Studies of the Quaternary Oxide System Bi_2O_3-CeO_2-Nb_2O_5 in Nanoparticle Form

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Background Information

- The Bi_2O_3-CeO_2-Nb_2O_5 system has been investigated for the first time, with data showing that nanoparticles containing all three metals have been produced.
- Each of the component metal oxides possesses useful properties. If all three metals can be contained in one particle they could show novel structures and characteristics.
- Due to the more relaxed crystal structure of nanoparticles, it is proposed that the crystal structures should be relatively tolerant to doping with each of the metal ions.
- A resin-gel synthesis was carried out to produce nanoparticles of size ranging from 7 to 10 nm (calculated from Scherrer analysis).

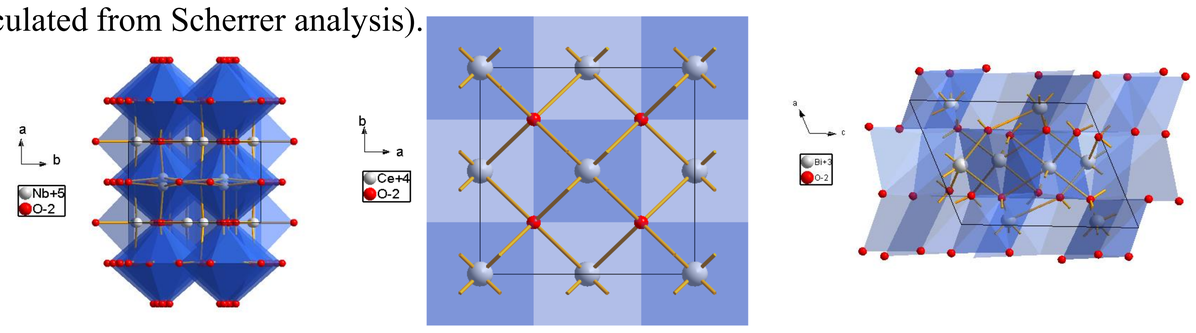

Figure 1. Crystal structures: T-Nb_2O_5, monoclinic (left); CeO_2, fluorite (centre); α-Bi_2O_3, monoclinic (right).

TEM Imaging and EDS

- EDS (below micrographs) indicates the presence of Ce, Nb and Bi ions in all nanoparticles.

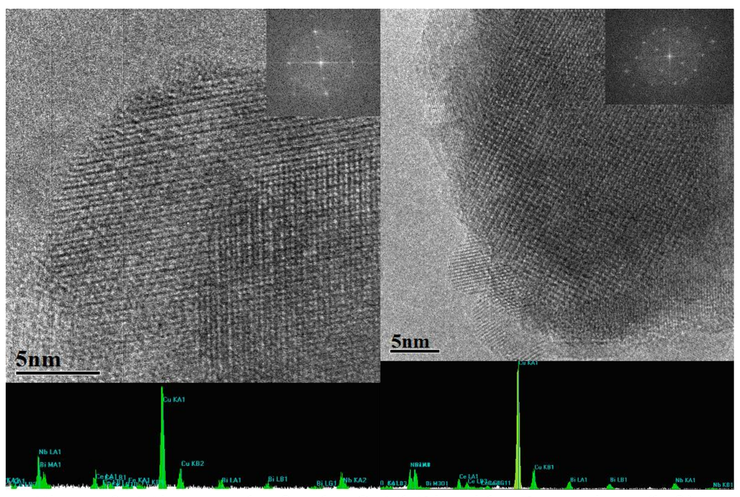

Figure 3. Micrographs for the CeNbBi oxide. D-spacings (left) match {111}, {220} for fluorite structure; d-spacings (right) match {111}, {311} and {400} for pyrochlore structure.

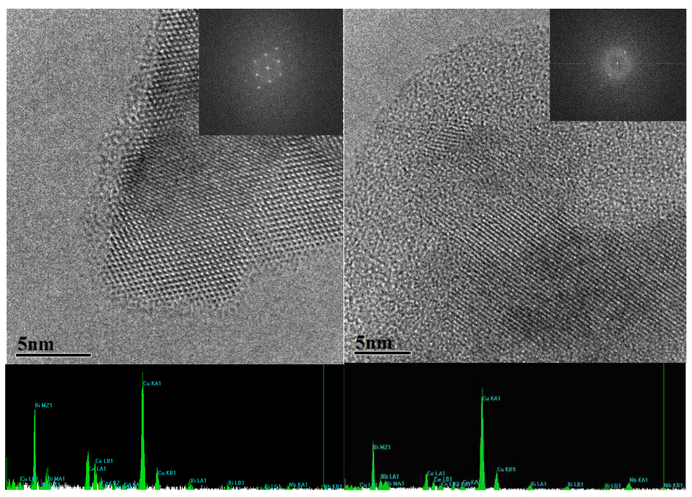

Figure 4. Micrographs for the Ce_2NbBi oxide. D-spacings (left) match {111} for fluorite structure. Micrograph (right) shows a crystalline area surround by a quasi-amorphous phase.

