

Direct observation of melting and solidification of
 $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_{1.9}\text{Ca}_{2.1}\text{Cu}_{3.5}\text{O}_x$ in various oxygen atmospheres
by high temperature optical microscopy

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Abstract

The melting and solidification processes of the $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_{1.9}\text{Ca}_{2.1}\text{Cu}_{3.5}\text{O}_x$ in various oxygen atmospheres have been observed in situ using a high temperature optical microscopy. In the melting process, the samples began to melt at 788°C in N_2 , 862°C in 8% O_2+N_2 , 880°C in air, 895°C in O_2 . Many dark needle-like crystals $(\text{Sr,Ca})_2\text{CuO}_3$ and the white bar-like crystals $(\text{Sr,Ca})\text{CuO}_2$ appeared in the liquid phase. When the temperature was raised, $(\text{Sr,Ca})\text{CuO}_2$ first melted and then $(\text{Sr,Ca})_2\text{CuO}_3$ melted peritectically ($(\text{Sr,Ca})_2\text{CuO}_3 \rightarrow \text{CaO}+\text{L}$). In the solidification process, two peritectic reactions $\text{CaO}+\text{L} \rightarrow (\text{Sr,Ca})_2\text{CuO}_3$ and $(\text{Sr,Ca})_2\text{CuO}_3 + \text{L} \rightarrow \text{Bi-2212}$ were observed in the atmospheres of air, 8% O_2+N_2 , and O_2 , whereas in N_2 , only a reaction of $\text{L} \rightarrow \text{Bi-2201}$ was observed.

Key words: Bi-superconductor; Oxygen; Melting; Solidification; Microstructure

1. Introduction

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Since Bi-Sr-Ca-Cu-O oxide was discovered to have a high transition temperature T_c [1], its preparation processes, structures, and superconducting properties have been investigated extensively. This system contains at least three kinds of superconducting phases, namely the Bi-2223 ($\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$) high- T_c phase, the Bi-2212 ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$) low- T_c phase, and the Bi-2201 ($\text{Bi}_2\text{Sr}_2\text{CuO}_x$) phase. The critical temperatures of these three phases are about 110 K, 80 K and 20 K, respectively. Although it has been found that partial substitution of Pb for Bi is favorable for obtaining the Bi-2223 phase [2], the synthesis of single Bi-2223 phase materials is still difficult due to poor understanding of its complex phase diagram, and solidification behavior [3,4]. Furthermore, the synthesis of Bi-2223 phase also critically depends on the atmosphere of the heat-treatments [5,6]. A reduced oxygen partial pressure was found to effectively enhance the efficiency of synthesizing Bi-2223 phase [5]. Recently [7], we reported the effect of oxygen partial pressure on the microstructure and formation of the (Bi,Pb)-2223 phase in the partial-melting and sintering process. Samples with the composition $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_{1.9}\text{Ca}_{2.1}\text{Cu}_{3.5}\text{O}_x$ were prepared by following sintering conditions after partially melted at 875°C for 1 h in air: (i) 760°C for 120 h in N_2 , (ii) 825°C for 120 h in $8\%\text{O}_2+\text{N}_2$, (iii) 840°C for 120 h in air and (iv) 845°C for 120 h in O_2 . In the samples sintered in pure N_2 and in pure O_2 , the Bi-2212 phase as a major phase existed without the Bi-2223 phase. The Bi-2223 phase appeared in the samples sintered in air and in $8\%\text{O}_2+\text{N}_2$, and the sample sintered in $8\%\text{O}_2+\text{N}_2$ had the highest fraction of the Bi-2223 phase. In this study, the melting and solidification processes of the $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_{1.9}\text{Ca}_{2.1}\text{Cu}_{3.5}\text{O}_x$ in various oxygen atmospheres have been observed in situ using a high temperature optical microscopy.

