

Reply to Comment on “ $\text{ALaMn}_2\text{O}_{6-y}$ ($A = \text{K}, \text{Rb}$): Novel Ferromagnetic Manganites Exhibiting Negative Giant Magnetoresistance”

The Comment by Hadermann et al.¹ on our manuscript² disputes the existence of $\text{KLaMn}_2\text{O}_{6-y}$ as a single phase; instead, it reports that the oxide sample of nominal composition $\text{KLaMn}_2\text{O}_{6-y}$ is a mixture of mainly two phases, a perovskite $\text{La}_{0.82}\text{K}_{0.18}\text{MnO}_3$ (LKMO) and K-birnessite, $\text{K}_{0.49}\text{MnO}_2 \cdot y\text{H}_2\text{O}$ (KMO).

Our conclusion that $\text{KLaMn}_2\text{O}_{6-y}$ prepared by us is a single phase was based on EDX analysis and powder XRD study. Our EDX analysis showed a uniform/homogeneous distribution of La, K, and Mn in the sample and not a heterogeneous mixture consisting of La-rich and La-poor/La-free constituents. Moreover, we found systematic changes in the powder XRD patterns of $\text{KLaMn}_2\text{O}_{6-y}$ phase and its Rb analogue. We could index both the patterns with reasonable accuracy on perovskite based supercells. Also, we did not find evidence for an obvious impurity phase in our XRD patterns. Accordingly, we came to the conclusion that both $\text{KLaMn}_2\text{O}_{6-y}$ and its Rb analogue are single phases with perovskite based superstructures. We however have not determined the crystal structures, and we therefore mentioned in our manuscript that “determination of actual structure of $\text{ALaMn}_2\text{O}_{6-y}$ manganites is required to confirm the structural model proposed”.

One possibility is that since our syntheses were made at a lower temperature (900 °C/24 h) and our samples were not annealed further [unlike the samples reported in the Comment which are prepared/annealed at a higher temperature (1000 °C)], we obtained a homogeneous phase, or the crystallites

of KMO in our samples were much smaller in size and hence could not be detected in our EDX study. Indeed, previous work (ref 7 in the Comment) has reported that KLaMnO perovskites are formed at as low a temperature as 873 K (600 °C) and “constituted of homogeneous particles ranging in size from 30–40 nm”. The particle size of KMO phase, judging from Figure 2 in the Comment, is much larger (in the micrometer range), presumably having been formed because of a higher temperature of synthesis and longer duration of annealing.

Comparing the XRD patterns of $\text{KLaMn}_2\text{O}_{6-y}$, we find that there is a distinct low angle peak at $d = 7.76 \text{ \AA}$ in our pattern, which is missing in the pattern (Figure 1) reported in the Comment. Also, only two reflections are identified as belonging to the birnessite, although the pattern of birnessite reported in the literature contains several reflections in the 2θ range 30–60°.

Considering that when our work was carried out, detailed studies of composition range, structure, and magnetic properties of KLaMnO perovskites were not reported [refs 3 and 7 in the Comment dealing with KLaMnO phases were published after our work was completed], we believe that our work has shown the formation of isostructural perovskite-like phases in the KLaMnO and RbLaMnO systems where a mixed valency of Mn(III)/Mn(IV) gives rise to magnetic and magnetoresistive properties similar to the lanthanum–alkaline earth metal manganites, although the details of the exact composition and structure of the perovskite phases in the KLaMnO and RbLaMnO systems have not been established by us.

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(2) Ramesha, K.; Smolyaninova, V. N.; Gopalakrishnan, J.; Greene, R. L. *Chem. Mater.* **1998**, *10*, 1436.