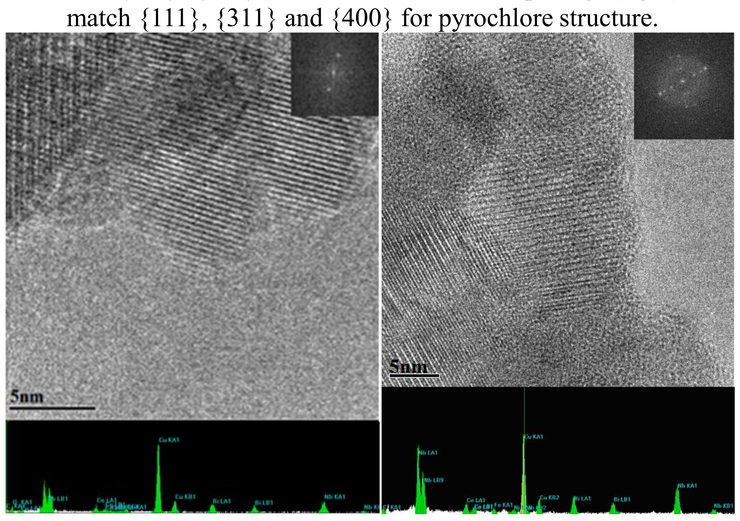

Figure 5. Micrographs for the $CeNb_2Bi$ oxide. D-spacings (left) match {111} for fluorite structure. D-spacings (right) match the {222} and {111} lattice planes of the pyrochlore structure.

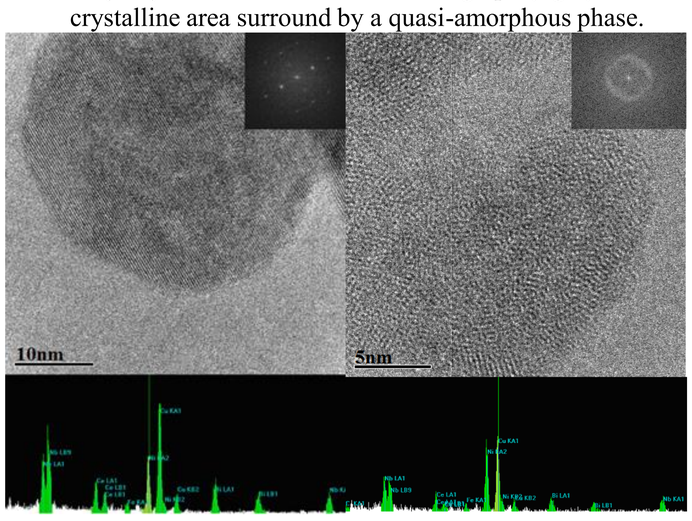

Figure 6. Micrographs for the $CeNbBi_2$ oxide. D-spacings (left) correspond to the {110}, {112}, {220} and {204} lattice planes of the perovskite structure. Micrograph (right) shows a quasi-crystalline area.

Conclusions

- It can be seen from this study that it is possible to synthesise a quaternary mixed metal oxide in nanoparticle form via a resin-gel synthesis.
- Two phases were seen from PXRD data, a fluorite phase and one consisting of pyrochlore and perovskite units.
- For high niobium concentrations, the perovskite units are energetically favourable because the oxygen anions occupy the octahedral interstices, rather than the smaller tetrahedral interstices. This contracts the structure making it more favourable for the small Nb^{5+} ions (supported by PXRD and TEM data).
- Quasi-crystalline regions were also observed, possibly due to the calcination temperature (350 °C) not being high enough to ensure a fully crystalline sample. A second theory is that in some regions, the long range ordering of the cations may be lost even if the oxygen ions are still ordered. This would not be seen in the TEM as only the cation arrangement is determined.

Synthesis via a Resin-Gel Method[1]

- $Bi(NO_3)_3.5H_2O$, $Ce(NO_3)_3.6H_2O$ and $NbCl_5$ were dissolved in acid to produce 4 samples with varying compositions.
- Polyethylene glycol (PEG - 20,000 MW) was added as a binding agent.
- The samples were dried using an IR lamp then pyrolyzed at 450 °C.
- The resulting powders were calcined at 350 °C for 24 hours under flowing oxygen to ensure the product was fully oxidised and no carbonaceous material remained.