2. Experiment details

High purity Bi_2O_3 , PbO , SrCO_3 , CaCO_3 and CuO powders (99.99% in purity) were weighed and mixed in the atomic ratio $\text{Bi:Pb:Sr:Ca:Cu} = 1.8:0.4:1.9:2.1:3.5$, which is the optimum composition for the preparation of (Bi,Pb)-2223 superconductor in the partial-melting and sintering processes in our previous experiment [8]. To increase sample's homogeneity, the initial powders were mixed and coarsely ground for 30 minutes in a ball mill with a little ethyl alcohol. The alcohol was then evaporated at 200°C . The remaining sediment was calcined at 800°C for 12 h in a muffle furnace in air, and reground for 30 minutes in the ball mill. The calcined powders consisted mainly of the Bi-2212 phase. The film samples were prepared by coating the suspension of the calcined powders and ethanol onto a $\phi 5\text{mm}$ MgO disc. The melting and solidification of these film samples in various oxygen atmospheres (N_2 , $8\%\text{O}_2+\text{N}_2$, air and O_2) at a heating and cooling rate of $2^\circ\text{C}/\text{min}$ were directly observed using a BHMJ-Olympus optical microscope with RHL-E-1R infrared rays condense furnace and Fujix HC-300Z digital camera.

3. Results and discussion

3.1. Melting process

Fig. 1 shows the optical microstructure changes of the calcined powders during heating in air. The micrograph in Fig.1a represents the starting materials. In the heating process, there was no apparent change below 870°C except for shrinkage by sintering. The sample began to melt at about 880°C and a lot of the dark needle-like phase and the white bar-like phase appeared in the liquid phase (Fig.1b). When the temperature was raised, crystals of the bar-like phase were firstly melted from 900°C to 920°C, and those of the needle-like phase were melted from 960°C to 980°C, but then the particle-like crystals appeared in the liquid phase (Fig.1c). Apparently, the sample was not melted perfectly at about 980°C (Fig.1d), where the particle-like phase existed in the liquid phase. According to analyses of SEM and EDS, the white bar-like crystals, dark needle-like crystals and the particle-like crystals are confirmed as $(\text{Sr,Ca})\text{CuO}_2$, $(\text{Sr,Ca})_2\text{CuO}_3$, and CaO , respectively.

Figs. 2-4 show the optical microstructure changes of the calcined powders during heating in N_2 , 8% O_2+N_2 and O_2 , respectively. By comparison with the melting process in air, these in N_2 , 8% O_2+N_2 and O_2 exhibit the same appearance but different melting temperatures. In the melting process, the samples began to melt at 788°C in N_2 , 862°C in 8% O_2+N_2 and 895°C in O_2 , and a lot of the dark needle-like crystals $(\text{Sr,Ca})_2\text{CuO}_3$ and the white bar-like crystals $(\text{Sr,Ca})\text{CuO}_2$ appeared in the liquid phase. When the temperature was raised, $(\text{Sr,Ca})\text{CuO}_2$ first melted and then $(\text{Sr,Ca})_2\text{CuO}_3$ melted peritectically ($(\text{Sr,Ca})_2\text{CuO}_3 \rightarrow \text{CaO}+\text{L}$).

3.2. Solidification process

Fig. 5 shows high-temperature optical micrographs of the sample during solidification in 8% O_2+N_2 . Above 950°C, the liquid phase was in equilibrium with CaO (Fig.5a). From 940°C to 870°C, the $(\text{Sr,Ca})_2\text{CuO}_3$ formed in a needle-like shape by the peritectic reaction of the liquid phase and CaO , or by crystallizing directly from the liquid phase (Figs.5b and 5c). From 865°C to 860°C, the plate-like 2212 phase was formed by the peritectic reaction of the liquid phase and $(\text{Sr,Ca})_2\text{CuO}_3$. The solidification process finished at about 860°C (Fig.5d). Solidification process in air or in O_2 exhibited the same appearance but different solidification temperatures.

Fig. 6 shows high-temperature optical micrographs of the sample in the solidification process in N_2 . Above 780°C, the liquid phase was in equilibrium with CaO (Fig.6a). From 775°C to 770°C, the plate-like 2201 phase was formed by crystallizing directly from the liquid phase (Figs.6b and 6c). Only a reaction of $\text{L} \rightarrow \text{Bi-2201}$ was observed during solidification in N_2 . The solidification process finished at about 770°C (Fig.6d).

