Crystal growth of $RuSr_2GdCu_2O_8$ compound

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Flux growth technique using Alkali halide flux and self flux, was investigated for the growth of $RuSr_2GdCu_2O_8$ single crystals under ambient pressure. In alkali halid flux method we have used NaCl, KCl, K_2CO_3 as flux material, but no single crystal of Ru-1212 could be found using these fluxes. In self flux method, the initial composition of reactants i.e. Ru:Sr:Gd:Cu is taken in ratio 1.8:2:1.4:3.7 and 1.6:2:1.4:3. The morphology of the single crystals was examined using scanning electron microscope (SEM). Compositional analysis of these crystals is done using EDX attached to SEM. The XRD technique confirmed 1212 phase formation.

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1. Introduction

A considerable research effort has been devoted recently to the understanding of the physical properties of the ruthenocuprate compounds with general composition $RuSr_2LnCu_2O_8$ and $RuSr_2(Ln_{1+x}Ce_{1-x})Cu_2O_{10}$ (Ln = Sm, Eu, and Gd) [1,2]. The interest in these materials was triggered by the observation of coexisting superconductivity (SC) and long-range magnetic order, including weak-ferromagnetism (wFM), at moderately high temperatures (T) [3,4]. The occurrence of long-range magnetic order has been determined by means of magnetic susceptibility, and muon spin relaxation, while details of the magnetic and crystal structure have been studied by neutron diffraction [5]. Heat capacity measurements and diamagnetic shielding fraction data indicate that SC is a bulk property, coexisting in a microscopic scale with magnetism in these materials [6, 7].

A major problem related to the understanding of the physical mechanisms involved in ruthenocuprates i.e $RuSr_2RCu_2O_8$ (Ru-1212) and $RuSr_2(R_{1+x}Ce_{1-x})Cu_2O_{10}$ (Ru-1222) with R = Gd, Eu or Sm, compounds, is the diversity of properties in different samples. Essentially it is needed to have pure samples to get information without the influence of the characteristic disorder of cuprate oxides. Because of that, single crystals provide the best tool to study the typical characteristic properties of these systems.

The single crystals of oxide materials can be grown by a number of techniques, such as, flux growth, Bridgman technique, Czochralski technique, top-seeded solution growth etc. Among these flux-growth is a simple and effective technique in particular for oxide material. In this method, the solute (a material of which crystals need to be grown) is dissolved in a specific flux at high temperatures. A slow cooling (of the solution) and/or continuous evaporation of flux (from the solution) leads to a supersaturated solution. This results in the nucleation and growth of the crystals. But ruthenocuprates melt incongruently. The crystal form at relatively high temperature (> 1100 °C) where it is difficult to achieve a sufficient solubility of Ru atoms in the crystal because the vapour pressure and escape rate of Ru is very high during growth process. Here, we have investigated the self-flux technique to grow the single crystals of $RuSr_2GdCu_2O_8$ superconducting compound.

2. Experimental

Alkali halide flux method

For growth of $RuSr_2GdCu_2O_8$ single crystals, alkali halide flux method was used. First, the solute (polycrystalline $RuSr_2GdCu_2O_8$ material) and the flux (NaCl 99.95 % pure) were mixed in different weight ratios, i.e. 1: 3, 1: 4, and 1: 5 and, put into an alumina crucible (inner diameter of 6 cm and 4 cm height). Then the crucible (covered with an alumina lid) was put into a vertical furnace (with a temperature controller that could control temperature with an accuracy of $\pm 1^oC$) and heated to 1050 ^oC for 5 h. Subsequently, the furnace was cooled very slowly at a rate of 1 ^oC/h to 800 ^oC and finally to room temperature at a rate of 60 ^oC/h. The solidified charge was dissolved in de-ionized water to separate crystals from the flux. This flux yields CuO oxide crystals. Several growth runs were carried out using different fluxes, such as, KCl, K_2CO_3, etc. But, no single crystal of Ru-1212 could be grown using these fluxes.

