

LOCAL STRUCTURE ANALYSIS OF CHROMOPHORE $\text{YGa}_{1-x}\text{Mn}_x\text{O}_3$

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ABSTRACT

This experiment investigates the local environment around Ga^{3+} and Mn^{3+} ions in $\text{YGa}_{1-x}\text{Mn}_x\text{O}_3$ chromophores. We explored the hypothesized structural origins of various hues of purple that can be formed over a range of small values of x in these solid solutions. Such understanding may lead to applications of this inorganic oxide material as a non-toxic pigment that could be used in coloring. While x-ray diffraction results provide an average description of the trigonal bipyramidal units about Ga/Mn atoms

with five oxygens surrounding the cation (Figure 1), the x-ray absorption near edge structure of these materials allow us to investigate the structural causes of these shades of purple (Figure 2). As such, these processes were used to study both the large scale and local structure of this chromophore.

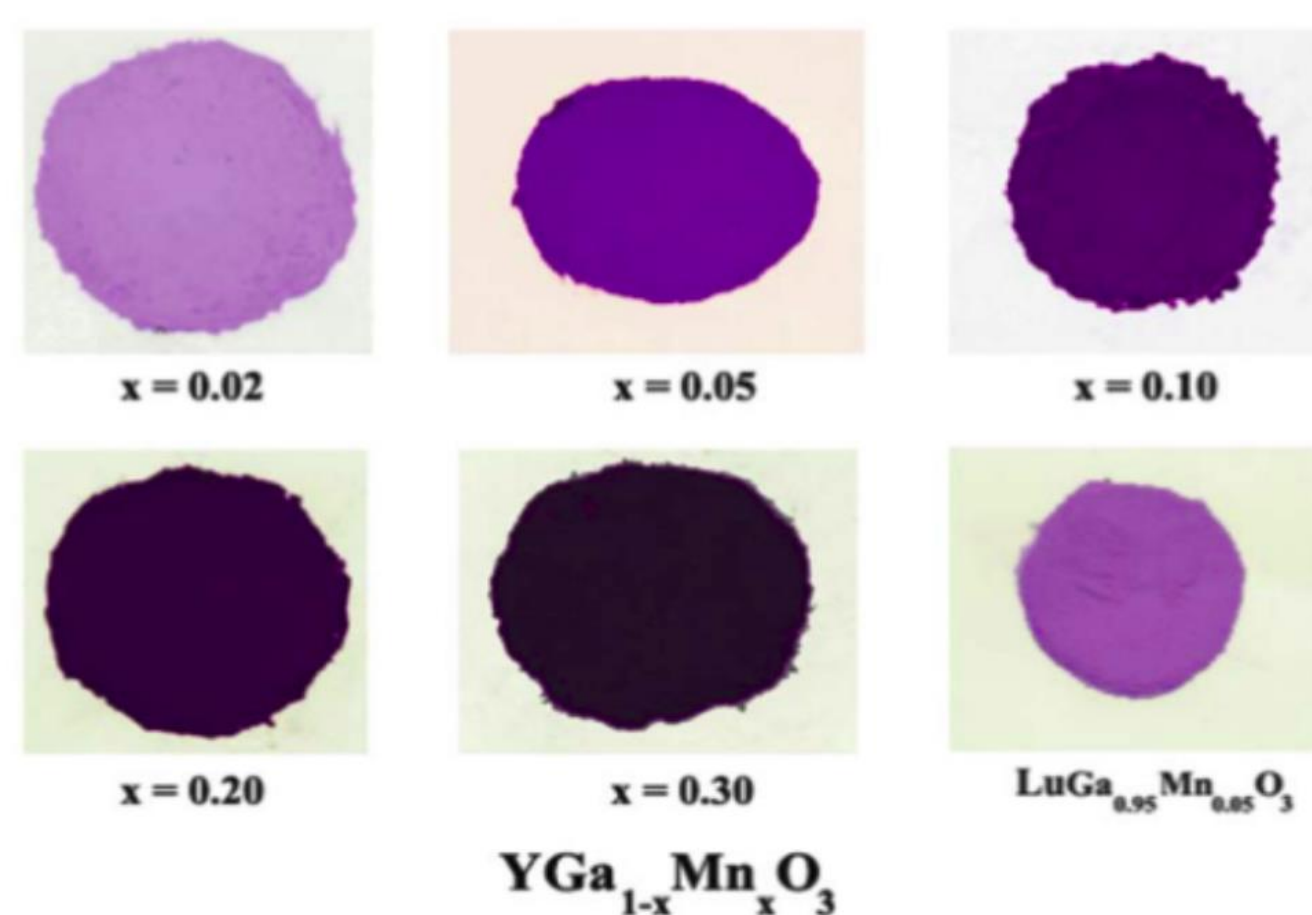


Figure 2. Color of $\text{YGa}_{1-x}\text{Mn}_x\text{O}_3$ oxides for various values of x as seen in the daylight.²