4. Conclusions

The melting and solidification processes of the $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_{1.9}\text{Ca}_{2.1}\text{Cu}_{3.5}\text{O}_x$ in various oxygen atmospheres have been observed. In the melting process, the samples began to melt at 788°C in N_2 , 862°C in $8\%\text{O}_2+\text{N}_2$, 880°C in air, 895°C in O_2 . Many dark needle-like crystals $(\text{Sr,Ca})_2\text{CuO}_3$ and the white bar-like crystals $(\text{Sr,Ca})\text{CuO}_2$ appeared in the liquid phase. When the temperature was raised, $(\text{Sr,Ca})\text{CuO}_2$ first melted and then $(\text{Sr,Ca})_2\text{CuO}_3$ melted peritectically ($(\text{Sr,Ca})_2\text{CuO}_3 \rightarrow \text{CaO}+\text{L}$). In the solidification process, two peritectic reactions $\text{CaO}+\text{L} \rightarrow (\text{Sr,Ca})_2\text{CuO}_3$ and $(\text{Sr,Ca})_2\text{CuO}_3 + \text{L} \rightarrow \text{Bi-2212}$ were observed in the atmospheres of air, $8\%\text{O}_2+\text{N}_2$ and O_2 , whereas in N_2 , only a reaction of $\text{L} \rightarrow \text{Bi-2201}$ was observed.