Self - flux method

In this method we have investigated the two starting compositions: (a) $Ru_{1.8}Sr_2Gd_{1.4}Cu_{3.7}O_8$ and $Ru_{1.6}Sr_2Gd_{1.4}Cu_3$. Usually 3-4 g of the mixture of RuO_2, $SrCO_3$, Gd_2O_3 and CuO were taken in stoichiometric ratio. This mixture is ground for 4-5 h in an agate mortar. This mixture is then transferred to a alumina crucible and heated in a raising hearth furnace in air at 880 ^oC for two

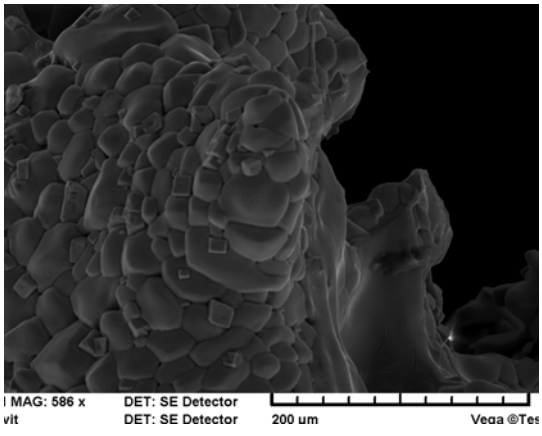
days. This calcined mixture is then grinded into fine powder and pressed into pellets and heated in oxygen flow at 920 °C for two days followed by furnace cooling. The resulting pellets then grinded again and put in a alumina crucible and put it in a raising hearth furnace. For initial composition (a) the mixture is heated to 1300 °C with a rate of 200 °C/h and kept for 2 h at this temperature. Then it cooled down to 930 °C with a rate of 1.5 °C/h and finally to room temperature with a rate of 200 °C/h. In the case of composition (b) the mixture is heated to 1325 °C with a rate of 200 °C/h and kept for 2 h at this temperature followed by cooling down to 950 °C with a rate of 1 °C/h and finally to room temperature with a rate of 60 °C/h. The morphology of the single crystals was examined using scanning electron microscope. Composition of these crystals is done using EDX analyzer attached to the same SEM. The XRD technique is used to confirm 1212 phase formation. The results thus obtained are presented and discussed in the next section

3. Results and discussion

Using alkali halide as flux, we did not get any Ru-1212 single crystal, but get CuO crystals. This might be due the decomposition of Ru-1212 in alkali halide. Thus alkali halide flux technique is unsuitable for the growth of Ru-1212 single crystals. The second technique that has been investigated for the single crystal growth is self flux growth. In this technique the off stoichiometeric composition of the various reactants was taken.

3.1 Crystal morphology

The morphology of the crystals in the melt is shown in Fig. 1. In this figure one can see the randomly distributed single crystals with tetragonal geometry. The crystal have well defined facet as evident from Fig. 2 in which the image of individual crystal with different orientation is shown.



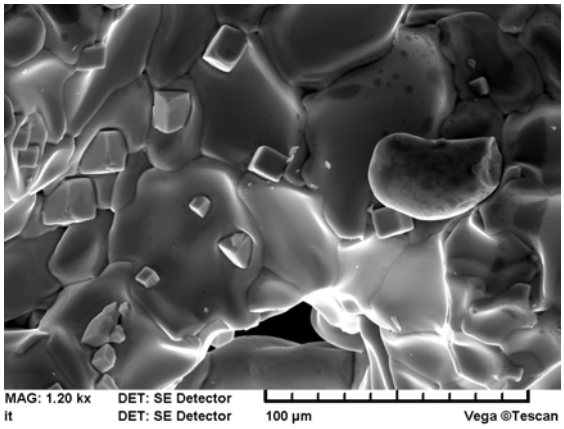
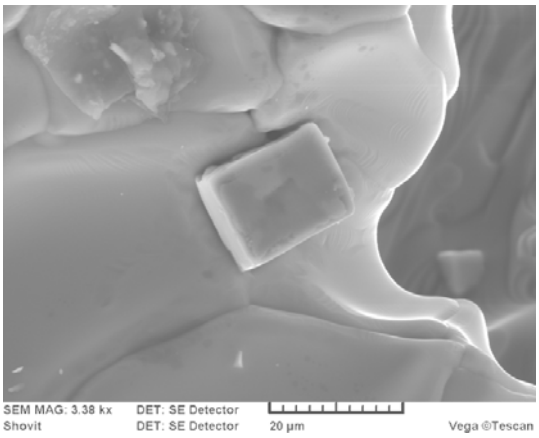


Fig. 1. Distribution of crystal in the flux matrix.



