperature range from 850 to 1000°C, we consider that each of the broad humps contains two endothermic peaks associated with the reactions based on equations (6.1) and (6.2) respectively. Using two Gaussians, the broad humps located in the temperature range of 700-950°C at three different heating rates are merged into two peaks. The Chi-square value of this fit is less than $4.2 \times 10^{-5}$. Thus, the first set of peaks is divided into two parts, marked $P_1$ and $P_2$ in Figure 6.6, which involve the reactions based on equations (6.1) and (6.2) respectively. Another set of peaks marked $P_3$, located in the temperature range of 1100-1200°C for all three heating rates, is attributed to the reaction based on Equation (6.4).

The maximum reaction temperature $T_m$, i.e., the temperature at which the largest reaction rate appears, changes as the heating rate is varied. Reich (1964) and Nae-Lih et al (1990) suggested that for a reaction occurring within a small temperature range, its activation energy $E$ can be estimated from the slope
Figure 6.3 XRD intensities ratio $I_{\text{Sr}-2116}/(I_{\text{Sr}-2116}+I_{\text{Gd}_2\text{O}_3})$ versus the sintering temperature

Figure 6.4 XRD intensities ratio $I_{\text{Sr}-2116}/(I_{\text{Sr}-2116}+I_{\text{Gd}_2\text{O}_3})$ versus the sintering time at 1070 °C
Figure 6.5  DTA curves measured for the stoichiometric mixture of SrO, Gd$_2$O$_3$ and RuO$_2$ according to the composition of Sr-2116 at the heating rate a) 2.5, b) 5 and c) 10 °C/min.

Figure 6.6  Decomposition of the broad hump obtained at the heating rate of 10°C/min. into two Gaussians P$_1$ and P$_2$ associated with the reactions based on Eqns. (6.1) and (6.2), respectively. P$_3$ is associated with the reaction based on Eqn. (6.4)
of the straight line, plotted for $\ln(T_m^2/\beta)$ versus $(1/T_m)$ as shown in Figure 6.7. This can be expressed as,

$$\ln\left(\frac{T_m^2}{\beta}\right) = (E/R)(1/T_m)$$  \hspace{1cm} (6.5)$$

where $\beta$ is the heating rate, and $R$ the gas constant. Figure 6.7 shows the curves of $\ln(T_m^2/\beta)$ versus $(1/T_m)$ for the solid state reactions based on a) Eqn.(6.1); b) Eqn.(6.2); c) Eqn.(6.4). The activation energies of the reactions, obtained using Eqn.(6.5) are listed in Table 6.1.

The results reveal that the values of activation energy for the formation of Sr$_4$Ru$_2$O$_9$ and Sr$_2$RuO$_4$ are close to each other. According to the XRD observations, Sr$_4$Ru$_2$O$_9$ is formed at a lower temperature than Sr$_2$RuO$_4$ and has the lower activation energy. In contrast, the formation of Sr-2116 has the high activation energy of 1033 kJ/mol. In the study of formation of R$_2$Ba$_4$Cu$_6$O$_{13}$ (R=Y, La, Nd, Sm, Eu or Er) using citrate precursors (Arul Antony et al 2001), an activation energy of 809 kJ/mol was estimated for the formation of Eu$_2$Ba$_4$Cu$_6$O$_{13}$ in the temperature range of 970-1010°C, and 445 kJ/mol. for Y$_2$Ba$_4$Cu$_6$O$_{13}$ under the same experimental conditions. The activation energy ($E$) is usually identified as the energy barrier (or threshold) that must be surmounted to enable the occurrence of the bond redistribution steps required to convert reactants into products. The higher the activation energy, the more difficult is the formation. Thus, Sr-2116 phase is stable at high temperature. Up to 1500°C, no change was observed for Sr-2116 by DTA measurement (Bauernfeind et al 1996, Braun et al 2002), and the same is confirmed in the present work. The high stability of Sr-2116 phase helps to prevent impurities from appearing in the preparation of RuSr$_2$GdCu$_2$O$_8$ and RuGd$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$O$_{10}$ via the precursor route.
Figure 6.7  The curves of $ln(T_m^{-2}/\beta)$ versus $(1/T_m)$ for the solid state reactions based on a) Eqn.(6.1), b) Eqn.(6.2) and c) Eqn.(6.4)

Table 6.1  Values of the activation energy $E$ and the transformed dimensionality $n$ for the solid state reactions related to Eqns. (6.1), (6.2) and (6.4)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activation energy, $E$ (kJ/mol)</th>
<th>Transformed dimensionality, $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4$SrO + $2$RuO$_2$ + $\frac{1}{2}$ O$_2$ = Sr$_2$Ru$_2$O$_9$</td>
<td>$188 \pm 12$</td>
<td>$2.6 \pm 0.2$</td>
</tr>
<tr>
<td>$2$SrO + RuO$_2$ = Sr$_2$RuO$_4$</td>
<td>$217 \pm 15$</td>
<td>$2.8 \pm 0.1$</td>
</tr>
<tr>
<td>Sr$_2$RuO$_4$ + $\frac{1}{2}$ Gd$_2$O$_3$ + $\frac{1}{2}$ O$_2$ = Sr$_2$GdRuO$_6$</td>
<td>$1033 \pm 104$</td>
<td>$2.7 \pm 0.1$</td>
</tr>
</tbody>
</table>
The width $\Delta T_p$ of the DTA peak taken at half maximum is predicted to be a qualitative measure for the dimensionality of the transformation, $n$, (Ray et al 1996, Augis and Bennet 1978),

$$n = 2.5R \left\{ \frac{T_p^2}{\Delta T_p \ E} \right\}$$  \hspace{1cm} (6.6)

Where $R$ is the gas constant, $T_p$ the peak temperature, and $E$ the activation energy. Using Eq.(6.6), the transformation dimensionalities $n$ can be calculated for the peaks $P_1$, $P_2$ and $P_3$ related to the reactions based on Eqns. (6.1), (6.2) and (6.4) respectively. These value of $n$ close to 3 (Table 6.1) suggests the solid state reaction is of bulk or three dimensional nature.

6.4 CONCLUSION

A systematic study has been carried out on the solid-state reaction synthesis of $\text{Sr}_2\text{GdRuO}_6$ (Sr-2116). The reactions were studied by thermal analysis and X-ray diffractometry. The formation of $\text{Sr}_4\text{Ru}_2\text{O}_9$, $\text{Sr}_2\text{RuO}_4$ and $\text{Sr}_2\text{GdRuO}_6$ are discussed and their activation energies have been estimated. The formation of Sr-2116 is having high activation energy of 1033 kJ/mol. Thus, the Sr-2116 phase is stable at high temperature. The high stability of Sr-2116 phase prevents impurities to appear in the preparation of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ and $\text{RuGd}_{1.5}\text{Ce}_{0.5}\text{Sr}_2\text{Cu}_2\text{O}_{10}$ via the precursor route. The values of the dimensionality of the transformation close to 3 suggest that the solid state reaction is of bulk or three dimensional nature.