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Fig. 1

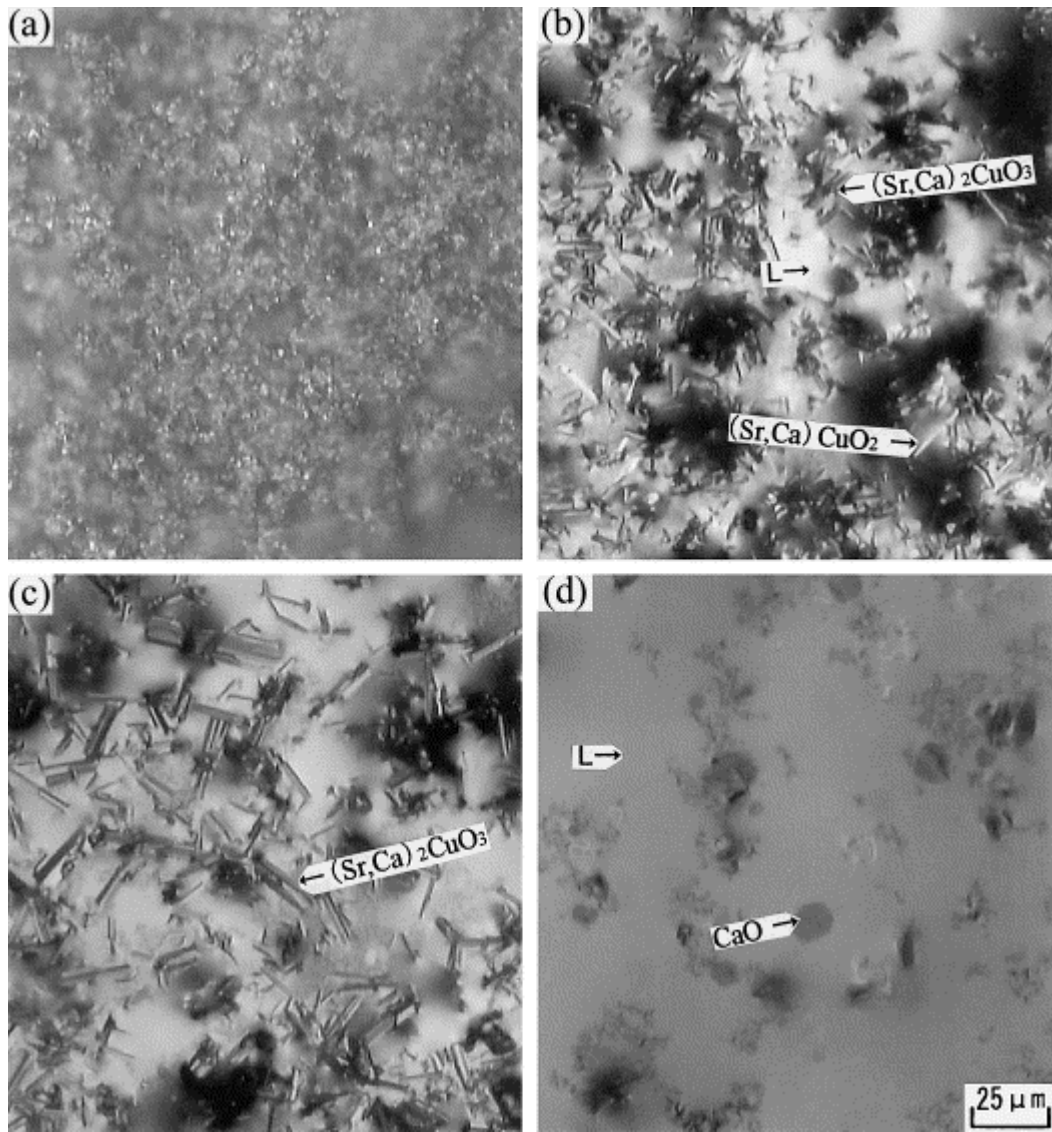


Fig. 2

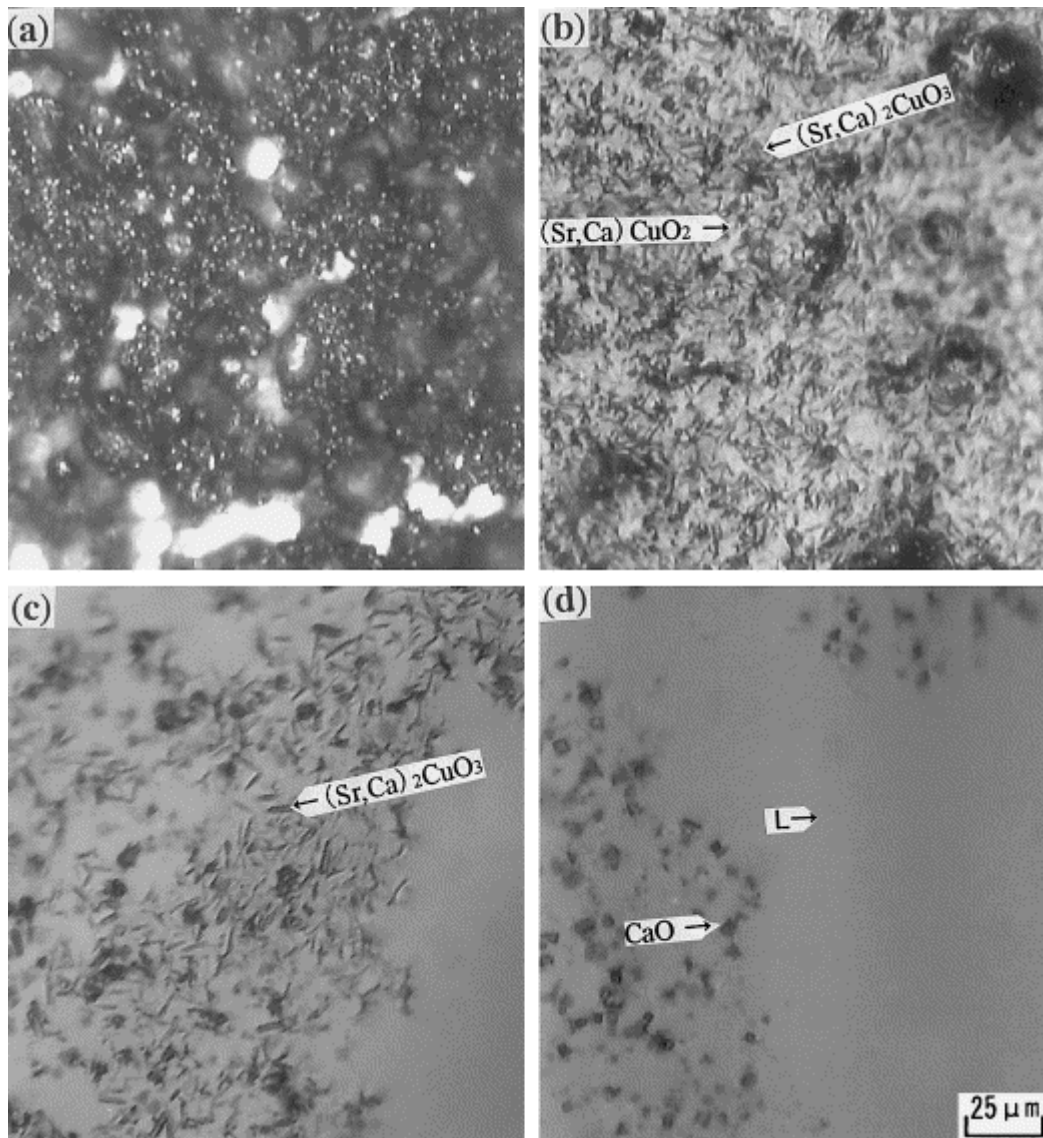


