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Single Crystal Growth and Domain Structure of $CsLaTa_2O_7$

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Abstract

A new layered perovskite compound of $CsLaTa_2O_7$ *was synthesized and grown in the forms of powder and single crystal by a conventional solid state reaction and a flux method, respectively. The Rietveld analysis based on the powder sample showed a tetragonal system, while the observation of the as-grown single crystal by a polarized light microscope showed an orthorhombic system. The orthorhombic as-grown single crystal transformed to a tetragonal phase on annealing at a high temperature. © 1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

The Dion–Jacobson phase with the general formula M $[A_{n-1}B_nO_{3n+1}]$ (M = alkali metal cation, A = trivalent cation, B = Nb, Ta, $n = 2, 3\ldots$), which is one of layered perovskite groups, has been attracted attention because of its unusual physical and chemical properties; ion-exchangeability, luminescence, superconductivity and so on.[1–3]

Recently, an unusual luminescent property was found in a new layered perovskite compound of $RbLaTa_2O_7$ ($n = 2$), which was the first example for the layered perovskite with tantalum atom as a B site ion.[4,5] In a $RbLaTa_2O_7$ phosphor doped with Eu^{3+}, a quite high luminescent efficiency was observed and found to be comparable with those of commercial high-brightness phosphors.[5] It was suggested that such a high efficiency could originate in a low dimensionality of the host crystal structure. In general, the concentration quenching in luminescence is strongly dependent on the structural dimensionality of the host material. The energy transfer of emission light occurs among neighboring luminescent centers. Sometimes, the energy transfer can be so depressed in such a case that a luminescent center is located in a lower dimensional environment because of the low probability of energy transfer, compared with a three dimensional one. Layered perovskite compounds can provide an effective circumstance for a luminescent center, which gives a high luminescent efficiency.

In our previous study,[4] the crystal structure of $RbLaTa_2O_7$ was determined by the Rietveld method using powder XRD patterns. In order to get much more detailed structural information which is necessary to understand the unusual luminescent efficiency of $RbLaTa_2O_7$, the structure determination by using a single crystal refinement should be needed. In this study, we were able to grow up single crystals of $CsLaTa_2O_7$, which has the same basic crystal structure as that of $RbLaTa_2O_7$, by a flux method. This is the first report on the single crystal of tantalum compounds with a layered perovskite structure.

2 Experimental

2.1 Synthesis and single crystal growth of $CsLaTa_2O_7$

Starting materials, Cs_2CO_3(99·99%), La_2O_3 (99·9%) and Ta_2O_5(99·9%), were mixed with acetone in an agate mortor. Considering the compensation for the loss of Cesium component by volatilization during the heating, a 50 mol% excess of Cs_2CO_3 was added to the mixture. After dried by using an infrared light in 10 min, the mixture was pressed into a pellet under a pressure of 30 MPa. The pellet was put into an alumina crucible

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*To whom correspondence should be addressed. Fax: +81-25-262-6768; e-mail: msato@cc.niigata-u.ac.jp and then fired at 1373 K for 24 h in air. To remove the excess Cesium component, the powder was washed with a deionized water and dried.

For the single crystal growth, a flux method was used. A Cs_2SO_4–CsF system with Cs_2SO_4: CsF = 30:70 (wt%) was used as the flux.[6] The ratio of the $CsLaTa_2O_7$ powder and the flux was 97:3 (wt%). The powder and the flux were put together into a platinum crucible and heated up to 1373 K. After holding at this temperature for 24 h, the molten solution was slowly cooled down to 973 K at a cooling rate of 5 K h^{-1} in air. Single crystals were collected by boiling the product with a deionized water. An effort to obtain single crystals of $RbLaTa_2O_7$ was not successful by this method.

The composition of the sample of powder and single crystal was checked by means of an electron probe microanalyzer (Shimadzu, EPMA-8705). Polarized light microscopic analysis was carried out to examine the optical property for the single crystals of $CsLaTa_2O_7$ by using a microscope (Olympus, BX60).

