

Single Crystal Growth of β -Ca_xCoO₂ ($x \approx 0.5$) by Flux Growth TechniqueX. Y. Huang¹, Y. Miyazaki^{1,2} and T. Kajitani^{1,2}¹ CREST, Japan Science and Technology Agency, Aramaki Aoba, Aoba-ku, Sendai 980-8579

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Single crystals of β -Ca_xCoO₂ ($x \approx 0.5$) were grown by the flux growth technique. Co₃O₄ and CaO or Co₃O₄ and CaCO₃ powders were used as starting materials. CaCl₂, KCl, CoCl₂ and K₂CO₃+KCl were separately used as the fluxes. Growth conditions were established for obtaining plate-like single crystals, which were about 8×8×0.05mm³ in size. The crystal structure of the products was identified by means of X-ray powder diffraction. It was found that CaCl₂ and CoCl₂ were beneficial to the growth of relatively large size single crystal β -Ca_xCoO₂ ($x \approx 0.5$). We have also measured the high temperature electrical transport properties.

Key words: flux, thermoelectric, single crystal, beta phase

1. INTRODUCTION

The need for environmental protection and utilizing the exhaust heat from industry department has been spurring study on thermoelectric materials. As we know, thermoelectric power generation should be worked at high temperature, and traditionally good thermoelectric materials, such as PbTe and SiGe, must be protected from oxidation because of their low chemical stability in air. Accordingly, it is worthwhile to look for a new kind of material that possesses both high stability and high dimensionless figure of merit ($ZT = S^2 \sigma T / \kappa$, where S , σ , κ and T are thermopower, electrical conductivity, thermal conductivity and absolute temperature, respectively).

In 1997, Terasaki *et al.* reported that NaCo₂O₄ with a layered structure had large S of 100 μ V/K and σ of 5×10⁵ Sm⁻¹ at 300K [1]. From then on many other kinds of thermoelectric cobaltites have been discovered [2-7], for example [Ca₂CoO₃]_{0.62}CoO₂, [Ca₂(Co_{0.65}Cu_{0.35})₂O₄]_{0.624}CoO₂, [Bi_{0.87}SrO₂]₂[CoO₂]_{1.82}, and so on. These cobaltites are of layered structure, which consists of CoO₂ layers of the CdI₂ type and block layers such as Na atoms layer for NaCoO₄ and NaCl-type three layered Ca₂CoO₃ block layers for [Ca₂CoO₃]_{0.62}CoO₂, respectively [3]. On the other hand, with different Na content, Na_xCoO₂ crystallizes into four different phases i.e. α -Na_xCoO₂ ($0.9 \leq x \leq 1$) having O3 structure (O is octahedral coordination of Na ion and 3 is the number of layers in repeat), α' -Na_{0.75}CoO₂, β -Na_xCoO₂ ($0.55 \leq x \leq 0.6$) having P3 structure (P is prismatic coordination of Na) and γ -Na_xCoO₂ ($0.55 \leq x \leq 0.74$) having P2 phase [8,9]. B. L. Cushing *et al.* reported that four Ca_xCoO₂ ($0.26 \leq x \leq 0.50$) oxides could be synthesized by the low-temperature ion exchange of layered Na_xCoO₂ oxide [9]. Y. Miyazaki *et al.* reported the preparation and thermoelectric properties of polycrystal β -Ca_xCoO₂ [10]. Unfortunately, there is no report on single crystal preparation and the thermoelectric properties about beta phase, β -Ca_xCoO₂. In this paper, we report the single crystal growth of

β -Ca_xCoO₂ ($x \approx 0.5$) by the flux growth technique, the electric conductivity and thermopower are also measured.

2. EXPERIMENTAL

Single crystals of β -Ca_xCoO₂ were grown from CaCl₂, CoCl₂, KCl and K₂CO₃+KCl fluxes, respectively. First, CaCO₃ (wako, 99.5%) and Co₃O₄ (wako, 66~74%) or CaO (calcined from CaCO₃ at 1000°C for 2h) and Co₃O₄ were mixed in a mortar in a molar ratio of 3:2, then the flux was added in the ratio of 1:9 (solute/flux). The mixture was placed in alumina crucibles 70mm in height and 80mm in diameter. The crucible was covered with an alumina disc to limit the evaporation of the flux and crystals were grown under relatively stable conditions. The solute-flux mixtures were melted at the temperature (Table 1) in air for 5h, then slowly cooled at a rate of -1.5K/h to 600K, and finally continued to cool to room temperature at a rate of about -100K/h. The grown crystals were separated from the flux by washing in distilled water, aided by the use of ultrasonic cleaning.

Table 1. Compositions and temperature of fluxes

Flux	Temperature (°C)
CaCl ₂ *	810
KCl	810
CoCl ₂	790
35mol%K ₂ CO ₃ +65mol%KCl**	660

* As the starting material, CaO was only used in the case of CaCl₂ flux.

