氏　　　　名	Zhijian TAN
学位(専攻分野)	博士(理学)
学 位 記 番 号	総研大甲第 2033 号
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学 位 論 文 題 目	The investigation of negative thermal expansion and magnetic structure in $La_{0.5}Ba_{0.5}Co_{O3-x}$ by neutron powder diffraction
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(Form 3)

Summary of Doctoral Thesis

Name in full Zhijian TAN

Title **The investigation of negative thermal expansion and magnetic structure in $La_{0.5}Ba_{0.5}CoO_{3-x}$ by neutron powder diffraction**
（負の熱膨張を示す $La_{0.5}Ba_{0.5}CoO_{3-x}$ の結晶構造と磁気構造の研究）

Negative thermal expansion (NTE) describes the phenomenon of lattice constriction as temperature increase. Since thermal expansion may cause significant problems in engineering fields, NTE is very important for industrial application, from large structural components such as railroad tracks and bridges, to precision instruments and electronic devices such as optical instruments and sensors. Recently, our group observed large NTE in cobaltite perovskite, $PrBaCo_2O_{5.74}$ below Neel temperature T_N =120 K. Moreover, NTE in $La_{0.5}Ba_{0.5}CoO_{3-x}$ can be tuned by changing the hole doping level x. Through the comprehensive study with multiple techniques, it is found this NTE is closely associated with the ferromagnetic (FM) and antiferromagnetic (AFM) competition. Now I am motivated to investigate NTE in the A-site disordered $La_{0.5}Ba_{0.5}CoO_{3-x}$. Firstly, the bandwidth can be control by changing to La. Secondly, compare with Pr, La has no magnetic moment so that it will be easier to analyze the relationship of NTE and magnetism in A-site disordered $La_{0.5}Ba_{0.5}CoO_{3-x}$ than in the $PrBaCo_2O_{5.5+x}$. Furthermore, since the structure of A-site disorder $La_{0.5}Ba_{0.5}CoO_{3-x}$ is cubic, this leads to the isotropic NTE. It will be simpler to understand the fundamental physics. So in this research I expect to search possible NTE in A-site disordered $La_{0.5}Ba_{0.5}CoO_{3-x}$ and investigate the new phenomenon of this sample.

This thesis is concerned with sample synthesis and investigation of magnetic structure and NTE property of the A-site disordered $La_{0.5}Ba_{0.5}CoO_{3-x}$. The present thesis contains five chapters. In the first chapter the application of NTE material as well as the common NTE material are introduced. Then the detailed properties and magnetism of NTE are reviewed. This chapter also includes the structure and the unusual properties of the cobaltite perovskites.

For the second chapter the focus changes to the experimental part. I prepared high-quality $La_{0.5}Ba_{0.5}CoO_{3-x}$ polycrystalline samples by solid-state reaction method and controlled the oxygen content by annealing as-synthesized sample in pure Ar atmosphere at various temperatures. The oxygen content is determined by the iodometric titration method. A combination of X-ray powder diffraction (XRD), high resolution neutron powder diffraction (NPD) and the superconducting quantum

interference device (SQUID) magnetometer (MPMS) was used to investigate the crystal structure and magnetic structure.

In the third chapter, the experiment results are presented. The crystal and magnetic structures are determined by the Z-Rietveld refinement. Based on the magnetization data and NPD data, the phase diagram of this $La_{0.5}Ba_{0.5}CoO_{3-x}$ is obtained. From the temperature dependence of volume, the large NTE is observed in the hole doping A-site disordered $La_{0.5}Ba_{0.5}CoO_{3-x}$. This NTE can be tuned by changing the oxygen content and the largest NTE occurs near the boundary between FM and AFM phases in the phase diagram. The phase separation of AFM and FM state or paramagnetic (PM) state was observed in very large range of oxygen content from 2.82 to 2.89. It is found that this NTE is related to the magnetic ordering. The transition of LV phase with AFM state to SV phase with FM or paramagnetic state results in the NTE. The results of NPD under magnetic field confirm that the large volume (LV) phase is related to the AFM and small volume (SV) phase is related to the FM. It is also found that the average volume is suppressed under magnetic field, which reveals that the NTE can be tuned by the magnetic field.

