

Structure identifications and magnetic measurements of CeAlO_3

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Abstract: Structure of CeAlO_3 was investigated by the single crystal structure refinements. The structure refinements, assuming the orthorhombic unit cell, $Z = 4$, space group *Ibam*, lattice parameters; $a = 0.5316(1)$ nm, $b = 0.5314(1)$ nm and $c = 0.7576(1)$ nm. The magnetic properties of this complex oxide were also studied; the present crystals basically consist of Ce^{3+} as expected.

Keywords: CeAlO_3 ; Perovskite-type oxide; Crystallography; Magnetism; Flux growth

1. Introduction

Rare-earth aluminates, REAlO_3 , crystallizes in a perovskite-type structure. Their structure with low-atomic numbers show a rhombohedral symmetry [1] and the others with high-atomic numbers take an orthorhombic symmetry [1, 2]. However, the CeAlO_3 structure is different from other structures of the series. There are a few reports on the structure of CeAlO_3 ; both Roth [3] and Kim [4] reported that the structure is rhombohedral with a cell dimension of $a = 0.5322$ nm and $\alpha = 60^\circ 21'$, and $a = 0.5327$ nm and $\alpha = 60^\circ 15'$, respectively. On the contrary, the structure with tetragonal symmetry, reported by Zachariassen [5], is very close to an ideal primitive cubic perovskite structure whose lattice constants are $a = 0.3760(4)$ nm and $c = 0.3787(4)$ nm. However, the details of the structures have not been clarified yet.

Recently we obtained single crystals by controlling the valence of Ce to be Ce^{3+} by applying a flux method [6].

In this paper, we report on the structure identifications and magnetic measurements of CeAlO_3 .

2. Experimental details

2.1. Sample preparations

Sample preparations [6] consisted of two stages. First of all, polycrystalline CeAlO_3 was prepared by sintering the mixture of CeO_2 (99.99%) and $\alpha\text{-Al}_2\text{O}_3$ (99.99%) in a molar ratio of 2:1. This mixture was put in a graphite crucible, heated by high frequency power in an He gas atmosphere up to 1600°C , kept at the temperature for 2 h, and then cooled down to room temperature.

Single crystals of CeAlO_3 were grown by the flux method as follows. The polycrystalline sample of CeAlO_3 , synthesized above, was used as a solute and flux material (KF) was used as a solvent. The solute and solvent were mixed in a weight ratio of 3:7. The mixture was placed in a platinum crucible of 40 mm in diameter and 40 mm in height. The crucible was set in an electric furnace with silicon carbide heaters. It was heated up to 1278 K (150 K higher than the melting point of KF) and kept for 8 days to obtain a denser solution by evaporation, and the temperature was decreased to room temperature. A purified He gas stream of 200 ml min^{-1} was applied while heating. Grown single crystals were separated from the solidified material by dissolving KF in warm water.

2.2. Characterizations

Structural identifications of both the sintered polycrystalline and single crystals were carried out by X-ray powder diffraction [7]. The crystal structure of the single crystal was also examined by a four-circle X-ray diffractometer. The static magnetization was measured by means of a vibrating sample magnetometer (VSM) and a superconducting quantum interference device (SQUID) system for polycrystalline and single crystals, respectively.

3. Results and discussions

Since the commercial cerium oxide reagent labelled as Ce_2O_3 was found to be a mixture of CeO_2 and Ce_2O_3 by analyses with X-ray powder diffraction, the stable reagent of CeO_2 was used as a starting material in order to synthesize the polycrystalline of CeAlO_3 . According to our preli-

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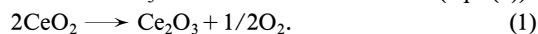
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minary experiments, CeO_2 is fully converted to Ce_2O_3 when heated at 1600°C in a graphite crucible under an He atmosphere (eqn.(1)). Therefore the synthesis of polycrystalline CeAlO_3 was carried out at 1600°C (eqn.(2)).



After sintering, greenish-yellow coloured polycrystallines were obtained. This product was examined by X-ray powder diffraction. The diffraction pattern indicated that the product was composed of a single phase of CeAlO_3 . It should be noted here that solvent KF acted as a good solvent for the growth of high-quality single crystals in comparison with the PbF_2 solvent. Oxide fluxes were not used in this study to avoid possible oxidation of Ce^{3+} to Ce^{4+} . Single crystals extracted from the KF flux were transparent or slightly pale yellow and almost cubic in shape [6, 8]. Flux growth method [9–10] is very suitable to prepare this compound.

Crystallographic data obtained from CeAlO_3 are summarized in Table 1. Data for the polycrystalline sample are almost the same as those for the single crystal. The structure refinements, assuming the orthorhombic unit cell, $Z=4$ and space group *Ibam*, lattice parameters are $a=0.5316(1)$ nm, $b=0.5314(1)$ nm and $c=0.7576(1)$ nm.