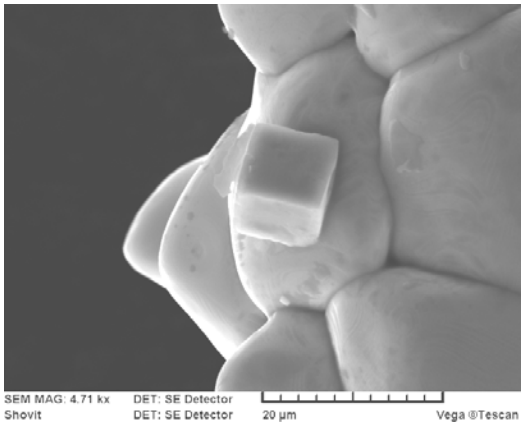


Fig. 2. SEM micrographs of individual crystals.

3.2 Compositional analysis

The compositional analysis of the grown crystals were performed using EDX technique. The typical sample used for EDX analysis is shown in Fig.3. In this figure the various scanned sites are marked as spectrum 1, spectrum 2, spectrum 3, spectrum 4, spectrum 5 and spectrum 6. The obtained results from this analysis are presented in table 1.

On inspection of Table 1 one can easily say that the crystals with sharp flat faces (spectrum 1, 3, 4, 5) are of nearly Ru-1212 stoichiometery, while spectrum 2 and 6 corresponds to the melt.

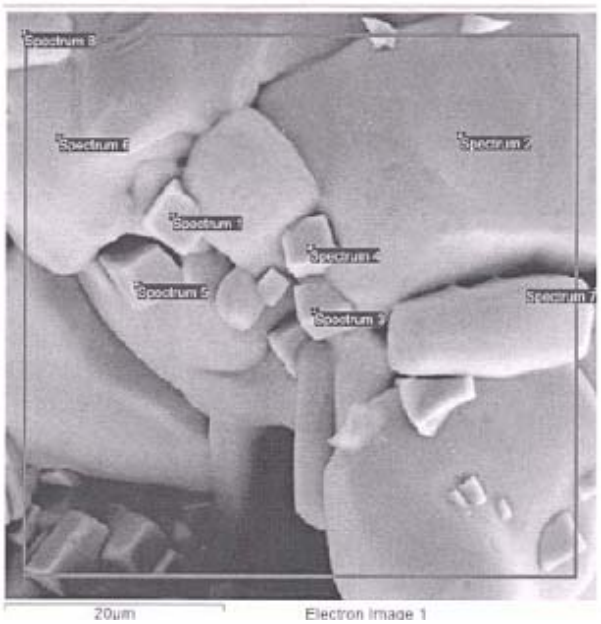


Fig. 3. The specimen of sample used for EDAX analysis.

Table 1. The Atomic percentage at different spectrum of the sample used for EDAX.

Site of Interest	Atomic percentage of cations			
	Ru	Sr	Gd	Cu
Spectrum 1	6.00	11.08	5.90	10.99
Spectrum 2	3.61	39.36	3.05	6.26
Spectrum 3	6.58	11.48	6.43	12
Spectrum 4	6.74	12.42	6.74	12.27
Spectrum 5	6.48	10.53	5.44	10.43
Spectrum 6	11.93	10.94	3.07	3.28
Spectrum 7	0.92	77.49	3.16	8.74
Spectrum 8	7.72	10.63	2.74	10.19

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3.3 XRD analysis

The XRD pattern of the powdered crystals is shown in Fig. 4. Excepting a few peaks all other peaks can be indexed to the tetragonal structure with lattice parameters a = 3.914 Å and c = 11.559Å. These values are in accordance with Lin. et. el. [8].

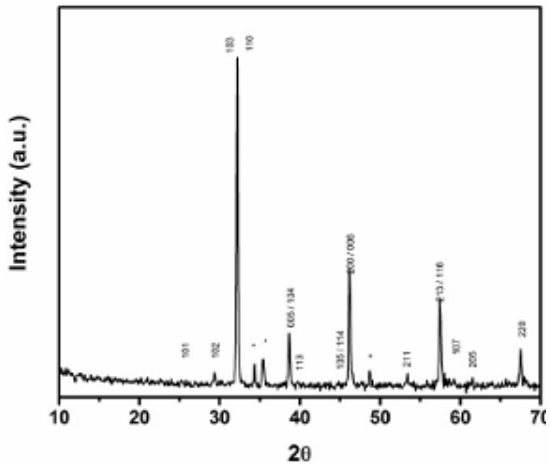

Fig. 4. XRD Pattern of powder of crystals.

4. Conclusion

The alkali-halide flux and self flux method have been investigated for the growth of Ru-1212 compound. In case of alkali haide flux method no Ru-1212 crystal formation was observed. Self flux method results in the formation of Ru-1212 crystal of sized of 50-100 μm.

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