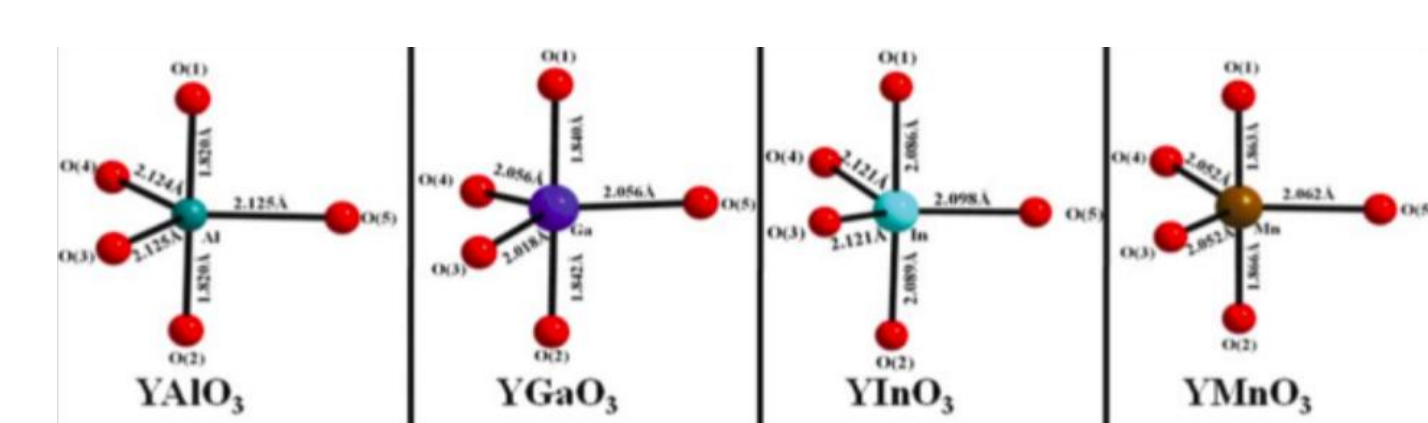


Figure 1. Trigonal bi pyramidal units for YMO_3 units.²

SAMPLE PREPARATION METHODS

Physical Combination Method

Based on stoichiometric relationships, we created a mixtures of yttrium III oxide, gallium III oxide, and manganese II oxide (or manganese IV oxide) following the relation (Mn compound) + (Ga compound) = 1 in proper stoichiometric proportions. When the compounds were mixed thoroughly using a grinding process, a binding agent was added. The mixture was then compressed into pellets and fired at temperatures between 850°C and 900°C.



Figure 4. Physical combination method used to mix compounds with mortar and pestle prior to firing.

Sol-Gel Method

Synthesis of the YMnO_3 ceramics was carried out by a citrate sol-gel route. Stoichiometric amounts of aqueous metal nitrates were prepared by dissolving Mn (CH_3COO)₂·4H₂O (99.5%) and $\text{Y}(\text{NO}_3)$ ₃·6H₂O (99.99%) powders in a minimum amount of concentrated nitric acid. The total metal ion concentration was kept at around 0.2 M by adding distilled water. The resulting solution was held for 4 h under constant stirring. The molar ratio of total metal ion to citric acid was kept at a ratio of 1:2; an appropriate amount of citric acid was added to this solution under constant stirring. The precursor powder (greyish brown) was then ground and heated at 300°C for 3 h in air. All of the powders calcined at 900°C for 10 h in air which enabled the formation of the desired oxides.

