

Relation between Structure and Magnetic Properties of Microstructured PrAlO_3

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The magnetic properties of both the praseodymium–aluminium perovskite PrAlO_3 crystal and its microstructured version in the form of a PrAlO_3 – $\text{PrAl}_{11}\text{O}_{18}$ eutectic have been investigated. It is shown that $R\bar{3}c \rightarrow Imma$ 205 K first-order and $Imma \rightarrow C2/m$ near 150 K second-order phase transitions in a PrAlO_3 single crystal are suppressed after structuring the material and embedding it in a $\text{PrAl}_{11}\text{O}_{18}$ matrix. This behavior is related to the $\text{PrAl}_{11}\text{O}_{18}$ matrix, which mechanically hinders expansion of the microrods and in this way suppresses the phase transitions.

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1. Introduction

Recently, the active area of research are oxide–oxide self-organized eutectics manufactured with the aim of obtaining unknown in nature properties such as negative refractive index [1], cloaking [2], artificial magnetism [3], or giant dielectric constant [4]. The example of such a material is the praseodymium aluminate (PrAlO_3) praseodymium hexaaluminate ($\text{PrAl}_{11}\text{O}_{18}$) eutectic, PrAlO_3 – $\text{PrAl}_{11}\text{O}_{18}$ [5] formed by PrAlO_3 microrods spaced hexagonally in the $\text{PrAl}_{11}\text{O}_{18}$ matrix.

At room temperature the PrAlO_3 crystal itself is a rhombohedrally-distorted perovskite characterised by space group $R\bar{3}c$ [6, 7], but it undergoes a series of complex phase transitions as the temperature is changed: $C2/m$ (monoclinic) $\xrightarrow{150\text{K}}$ $Imma$ (orthorhombic) $\xrightarrow{205\text{K}}$ $R\bar{3}c$ (rhombohedral) $\xrightarrow{1650\text{K}(1770\text{K})}$ $Pm\bar{3}m$ (cubic) [7, 8]. The phase transitions at low temperatures [8, 9] are a first-order one (discontinuous) at about 205 K and a second-order one (continuous) near 150 K. On the other hand, at high temperatures the rhombohedral distortion is reduced, and above about 1770 K, PrAlO_3 exhibits the cubic structure of the ideal perovskite [8].

In the present work, we investigate the magnetic properties of a PrAlO_3 crystals and compare them with the

properties of a PrAlO_3 – $\text{PrAl}_{11}\text{O}_{18}$ eutectic. As it will be shown, due to the influence of microstructure, some phase transitions of pure PrAlO_3 are completely absent when it grows in the form of microrods hexagonally embedded in a matrix of $\text{PrAl}_{11}\text{O}_{18}$.

2. The experiment

The PrAlO_3 single crystals with the stoichiometric composition have been obtained by the Czochralski method described elsewhere [10]. The PrAlO_3 – $\text{PrAl}_{11}\text{O}_{18}$ eutectics were grown by means of the micro-pulling down method [11]. The specification of the thermal system used and the growth conditions can be found in Ref. [12]. The eutectic crystals were seed-grown with a YAlO_3 single crystal and Al_2O_3 , Pr_6O_{11} oxide powders (99.995% purity) were used as starting materials.

The PrAlO_3 – $\text{PrAl}_{11}\text{O}_{18}$ eutectic rod obtained by the micro-pulling down method is presented in the inset to Fig. 1, whereas the main part shows eutectic microstructure composed of the PrAlO_3 microfibers hexagonally placed in the $\text{PrAl}_{11}\text{O}_{18}$ matrix. The details of this microstructure strongly depends on the pulling rate — the cross-section of the PrAlO_3 microrods and their distribution becomes more regular as the pulling rate increases. Simultaneously, the diameter of microrods decreases with the increase of the pulling rate.

Magnetization measurements were performed by means of Quantum Design MPMS system (SQUID). For

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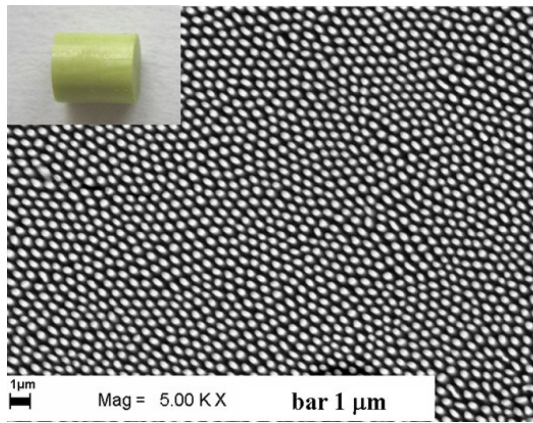