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RAD-rA diffractometer equipped with a curved crystal graphite monochrometer using CuK_α radiation. The data were collected by a step-scanning mode in the range of $2\theta = 5$–$100°$ with a step width of 0·02° and a step time of 4 s. The powder XRD patterns obtained was indexed with the aid of the computer program CELL.[7] Data analysis was carried out by the Rietveld method, using the RIETAN94 profile refinement program.[8]

3 Results and Discussion

From the indexing of the powder XRD patterns, a possible space group for $CsLaTa_2O_7$ was deduced to be P4/mmm, similar to that found in $RbLaTa_2O_7$.[4] The Rietveld refinement on the basis of this space group was reasonably converged to acceptable values of R-factors. Figure 1 shows the XRD pattern fitting of $CsLaTa_2O_7$. In Table 1 is shown crystallographic data finally obtained by the Rietveld refinement for the compound. The crystal structural model is represented in Fig. 2.

Armstrong *et al.*[9] claimed that the crystal system for $RbLaNb_2O_7$ is orthorhombic, different from those found in $RbLaTa_2O_7$ and $CsLaTa_2O_7$. This could be due to the difference of bond character between Ta-O and Nb–O. Niobium atom has stronger interaction with oxygen than tantalum atom does, because the Nb-O bond approximately consists of oxygen 2p orbital and niobium 4d orbital which is not so spatially expanded compared with tantalum 5d orbital. As a result, niobates have a narrower band gap than the corresponding tantalates do. Such a difference of bonding characters between niobium and tantalates may make crystal system different from each other.

As already reported in the previous study,[5] the phosphors consisting of $RbLaTa_2O_7$ as a host and Eu^{3+} as an activator show a quite high luminescence due to a layered structure of the host. Eu^{3+} activators are located at a nearly two-dimensional space of the layered structure. In this phosphor, the emission peak intensities of $^5D_0-^7F_1$ and $^5D_0-^7F_2$ transitions are almost same. However, as long as the structure of the host has a tetragonal crystal system with a point group of inversion center, the intensity of $^5D_0-^7F_2$ transition should be weaker than that of $^5D_0-^7F_1$ transition.[10] Nieuwpoort *et al.*[11] also suggested that the presence of inversion center brings no $^5D_0-^7F_2$ emission except for weak vibronic transitions. Contrary to this, with increasing the deviation from inversion symmetry, the intensity of the $^5D_0-^7F_2$ transition becomes stronger and finally compatible to that of $^5D_0-^7F_1$. Nieuwpoort *et al.*[11] claimed that the intensity of $^5D_0-^7F_2$ is so sensitive that small changes in the surroundings of the Eu^{3+} ion influence the emission behavior. Consequently, both of the experimental facts and the above considerations for the luminescence behavior of $RbLaTa_2O_7$ strongly suggest a crystal system with a lower symmetry than tetragonal one, which is deduced from the Rietveld refinement.

We tried and succeeded to grow single crystal of $CsLaTa_2O_7$, which has almost the same structural features as $RbLaTa_2O_7$, although the effort to grow $RbLaTa_2O_7$ crystals was failed. One of the crystals obtained was the largest one among the single crystals ever grown for Dion–Jacobson series. The size of the largest single crystal was 4×4×0·05 mm. Figure 3 shows a photograph of the $CsLaTa_2O_7$ single crystal, which is a transparent, thin rectangular plate crystal. The crystal is well oriented along with (001) plane, suggesting a preferential two-dimensional growth mechanism reasonable to the layered structure feature. The average size of the crystal is about 2×2×0·05 mm.