Fig.3

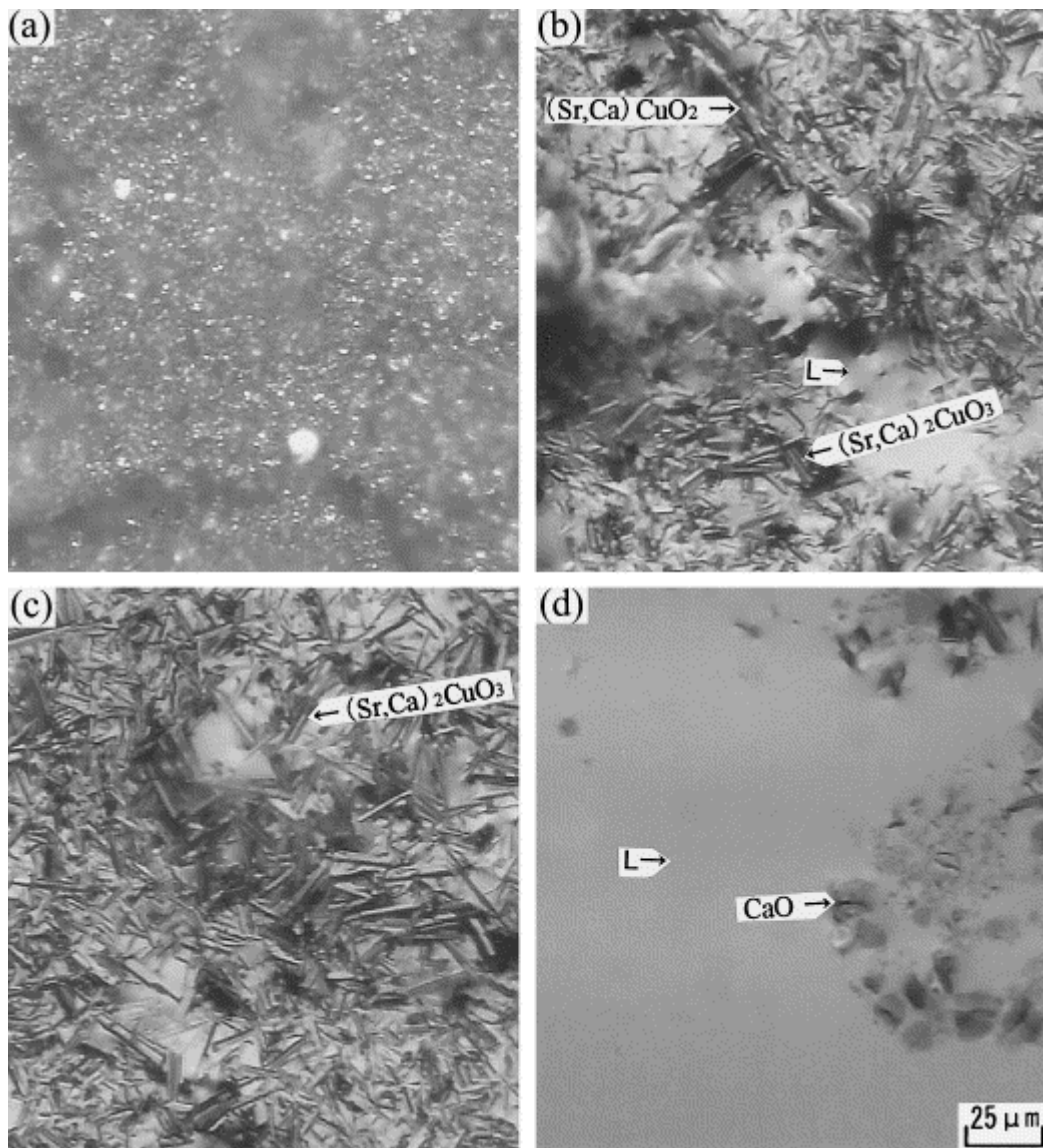


Fig.4

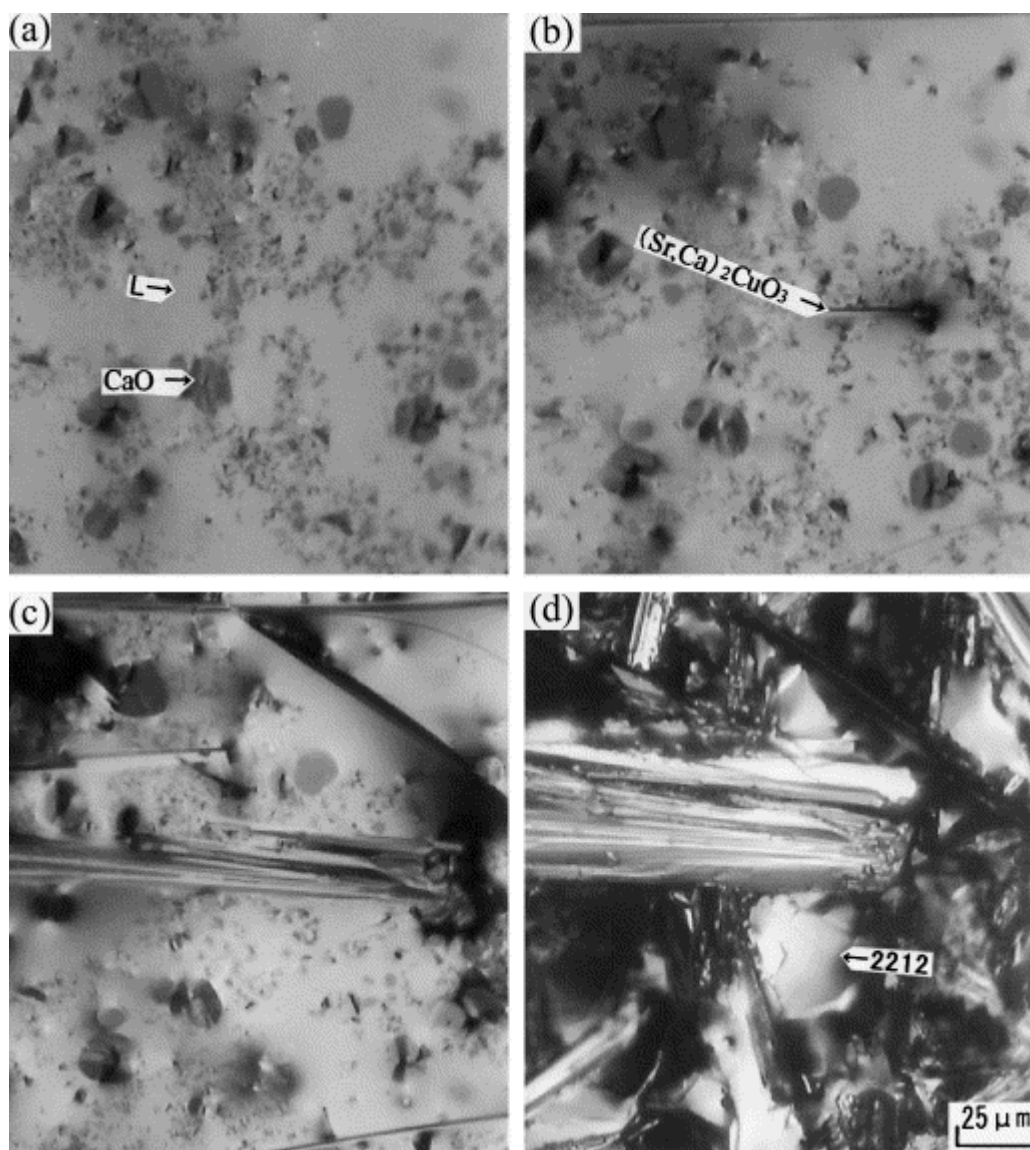