Fig. 1. The $\text{PrAlO}_3\text{-PrAl}_{11}\text{O}_{18}$ eutectic: the rodlike microstructure of the eutectic; inset is the sample cut from an as-grown eutectic rod.

the measurements, a set of three $\text{PrAlO}_3\text{-PrAl}_{11}\text{O}_{18}$ eutectic samples and one single PrAlO_3 crystal for comparison were selected. To obtain proper dimensions for SQUID the eutectic samples were cut perpendicular to the crystal growth direction and perpendicular to PrAlO_3 microrods. The $\text{PrAlO}_3\text{-PrAl}_{11}\text{O}_{18}$ eutectic samples were as follows: sample “0.3” — pulled at the rate p.r. = 0.3 mm/min, mean radius of microrods $\langle r \rangle = 1.35 \pm 0.01 \mu\text{m}$; sample “0.45” — p.r. = 0.45 mm/min, $\langle r \rangle = 1.06 \pm 0.01 \mu\text{m}$; sample “5” — p.r. = 5 mm/min, $\langle r \rangle = 0.39 \pm 0.01 \mu\text{m}$ [5]. The magnetic field was applied parallel to the microrods. The PrAlO_3 sample was cut perpendicular to crystal growth direction from the as-grown PrAlO_3 crystal. The magnetic field was applied parallel to the growth direction.

3. Results and discussion

Figure 2 shows the results of susceptibility $\chi(T)$ measurements for PrAlO_3 single crystal recorded for applied magnetic field 1 T. The zero field cooling (ZFC) and field cooling (FC) $\chi(T)$ data mostly coincide, except the range from ≈ 140 K to ≈ 200 K. This suggests that there are no irreversible magnetization processes related to, for example, domain reorientations [9, 13]. The step discontinuity in $\chi(T)$ at 205 K corresponds to the $Imma \rightarrow R\bar{3}c$ first-order structural transition whereas the change near 150 K is associated with a $C2/m \rightarrow Imma$ second-order structural transition. Like in a few reports [13], we have not observed here both distinct structural transitions in a single measuring procedure i.e. ZFC or FC. This behavior is caused by internal strains which can smear the transition or even change it from first-order to second-order like or opposite [13]. This is really observed in Fig. 2. Below 40 K the susceptibility is practically constant because of the Van Vleck temperature-independent paramagnetism [14].

Obviously, the transitions discussed here are structural and rely on rotation of the AlO_6 octahedra about

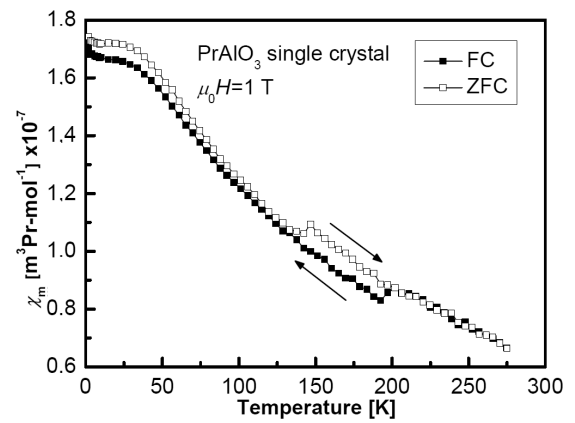


Fig. 2. Magnetic properties of PrAlO_3 single crystal recorded for ZFC and FC mode for applied magnetic field $\mu_0 H = 1$ T.

corresponding crystallographic axes. However, they can be monitored with magnetometric measurements due to the strong coupling of Pr^{3+} ion levels to the crystal lattice, which leads to changes in the magnetic moment of praseodymium when the lattice distorts during the transitions.

The main part in Fig. 3 presents the temperature dependences of ZFC susceptibility $\chi(T)$ for three selected $\text{PrAlO}_3\text{-PrAl}_{11}\text{O}_{18}$ eutectic samples. The FC susceptibility curves, coincides well to ZFC ones and are omitted here for clarity of the picture. Unlike the behavior of single crystals of PrAlO_3 , in these eutectics the 205 K transition is completely absent. Weak trace of 150 K phase transition appears in the inverse of susceptibility $1/\chi(T)$, only (inset to Fig. 3). Moreover, instead of a Van Vleck regime of constant magnetization observed in PrAlO_3 , in the eutectic samples substantial increase of susceptibility appears in low temperature.