The observation of the crystal under the polarized light microscope, as shown in Fig. 4(a), shows an optically biaxial characteristic, indicating a crystal system with a lower symmetry than tetragonal. This is contradictory to the result obtained from powder sample. An another interesting phenomenon can be seen in the single crystal. The as-grown crystal has a complicated plural domain structure, where there are two kinds of streaks which are perpendicular to each other, implying an orthorhombic system. When annealing the

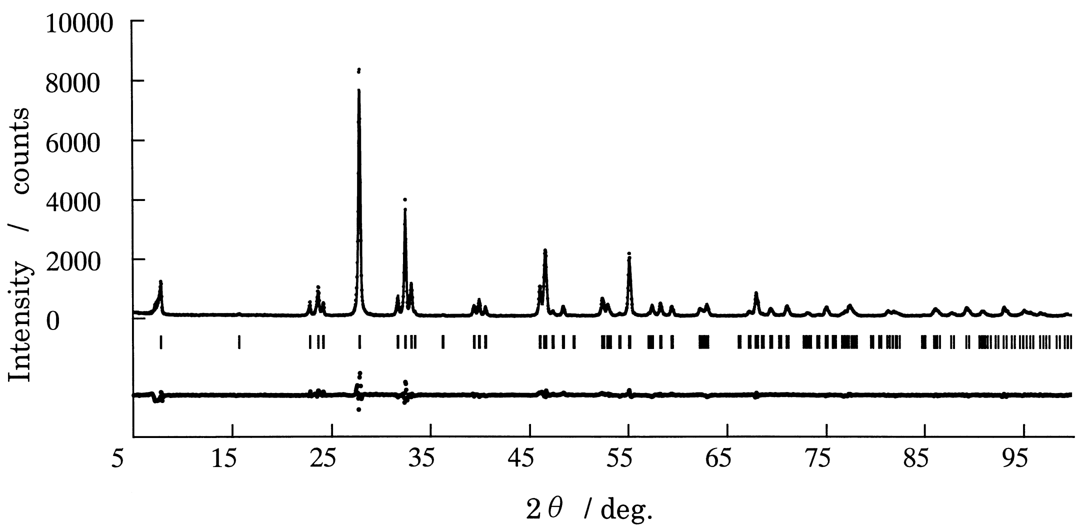


Fig. 1. Powder X-ray pattern fitting for $CsLaTa_2O_7$. The calculated and observed patterns are shown on the top solid line and dots, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The trace on the bottom is a plot of the difference between calculated and observed intensities.

Table 1. Crystallographic parameters refined by Rietveld method for $CsLaTa_2O_7$

Sample	*Atom*	*Site*[a]	g	x	y	z	*B*/*nm*^{2}
$CsLaTa_2O_7$	Cs	1d	1·0	0·5	0·5	0·5	0·012(2)
P4/mmm (no. 123)	La	1c	1·0	0·5	0·5	0	0·005(2)
a = 0·3899(1) nm	Ta	2g	1·0	0	0	0·2007(4)	0·002(2)
c = 1·1292(5) nm	O(1)	1a	1·0	0	0	0	0·04(3)
Rwp = 10·23%	O(2)	2g	1·0	0	0	0·373(5)	0·01(1)
R_F = 2·46%	O(3)	4i	1·0	0	0·5	0·183(3)	0·01(1)

[a] Multiplicity and Wyckoff notation.

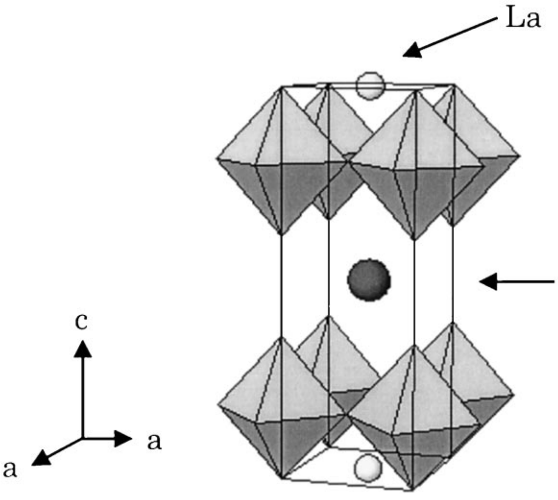


Fig. 2. Structural model of $CsLaTa_2O_7$. The octahedra are TaO_6 units.