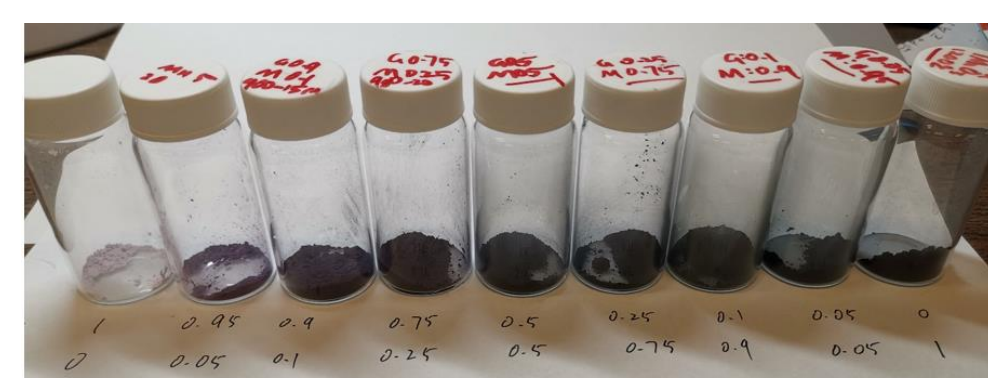


Figure 5. Sol-gel samples created with various x -values representing amounts of Mn and Ga.