** The melting point is 620°C [11].

The crystal phase of the grown crystals was identified by means of X-ray powder diffraction with a Rigaku2000 diffractometer using Cu K α radiation in the 2 θ angular range of 5-70°. The lattice parameters were got from Rigaku four-circle diffractometer. The morphology of the crystals was characterized with Hitachi SEM S-3100H and Olympus microscope BX60. Electrical

conductivity and thermopower were measured using a commercial instrument Ozawa RZ2001i in the temperature range 300-1000K, silver paste was used for terminal connection.

3. RESULTS AND DISCUSSION

Being different from $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_3\text{Co}_2\text{O}_6$ phases, β - Ca_xCoO_2 is a low temperature phase which decomposes at about 800°C [12], therefore some compounds (or mixture) possessing relatively low melting point were selected as the fluxes. In the case of CaCl_2 flux, being independent of the starting materials, the grown single crystals are black in color with mirror like shining surfaces, and are platelet-shaped. The typical size of the grown crystals is $8 \times 8 \times 0.05 \text{ mm}^3$, some crystals have size about $30 \times 20 \times 0.1 \text{ mm}^3$ (Fig. 1).

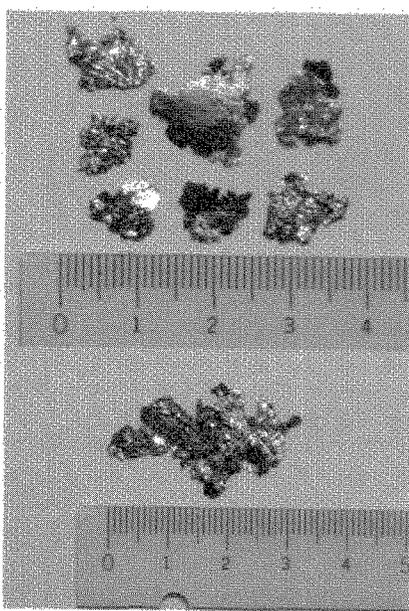


Fig. 1 Photographs of the grown β - Ca_xCoO_2 crystals.

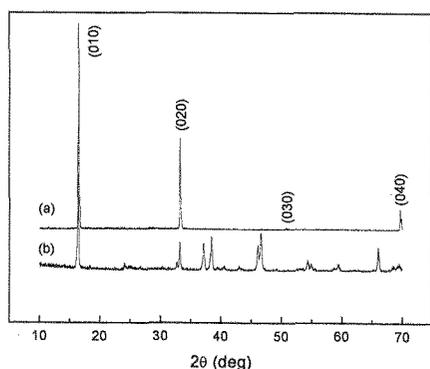


Fig.2 XRD patterns of the grown β - Ca_xCoO_2 single crystals (a) and polycrystal (b), respectively.

Fig. 2 is the XRD pattern of the β - Ca_xCoO_2 single crystals (a) and polycrystals (b) [12], respectively. The Ca composition, x , was estimated to be 0.48 from the crystal structure analysis. The lattice constant for

β - Ca_xCoO_2 single crystal are $a=4.9058(4)$ Å, $b=5.6584(6)$ Å, $c=5.6627(7)$ Å, $\alpha=75.45(1)^\circ$, $\beta=89.96(1)^\circ$ and $\gamma=80.91(1)^\circ$, which are in good agreement with our previous results for the polycrystals [12], the lattice constants for the polycrystals are $a=4.9047(4)$ Å, $b=5.6586(6)$ Å, $c=5.6612(5)$ Å, $\alpha=75.37(1)^\circ$, $\beta=89.97(1)^\circ$ and $\gamma=80.91(7)^\circ$. It is shown that there are only $(0\ n\ 0)$ reflections of β - Ca_xCoO_2 polycrystals in the pattern (a). It means that the single crystal possesses the β - Ca_xCoO_2 structure with an ac -plane parallel to the flat plane. Owing to layered structure, one might expect only $(0\ 0\ n)$ reflections in the XRD pattern. However our previous neutron diffraction measurement indicated that β - Ca_xCoO_2 is of space symmetry $P1$ (No.1), belonging to triclinic system and differing from $\text{Ca}_3\text{Co}_4\text{O}_9$, latter belongs to monoclinic system.

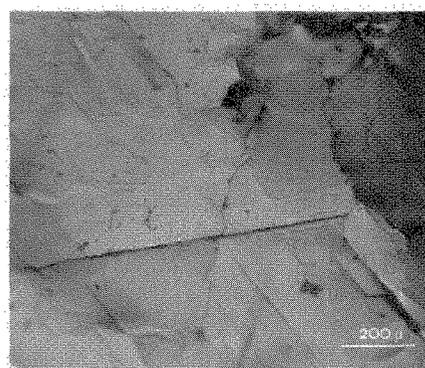


Fig. 3 Optical micrograph of grown β - Ca_xCoO_2 crystals. There are the boundaries of domains on the surface of the single crystal.