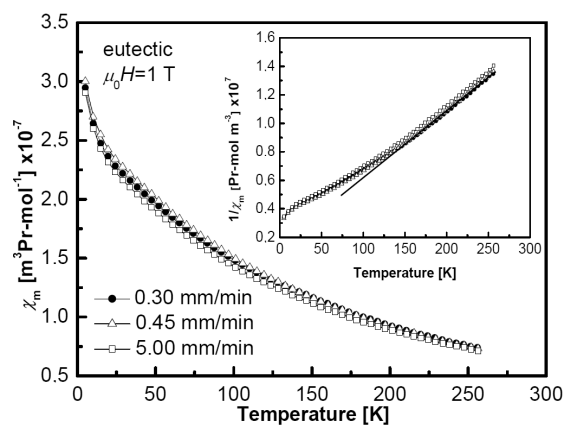


Fig. 3. ZFC susceptibility vs. temperature, $\chi(T)$, of $\text{PrAlO}_3\text{-PrAl}_{11}\text{O}_{18}$ eutectics grown with pulling rates; 0.3 mm/min, 0.45 mm/min and 5 mm/min. The inset shows the inverse of susceptibility $1/\chi(T)$. The applied magnetic field was $\mu_0 H = 1$ T.

The exact interpretation of these data is difficult because, besides PrAlO_3 , the eutectic sample also contains a $\text{PrAl}_{11}\text{O}_{18}$ phase, whose magnetic properties are completely unknown. Therefore it is impossible to separate the magnetic contribution of the PrAlO_3 microrods out of the total signal and to compare it with magnetic properties of single PrAlO_3 crystals. However one can expect that the strong increase in the magnetic susceptibility $\chi(T)$ of the eutectics at low temperatures, which probably mask the constant Van Vleck susceptibility of PrAlO_3 microrods, is due to a strong paramagnetic moment of $\text{PrAl}_{11}\text{O}_{18}$ matrix.

The absence of a high-temperature transition at 205 K in eutectics is probably related to their microstructure which consists of hexagonal network of PrAlO_3 microrods embedded in $\text{PrAl}_{11}\text{O}_{18}$ matrix phase. The presence of matrix stabilize the crystallographic structure of PrAlO_3 microrods because it hinders lateral expansion of microrods due to changes in lattice constants of PrAlO_3 phase associated with the structural transitions. It can also pin the PrAlO_3 microstructures to the $\text{PrAl}_{11}\text{O}_{18}$ matrix at the microrods/matrix interface. The $\text{PrAl}_{11}\text{O}_{18}$ matrix surrounding the PrAlO_3 microrods can inhibit the relatively weak thermal changes of their dimensions at $R\bar{3}c \rightarrow Imma$ ($Imma \rightarrow R\bar{3}c$) phase transition near 205 K. This is however, impossible at the phase transition near 150 K ($Imma \rightarrow C2/m$), where the changes in dimensions of microrods are much more substantial. Therefore, in the eutectics, the first order 205 K phase transition is completely suppressed but there are still visible small traces of the second-order 150 K transition in the $1/\chi(T)$ plot.

The size of microrods, and thus the surface-to-rod volume ratio, does not influence the transitions significantly. This gives evidence that the mechanical effect of the $\text{PrAl}_{11}\text{O}_{18}$ matrix dominates over the interfacial pinning of PrAlO_3 and is responsible for the reduction of magnitude of phase transitions in the eutectics.

4. Conclusions

The PrAlO_3 crystal and PrAlO_3 - $\text{PrAl}_{11}\text{O}_{18}$ eutectic composed of PrAlO_3 microrods embedded in $\text{PrAl}_{11}\text{O}_{18}$ matrix were successfully grown by the Czochralski and the micro-pulling down method, respectively. In the magnetic measurements, we have observed both $Imma \rightarrow C2/m$ (at 150 K) second-order and $R\bar{3}c \rightarrow Imma$ (at 205 K) first-order structural phase transitions in PrAlO_3 single crystal. As opposed to single crystals PrAlO_3 - $\text{PrAl}_{11}\text{O}_{18}$ eutectics exhibit lack of high-

-temperature transition at 205 K and only very weak trace of transition at 150 K. This behavior is explained assuming that $\text{PrAl}_{11}\text{O}_{18}$ matrix prevents lateral expansion of microrods during the structural transitions and in this way stabilizes the crystallographic structure of PrAlO_3 phase.

Acknowledgments

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