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$^{18}O/^{16}O$ Exchange Studies in $Bi_2(Ga_xAl_{1-x})_4O_9$: Oxygen Diffusion Coefficients Estimated from Infrared Absorption and XRD Powder Data

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The ternary oxides $Bi_2(M'_xM_{1-x})_4O_9$ with M′, M = Al, Fe or Ga, Fe, which belong to the mullite type family [1], show interesting conducting properties at intermediate temperatures [2,3,4]. Abrahams *et al.* [3] and Zha *et al.* [4] suggested the formation of oxygen vacancies on the structurally preferred O_c site. O_c denotes the common oxygen of the characteristic double tetrahedral M_2O_7 units in this structure. In the present contribution the role of the O_c was investigated via $^{18}O_c/^{16}O_c$ exchange experiments at 800 °C by means of infrared absorption spectra and XRD. The new results enable to estimate the O_c tracer diffusion coefficient in these systems.

Polycrystalline samples of series $Bi_2(Ga_xAl_{1-x})_4O_9$, ($x = 0, 0.1, \ldots 1$) were prepared from the nitrates by a special glycerine solution route [5, 6]. The dried gel was finally heated in an open Pt crucible at 850 °C for 48 h in air. According to X-ray analysis (Stoe Stadi P diffractometer, Rietveld software Diffrac Plus TOPAS; Bruker AXS, Karlsruhe, Germany) the products show a linear dependence of the lattice parameters on the nominal composition x as described by the coefficients given in Table 1. $^{18}O/^{16}O$ exchange experiments were carried out as follows: preheated samples (96 h at 800 °C in air) were annealed at 800 °C for 16 hours in $^{18}O_2$ (enrichment: 95 %, total pressure: 200 mbar).

Infrared absorption spectra were taken (FTIR spectrometer Bruker Vertex 80v) using KBr pressed pellet technique in the spectral range 370 – 1100 cm^{-1}. In Fig. 1 the FTIR spectra of samples $Bi_2(Ga_xAl_{1-x})_4O_9$ with $x = 0$, 0.6 and 1 heated in $^{18}O_2$ atmosphere are compared to spectra obtained before the $^{18}O_2$ treatment. It is seen that the $^{18}O_2$ treatment results in an additional peak as marked by an arrow, which can be assigned to the vibration of the structure specific short M-O_c bonding within the double tetrahedral unit M_2O_7 [7]. According to Beran *et al.* [7] the direction of the Ga-O_c bonding deviates only slightly from the [110] direction. Therefore, the observed normal modes only slightly deviate in frequency (848 cm^{-1} for $E \parallel b$; 852 cm^{-1} for $E \parallel a$), which is not further separated in the powder spectra. From inspection we obtain peak positions for Ga-O_c and Al-O_c of 851 and 922 cm^{-1}, respectively. Therefore, the observed splitting of the M-O_c peak in the mixed system must be related to the different M-O_c length of the Al_2O_7 and Ga_2O_7 double tetrahedral units. Consequently, a third M-O_c related peak as observed for the $Bi_2(Al_{1-x}Fe_x)_4O_9$ series [5,6] implies a third type of M-O_c bonding length, which is related to an Al-O_c-Fe mixed occupation of the M_2O_7 unit and accordingly to an aver-

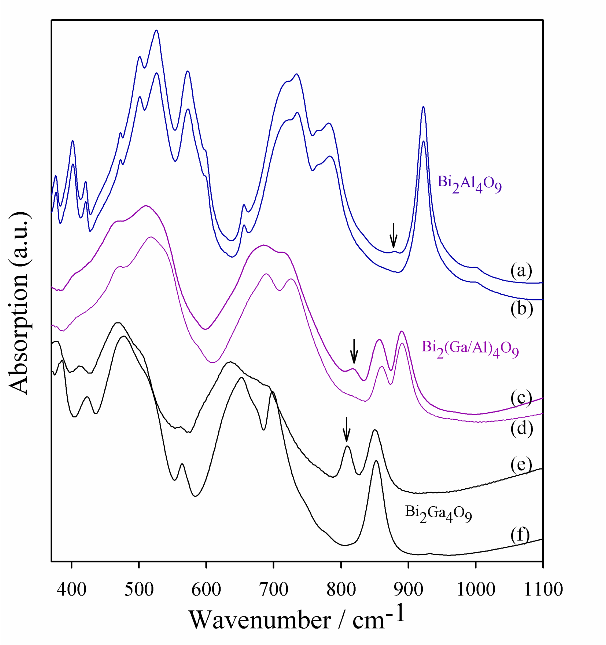

Fig. 1 FTIR absorption spectra of samples with compositions $Bi_2Al_4O_9$ (a, b), $Bi_2(Ga_{0.6}Al_{0.4})_4O_9$ (c, d) and $Bi_2Ga_4O_9$ (e, f) in air heated (96 h at 800 °C) before (a, c, e) and after (b, d, f) heating in $^{18}O_2$ (16 h at 800 °C).

Table 1 List of coefficients (m, p) in the equation, $f(x) = mx + p$, obtained from the linear regression plot of the lattice parameters of the $Bi_2(Ga_xAl_{1-x})_4O_9$ solid-solution series

axis	*m*	*p*
a	0.209	7.7194
b	0.184	8.1036
c	0.202	5.6835

aging of the two shortest bonding lengths. Therefore, we may also expect a third peak in the range of M-O_c vibrations of the $Bi_2(Ga_xAl_{1-x})O_9$ system. In any case for the $x = 0$ and $x = 1$ sample the peak marked by an arrow is assigned to the isotope effect Al-$^{18}O_c$ and Ga-$^{18}O_c$. For $x = 0.5$ the extra peak can be assigned to the Ga-$^{18}O_c$ bond. The possible effect of the presence of Al-$^{18}O_c$-Ga and Al-$^{18}O_c$ related modes is superimposed by the Ga-$^{16}O_c$ related peak as can be suggested observing the appropriate peak broadening. The big isotope shift shows the extraordinary influence of the oxygen in this vibration, whereas all other absorption peaks of the $^{18}O_2$ treated samples are only slightly affected by the exchange. This shows that the O_c is not the only oxygen site involved in the oxygen diffusion. However, the well separated M-$^{18}O_c$ related peak in the KBr-spectra enable an easy estimate of the O_c related diffusion coefficient. From evaluation of our X-ray data we obtained an average crystal size between 400 and 600 nm for the $^{18}O_2$ treated samples. The obtained M-$^{18}O_c$/M-$^{16}O_c$ absorption intensities imply an exchange of not more than 5 % in $Bi_2Al_4O_9$ and 30 % in $Bi_2Ga_4O_9$. Assuming an average crystal size of 500 nm and an exchanged surface layer of about $z = 25$ nm and 150 nm we may estimate ($z = \sqrt{D \cdot t}$, $t = 57600$ s) diffusion coefficients of $D = 1 \times 10^{-16}$ cm^{2}s^{-1} and $D = 4 \times 10^{-15}$ cm^{2}s^{-1} for $Bi_2Al_4O_9$ and $Bi_2Ga_4O_9$, respectively. The value estimated for $Bi_2Ga_4O_9$ is in acceptable agreement with the diffusion coefficient $D = 2 \times 10^{-14}$ cm^{2}s^{-1} obtained from single crystal isotope exchange experiments and SIMS depth profile measurement on a (010) plate [8].

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