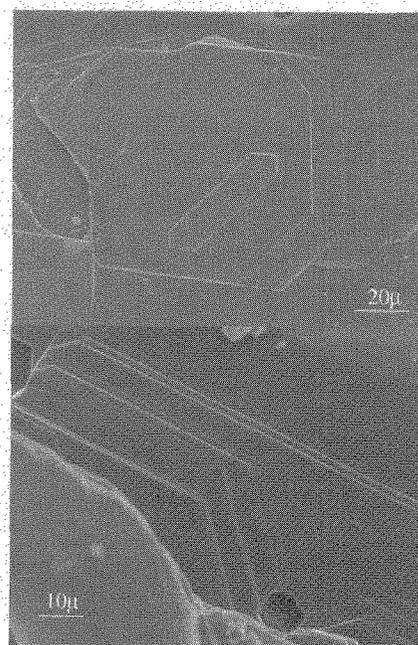


Fig. 4 SEM images of the β - Ca_xCoO_2 crystals.

In order to know the growth habit of β - Ca_xCoO_2 single crystals, optical microscope and SEM were used

to observe the morphology (Fig. 3 and Fig. 4). It is evident that there are the boundaries of domains on the surface of the single crystal.

On the other hand, the single crystals show polygonal morphology (Fig. 4, upper). In the edge, all single crystals possess the features similar to that shown in Fig. 4 (lower), this is typical step-and-terrace surface structure of crystal growth. Unfortunately, we could not get one step height in Fig. 4, but the width of the terrace is clearly presented to be about 0.5~1.5 μm . Based on the optical microscope and SEM images, it was concluded that growth of the crystals occurred via two-dimensional, being parallel to the ac-planes, layer-by-layer mechanism.

In the case of KCl flux, the solute ($\text{CaCO}_3+\text{Co}_3\text{O}_4$) did not dissolve, even up to 860°C, being much higher than melting point of KCl, we just obtained some KCl single crystals. When CoCl_2 was used as flux constituent, we got some very small $\beta\text{-Ca}_x\text{CoO}_2$ single crystals. It was unexpected that it is $\text{Ca}_3\text{Co}_4\text{O}_9$ single crystals rather than $\beta\text{-Ca}_x\text{CoO}_2$ single crystal in the presence of 35mol% $\text{K}_2\text{CO}_3+65\text{mol}\%\text{KCl}$ flux, because the starting materials were $\text{CaCO}_3+\text{Co}_3\text{O}_4$ rather than $\text{Ca}_3\text{Co}_4\text{O}_9$ and temperature was only 660°C, much lower than 950°C at which $\text{Ca}_3\text{Co}_4\text{O}_9$ single crystals were generally grown by a flux method [13]. We don't know the exact reason. However from another point of view, it is of significance because of the single crystals growth of $\text{Ca}_3\text{Co}_4\text{O}_9$ at considerably lower temperature. These experimental results indicate that single crystal structure varies with the composition of flux.

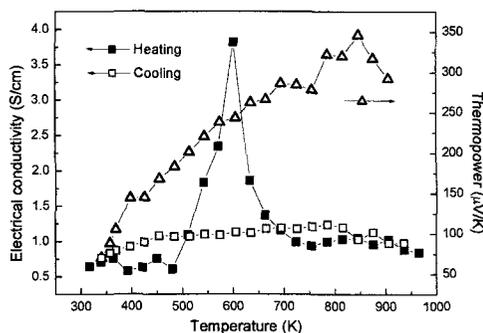


Fig. 5 Temperature dependence of the electrical conductivity and thermopower in the ac-plane for $\beta\text{-Ca}_x\text{CoO}_2$ single crystals.

Fig. 5 shows the temperature dependence of the electrical conductivity and thermopower in the ac-plane for $\beta\text{-Ca}_x\text{CoO}_2$ single crystals. It was found that the electrical conductivity for single crystal in ac-plane is almost five times higher than that for polycrystals [12]. Similar to polycrystalline sample, there is a peak between 480K and 750K in the conductivity curve in the heating process. The peak temperature 600K is 30K higher than that of polycrystals sample. This difference is expected due to their slight difference in the lattice parameter. Based on our previous experimental results about polycrystalline sample, we believe that this phenomenon might relate to the structural water, -OH. For the $\beta\text{-Ca}_x\text{CoO}_2$ phase, in despite of single crystals or

polycrystals, the elimination of -OH and following by structural arrangement lead to sharp change in electrical conductivity during that temperature range. Further experiments and analyses are required to clarify the interesting behavior. On the other hand, the thermopower is almost the same as that for polycrystalline sample.

4. CONCLUSIONS

We grew the $\beta\text{-Ca}_x\text{CoO}_2$ single crystals by employing the flux technique and obtained many large size crystal samples in the case of CaCl_2 flux. The single crystals are plate-like and have typical size of $8\times 8\times 0.05\text{mm}^3$. The growth of the small crystals, parallel to the ac-plane, took place as the fundamental growth mechanism. Single crystal structure is closely relevant to the flux compositions. Additionally, $\beta\text{-Ca}_x\text{CoO}_2$ single crystals show the similar electrical transport properties as the polycrystal samples.

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