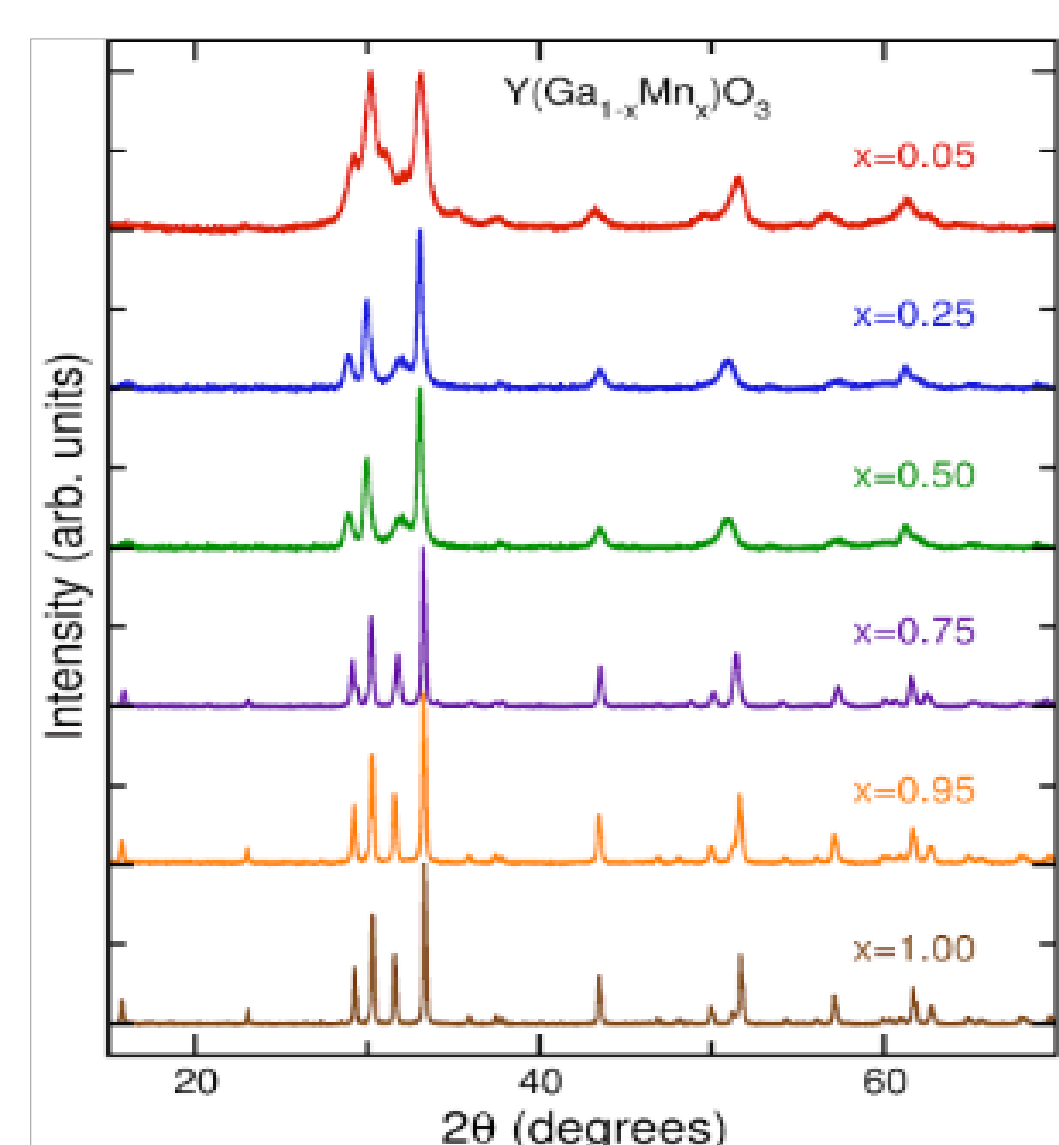


Figure 6. X-ray diffraction data for sol-gel samples of various x -values.

Figure 6 compiles all of the x-ray diffraction data for the sol-gel samples in one image. Broader peaks in a sample typically mean that the sample has small lattice structures in contrast to the sharp peaks found in the data. This means that as x , and therefore the Mn concentration, increases the lattice structure gets larger.

ACKNOWLEDGMENTS

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MOTIVATION FOR HIGH SCHOOL RESEARCH

This experiment afforded Glenbrook South students (Figure 3) the opportunity to engage in high level materials research that involved learning how to make inorganic oxide pellets, how to use x-ray diffraction to view the structure of the dyes, and how to use x-ray absorption techniques to explore the local and electronic structure of the solutions. While uncovering how a chromophore's local structure gives rise to its visible color is important in itself, there are many applications that can emerge from this work. Dyes and pigments of purple color are somewhat rare. This experiments and ones like it can possibly lead to manufacturing pigments used in paints, crayons, and for other applications. Furthermore, the current large-scale manufacturing of some pigments produce

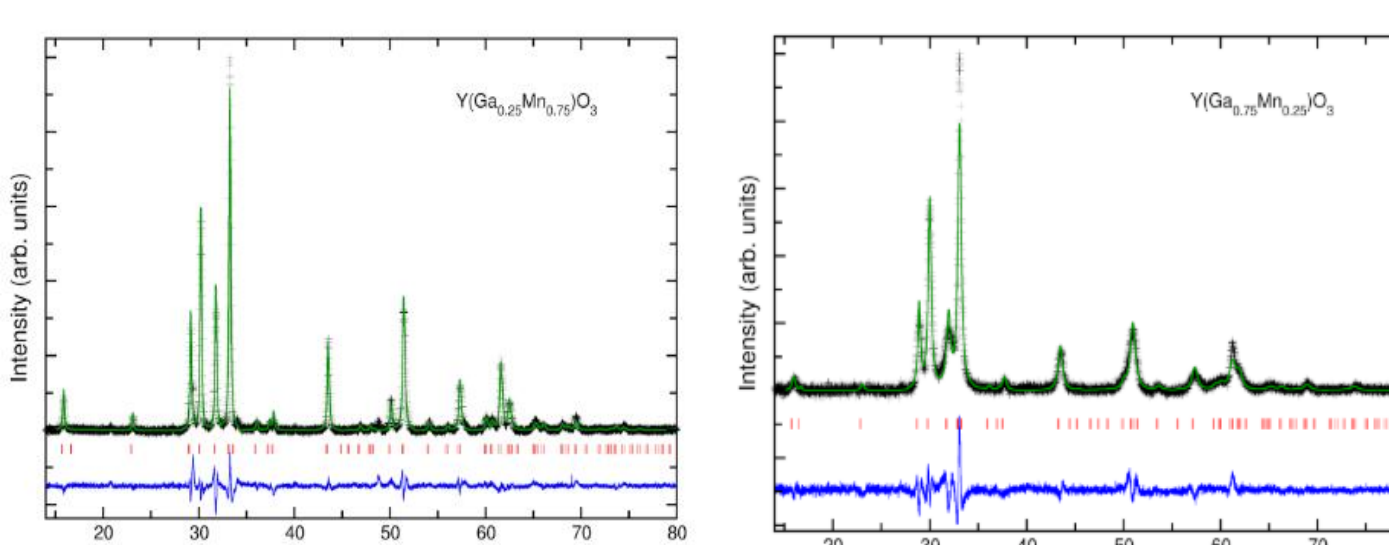
and emit significant amounts of sulfur dioxide into the atmosphere. Many textile and painting companies may be interested in manufacturing inorganic oxide chromophores to produce environmentally friendly and readily available pigments. Through working with a professional scientist, using primary resources in professional journals, and conducting such an experiment, this work gave high school students the rich opportunity to understand how scientific research is conducted today.