PXRD Analysis

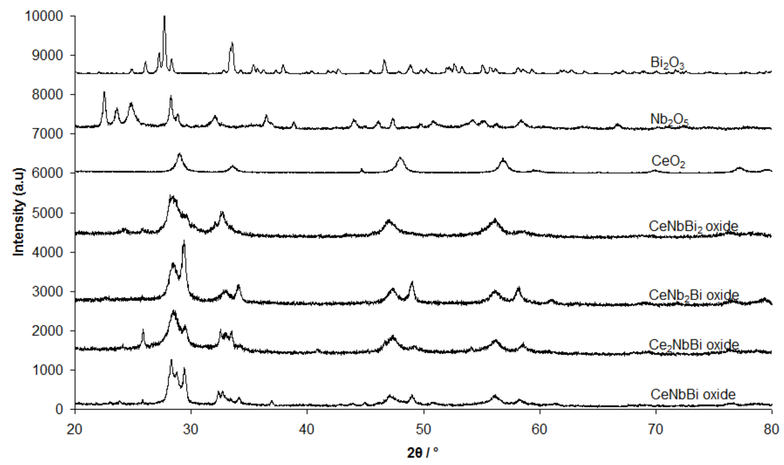

Figure 2. PXRD patterns for the four samples synthesised compared to the PXRD patterns of the parent oxides.

PXRD data shows that the crystal structure of the Ce-Nb-Bi oxide system is based mainly on the CeO_2 fluorite phase.[2]

However, some of the peaks are split indicating that another phase is present. The new peaks are to the right of the fluorite peaks indicating the unit cell of the new phase is smaller.

This new phase is likely to be based on pyrochlore and perovskite units which has been seen previously.[3] These conclusions are verified by the calculated d-spacings from the micrographs.

EDS Analysis

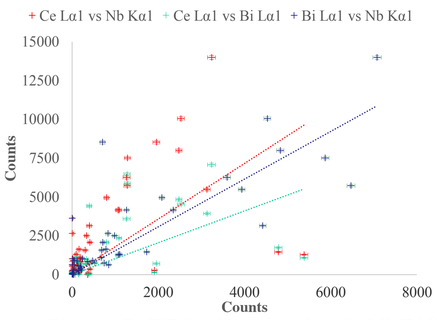

Figure 7. EDS plots for the $CeNbBiO_y$ sample.

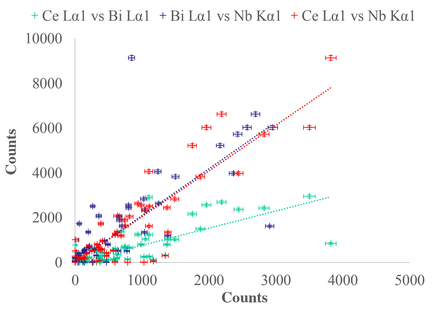

Figure 8. EDS plots for the Ce_2NbBiO_y sample.

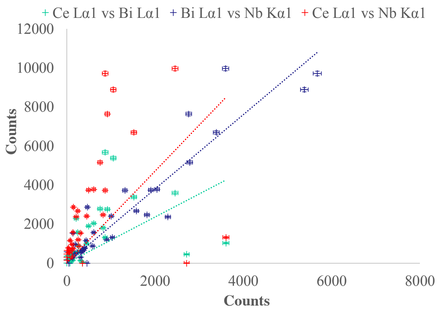

Figure 9. EDS plots for the $CeNb_2BiO_y$ sample.

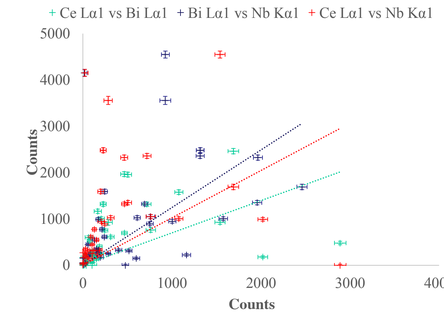

Figure 10. EDS plots for the $CeNbBi_2O_y$ sample.

The EDS data (Figs. 7-10) is conclusive evidence for quaternary metal oxide nanoparticles being formed rather than just the parent oxides. The large amount of scatter on the plots could indicate that the metal ions are in solid solution.

References

1. X. Li, H. Zang, F. Chi, S. Li, B. Xu and M. Zhao, *Mat. Sci. Eng. B.*, **10**, 209-213, (1993).
2. V. M. Goldschmidt and L. Thomassen, *Naturvidenskapelig Klasse*, 1-48, (1923).
3. D.A. Jefferson, J.M. Thomas, W. Zhou, *J. Solid State Chem.*, **70**, 129-136, (1987).

Acknowledgements: KLM would like to acknowledge the financial support of EPSRC.