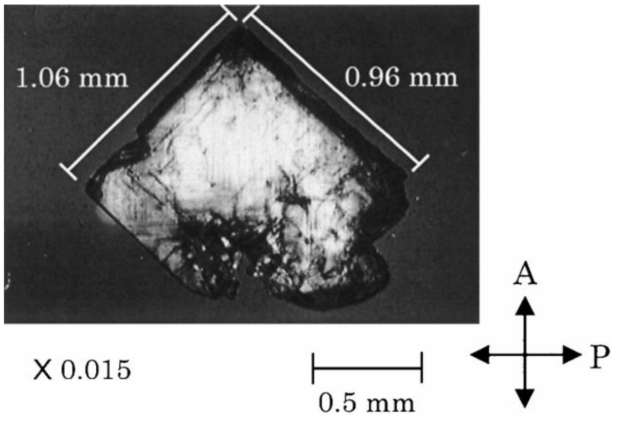
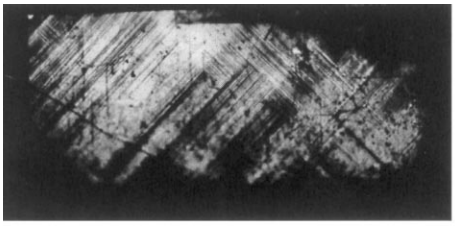
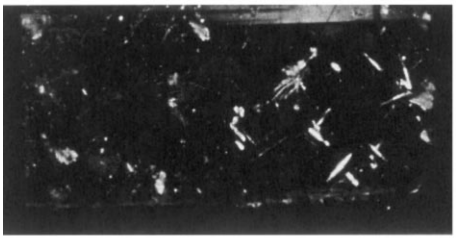


Fig. 3. Photograph of single crystal $CsLaTa_2O_7$ under polarized light microscope.

crystal at 1123 K for 24 h, the plural domain disappeared to become a single one, indicating a crystal system change from orthorhombic to tetragonal as shown in Fig. 4(b). These facts seem to suggest that not only the free energy difference but also the cell parameter difference between orthorhombic and tetragonal phases are quite small. It should be reasonable to conclude that the orthorhombic phase is thermodynamically metastable one at ambient temperature and pressure. During the cooling process usually used in conventional experimental condition, the orthorhombic phase seems to be frozen down to room temperature. Powder XRD can not distinguish such a pseudotetragonal symmetry from the corresponding tetragonal one. The same situations could be realized in the $RbLaTa_2O_7:Eu^{3+}$ phosphor, where Eu^{3+} ions are located at acentrosymmetrical sites in consistent with the results of the luminescent behavior. A similar phase transition accompanied with such



(a) Before annealing



(b) After annealing

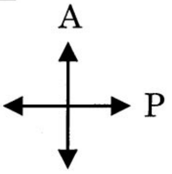


Fig. 4. Domain structure of $CsLaTa_2O_7$ observed under polarized light microscope for (a) as-grown single crystal and (b) annealed single crystal.

a domain structure was observed in a Dion–Jacobson phase of $CsCa_2Nb_3O_{10}$.[12] In this case, however, a mechanical force is necessary to drive the transition from orthorhombic to tetragonal, so called ferroelastic behavior. Although the precise crystal structure of $CsLaTa_2O_7$ can not be determined due to the domain structure, the degree of distortion from tetragonal to orthorhombic in the tantalate should be smaller than that of niobate, because the distortion in tantalate can be easily erased by annealing.

4 Conclusion

A new layered perovskite compound of $CsLaTa_2O_7$ was synthesized and grown successfully in the forms both of powder and single crystal. The Rietveld analysis using the powder sample showed a tetragonal system with P4/mmm space group, which is exactly the same crystal structure as that of the high brightness phosphor host of $RbLaTa_2O_7$. On the other hand, the observation of the $CsLaTa_2O_7$ single crystal under the polarized light microscope strongly suggested an orthorhombic crystal system. On annealing the single crystal, a clear phase transition from orthorhombic to tetragonal was observed. This suggests that the orthorhombic phase is a thermodynamically metastable one at room temperature. Such a situation could be true in the case of iso-structural $RbLaTa_2O_7$, because the behavior of its luminescence property is quite reasonable to orthorhombic system.

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