Figure 3. Glenbrook South student team.

RESULTS AND ANALYSIS

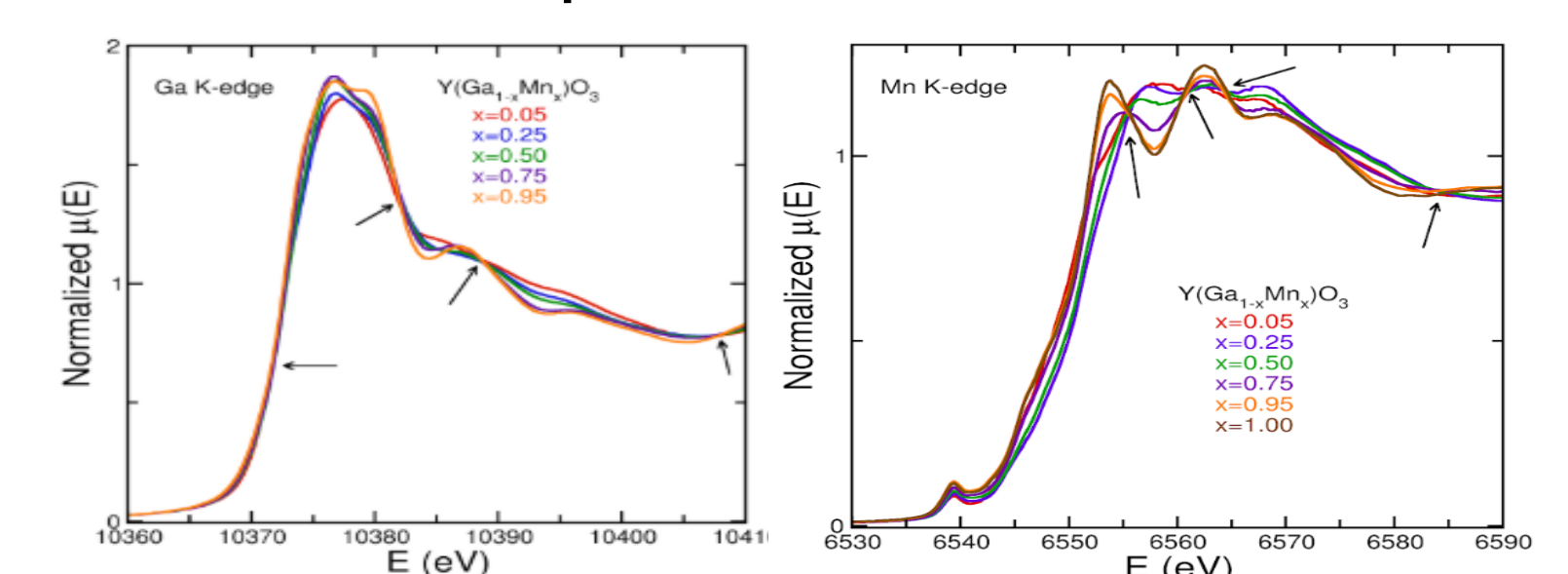
Figures 7 and 8 show x-ray diffraction data and fits for the sol-gel samples for $x=0.25$ and $x=0.75$. The red lines on the bottom indicate the expected presence of peaks. The slight difference of placement is due to some irregularity of the material as a perfect uniform solution is difficult to make. The difference between the two materials is that one is made of 3:1 ratio of Ga:Mn and the other 1:3 Ga:Mn. This is evident in the graphs as the material with more Mn has sharper peaks and less disruptions. This is due to the larger lattice of the higher Mn material. In the lower Mn concentration, the lattice is smaller so the peaks are broader and there is more interference in the material.



Figures 7 (left) and 8 (right). X-ray diffraction analysis for sol-gel samples.