The temperature dependence of the inverse static magnetic susceptibility, χ^{-1} of the polycrystalline sample is

shown in Figure 1. The susceptibility deviates slightly from the Curie-Weiss law, below about 100K, suggesting some magnetic ordering. Figure 2 shows χ^{-1} as a function of temperature for the single crystal. Behaviour, similar to that of the polycrystalline sample is seen through the small swelling around 80K, does not appear. The temperature dependence of χ^{-1} obeys the Curie-Weiss law $\chi^{-1}=C/(T-\theta)$ at higher temperature above 70 K. The effective magnetic moment of the Ce ion and Curie-Weiss temperature θ_p were determined from the slope and the intercept of the straight line with T -axis, respectively. The values obtained are $\mu_{\text{eff}}=2.34 \mu_B$ and $2.17 \mu_B$ and $\theta_p=-33$ K and -48 K for polycrystalline and single crystals, respectively. These

Table 1 Crystallographic data for the CeAlO_3 single crystal

Chemical formula	CeAlO_3
Crystal system	Orthorhombic
Structure type	Perovskite
Space group	<i>Ibam</i>
a (nm)	0.5316 (1)
b (nm)	0.5314 (1)
c (nm)	0.7576 (1)
Z	4

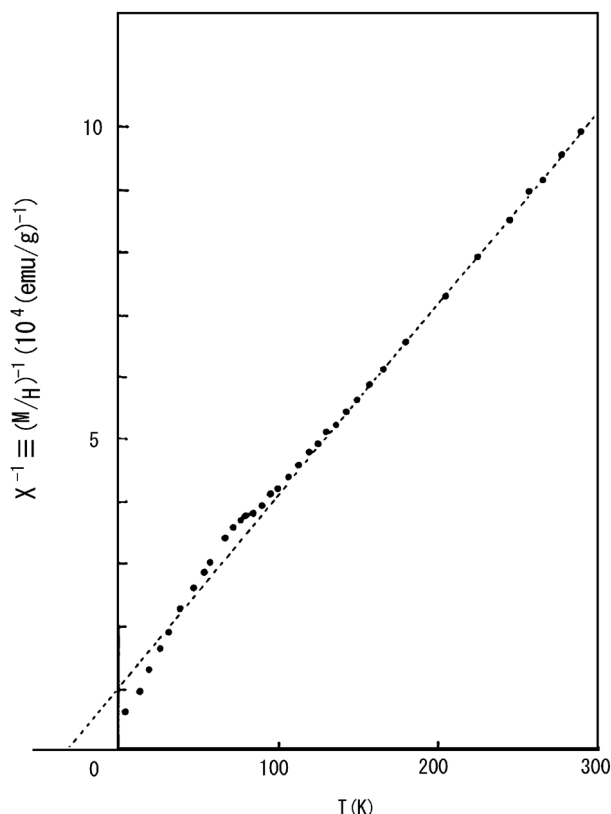


Fig. 1. Temperature dependence of the inverse magnetic susceptibility χ^{-1} for polycrystalline CeAlO_3 measured by vibrating sample magnetometry.

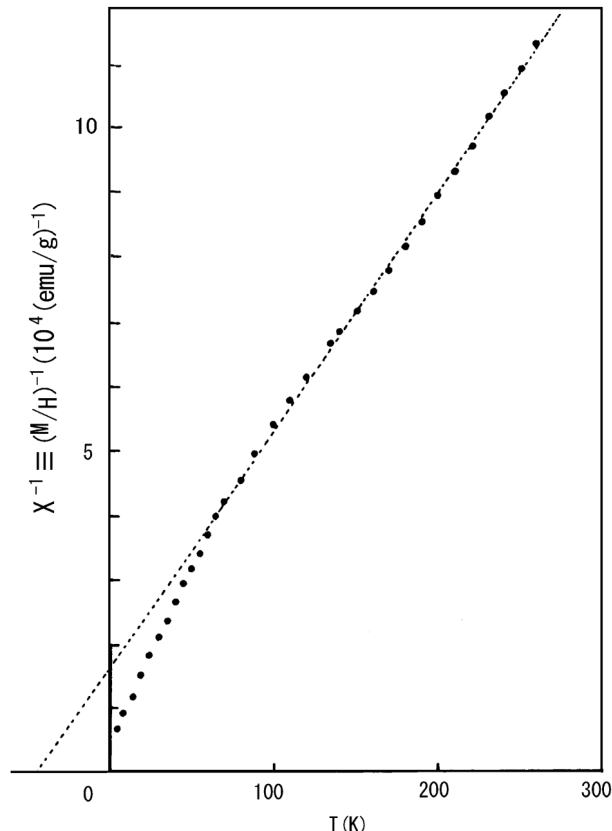


Fig. 2. The temperature dependence of the inverse magnetic susceptibility χ^{-1} for single crystal CeAlO_3 measured by SQUID.

Table 2 Magnetic properties of CeAlO_3

Sample	Effective magnetic moment, μ_{eff} (in unit of μ_{B})		Extrapolated Curie-Weiss temperature θ_{p} (K)
	Experiment	Hund rule	
Polycrystalline sample	2.34 ^a	2.54	−33
Single crystal	2.17 ^b	2.54	−48

^a Measured by VSM method.^b Measured by SQUID method.

values of the effective magnetic moment are close to the theoretical Hund rule value of $2.5 \mu_{\text{B}}$ for the free trivalent ion (Ce^{3+}) and the valence of the Ce ion seems to be almost +3.

Since Ce^{4+} is a non-magnetic ion ($\mu_{\text{B}}=0$), the present crystals basically consist of Ce^{3+} as expected. The reason why the observed effective magnetic moment is slightly smaller than the free moment might be ascribed to the crystalline field effect. Although the negative value of θ_{p} suggests that the antiferromagnetic order among the Ce moment might appear, further studies of the crystalline field effect are necessary to clarify the magnetic anomaly below 100–70 K.

Acknowledgements

The authors would like to express thanks to Dr M. Tanaka of Spring-8 for his fruitful discussions. The authors are indebted to Miss A. Nomura, Messrs T. Sugawara, S. Tozawa, Y. Murakami, S. Itoh, N. Ohtsu and K. Obara of IMR in Tohoku University for their technical contributions.

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