In the fourth chapter, I discuss about the new phenomenon of this sample. From the phase diagram of $La_{0.5}Ba_{0.5}CoO_{3-x}$ and $Pr_{0.5}Ba_{0.5}CoO_{3-x}$, the phase separation is observed in a much larger range of oxygen content from 2.82 to 2.89 in $La_{0.5}Ba_{0.5}CoO_{3-x}$. The Curie temperatures T_C of the two samples are very close while the T_N in $La_{0.5}Ba_{0.5}CoO_{3-x}$ is much high than that of $Pr_{0.5}Ba_{0.5}CoO_{3-x}$. The phase diagram shows large differences in the two samples. It may come from the different radius of La and Pr or from the A-site disordered effect. I also found that the relative difference of volume between the LV and SV ($\Delta V_{LV\text{-}SV}/V$) in $La_{0.5}Ba_{0.5}CoO_{3-x}$ is much larger than that in $Pr_{0.5}Ba_{0.5}CoO_{3-x}$. From the phase diagram and the analysis of the volume in AFM and FM phase between these two samples, it is suggested that the much larger $\Delta V_{LV\text{-}SV}/V$ is related to the much stronger AFM in $La_{0.5}Ba_{0.5}CoO_{3-x}$.

In the last chapter, the summary and future work of the thesis are presented.

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（様式８・別紙）

Results of the doctoral thesis screening

博士論文審査結果

Name in Full
氏　名　Zhijian TAN

Title
論文題目　The investigation of negative thermal expansion and magnetic structure in $La_{0.5}Ba_{0.5}CoO_{3-x}$ by neutron powder diffraction

Zhijian TAN氏は、$PrBaCo_2O_{5+x}$で報告された負の熱膨張（NTE）の起源を明らかにするために、無秩序型$La_{0.5}Ba_{0.5}CoO_{3-x}$に着目し、酸素欠損量を制御した試料を合成、高分解能粉末中性子回折、Ｘ線回折、磁化測定等により、NTEや相分離現象について研究を行った。

酸素欠損量を制御した試料（x = 0.09-0.34）を合成し、高分解能粉末中性子回折やＸ線回折を用いて、酸素欠損量の広い範囲においてNTEが発現することを発見した。さらに、低温で相分離が発現すること、相分離が強磁性（F）相と反強磁性（AF）相の共存によること、AF相の単位胞がF相のそれより大きいこと、F相とAF相の比率が温度により変化し低温でAF相の比率が増大することを見出した。これらのことから、NTEの発現は、「低温で、小さな単位胞を持つF相の比率が減り大きな単位胞を持つAF相の比率が増大する」ことに起因すると突き止めた。さらに、磁場14 Tまでの中性子回折によりAF相とF相の基底状態のエネルギー差が小さく、強磁場下で（単位胞が大きい）AF相が抑制され、（単位胞が小さい）F相が増大すること、その結果、強磁場下でNTEが抑制されることを示した。

本研究の無秩序型$La_{0.5}Ba_{0.5}CoO_{3-x}$の結果を$PrBaCo_2O_{5+x}$と比較すると、$La_{0.5}Ba_{0.5}CoO_{3-x}$の方が相分離領域が広いこと、キュリー温度は殆ど同じだがネール温度は$La_{0.5}Ba_{0.5}CoO_{3-x}$で2倍程度になることを示した。AF相の発現による単位胞体積の増大が$PrBaCo_2O_{5+x}$より$La_{0.5}Ba_{0.5}CoO_{3-x}$で大きい理由について考察し、後者のAF相互作用が大きいことによる、と推測した。

本審査では、予備審査での指摘事項に適切に対応したことが示され、これらを反映した発表が行われた。Tan 氏の研究は、当該分野における進展に新たな貢献を行ったと判断された。

以上の理由により、審査委員会は、本論文が学位の授与に値すると判断した。