Fig.5

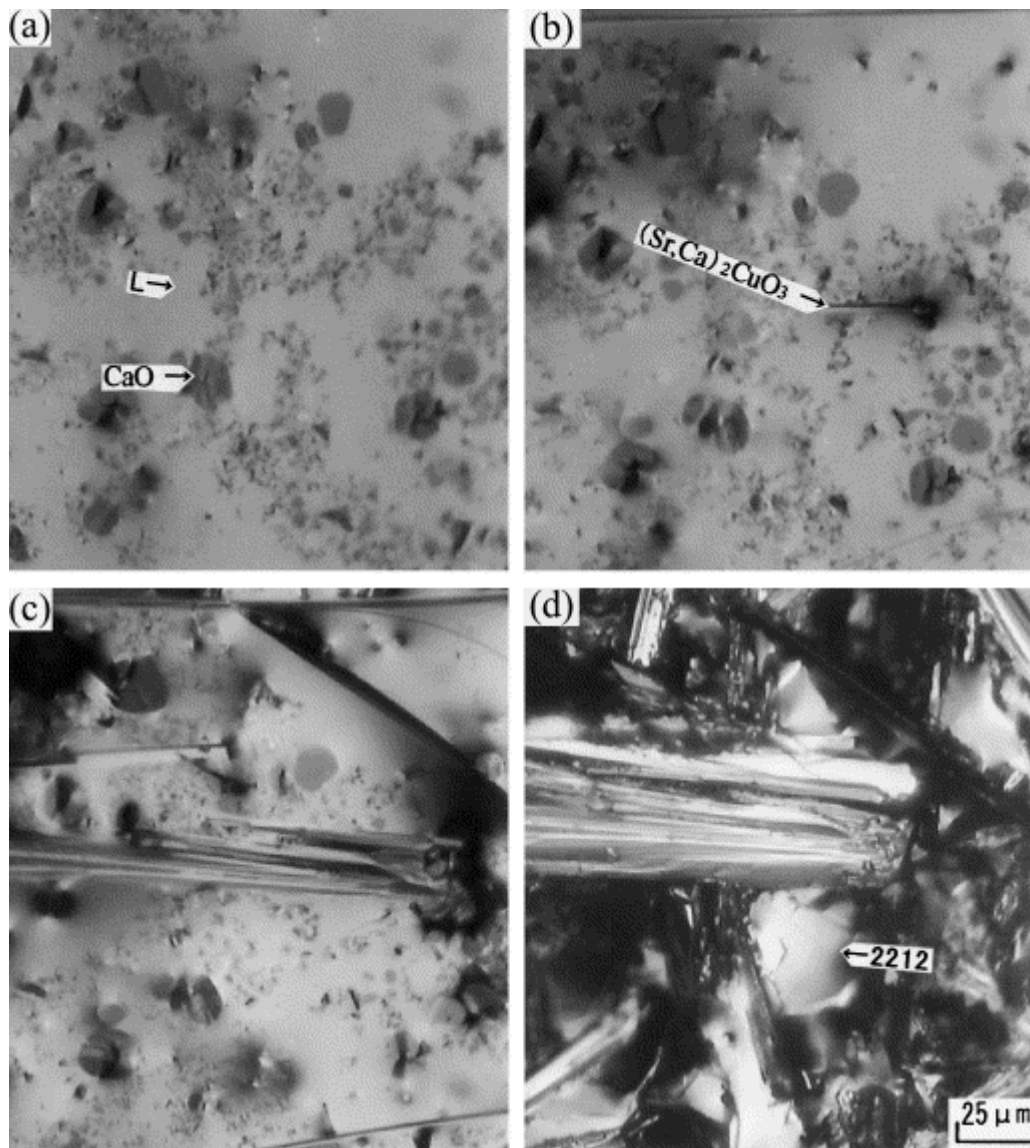


Fig.6