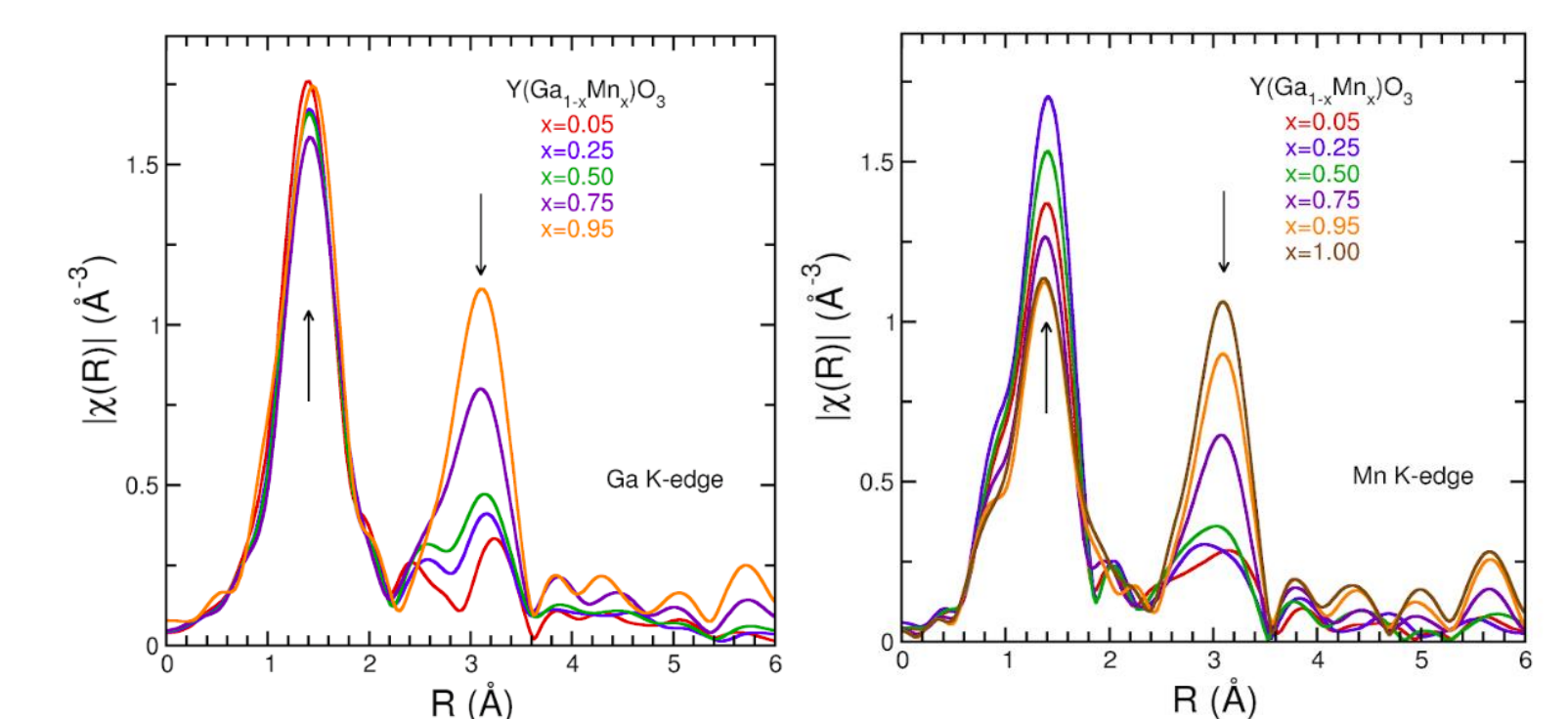
Figure 9 to the right shows the Ga XANES data for the relevant samples. The arrows indicate the isosbestic points that hint at the presence of two distinct environments for the Ga atoms. As the ratio of Mn to Ga increases, there is an emergence of a double peak at the highest point. This is likely due to the larger lattice formed when more Mn is added to the substance. At another point in the graph, there is another emergence of a double peak, once again likely due to

the difference in lattice size. Figure 10 is the corresponding plot for the Mn edge, with isosbestic points noted.



Figures 9 (left) and 10 (right). Ga and Mn XANES data.

The upward arrow shown in Figure 11 illustrates the Ga-O bond that does not vary significantly throughout the series. The downward arrow indicates the Ga-M (M=Ga,Mn) bond which shows a significant shift as the composition changes. This is consistent with two local environments where the predominance of a Ga-Ga bond is in one environment and the predominance of Ga-Mn in the other. Figure 12 illustrates a change in the Mn-O environment--the peak indicated with the upward arrow as well as the Mn-M (M=Mn,Ga) peak indicated with the downward arrow. The Mn-O bond changing is the reason for the samples showing color.



Figures 11 (left) and 12 (right). Ga and Mn K-edge data.

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