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Characterization of columbite ceramics $A_{1-x}Nb_2O_6$ by positron annihilation spectroscopy

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Columbite ceramics $A_{1-x}Nb_2O_6$ (where A = Mg, Co, Zn and x = 0, -0.005, -0.01, -0.03, -0.04) were studied by means of positron annihilation spectroscopy. The lifetime spectra revealed the presence of two lifetime components. The first component originates from positron annihilation inside of the grains. The second component is due to annihilations in the grain boundary regions. From the intensity of the second component and simulations (C. Hübner, T. Staab, and R. Krause-Rehberg, Appl. Phys A **61**, 203 (1995) [1]) the diameter of the grains is estimated as 2-5 μm, ~ 10 μm and 5-7 μm, respectively for Mg-, Co-, and Zn-containing columbites, in agreement with the results of microscopy measurements. In order to facilitate explanation of experimental results, theoretical calculations were conducted on columbite samples.

1 Introduction Development of communication systems requires the use of new materials with high permittivity, low microwave (MW) loss and good temperature stability of material properties. Until recently materials like Ba(Zn,Ta)O and Ba(Mg,Ta)O were widely used in filtering and oscillating devices. But the high cost of tantalum containing materials makes researchers look for other, cheaper, materials. One of the candidates is $Ba_3ANb_2O_9$ perovskite (where A = Mg, Co or Zn).

Microwave properties of $Ba_3ANb_2O_9$ strongly depend on the properties of $A_{1-x}Nb_2O_6$, an intermediate stage in the preparation process. MW loss depends on the defects concentration in material.

In the last decade positron lifetime spectroscopy became standard method for studying material defects. To our best knowledge there are no experimental results on the positron measurements of Mg, Co and Zn columbites. So, the objective of this work is to study defects in columbite type materials by means of positron annihilation spectroscopy in order to give further suggestions on the preparation of perovskite type material with low defect levels.

2 Experimental procedure All samples under investigation were obtained from the V.I.Vernadskii Institute of General and Inorganic Chemistry of NAS of Ukraine. Powder samples after thermal treatment (1100-1200 ºC) were pressed into pellets and then annealed under 1400 ºC for 4-8 hours to obtain single phase composition.

To study the influence of initial reagents on the final product, samples were prepared from reagents with different degrees of purity ($BaCoO_3$:extra pure "OSCh" grade "Ukraine" and high purity (99.9%) from Japan; Nb_2O_5: "OSCh" grade "Ukraine" and high purity (99.9%) from Japan; MgO: chemical pu-

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rity (Ukraine) and high purity (99.9%) from Japan; Co_3O_4: chemical purity (98.5%, Ukraine) and high purity (99.9%) from Japan).

The experimental setup has been described elsewhere in the literature (for example in [2]) and thus is not provided here.

A sodium-22 source was sandwiched in a way to minimize positron annihilation through the edges of the samples. Each recorded spectrum contains around 6 million counts and at least 3 spectrums were collected for each pair of the samples.

Experimental curves were analyzed by using the PATFIT88 program [3]. After source correction and background subtraction spectrums were decomposed into three components: the first is the so called "reduced bulk lifetime", the second contains information about defects inside the samples, and the last is responsible for the positron annihilation on the surface of the samples. This last component depends on the surface state and the position of sodium source relative to the center of the samples, and is not considered in further discussion.

3 Results and discussion The experimentally obtained lifetime components and their intensities are presented in Table 1 below.

Table 1 Lifetime components obtained from the experimental spectra.

material	x	τ_1, ps	τ_2, ps	I_1,%	I_2,%	τ_{av}, ps	comment
$Mg_{1-x}Nb_2O_6$	0	172	372	94	5.3	192	Nb_2O_5Ukr
	0	174	385	93	5.3	197	Nb_2O_5Jap
	0	173	365	90	8.3	204	Ukr reagents
	-0.01	176	415	91	7.6	215	Ukr reagents
$Co_{1-x}Nb_2O_6$	0	167	412	95	3.5	186	Co_3O_4Jap Nb_2O_5Ukr
	-0.01	163	365	94	5.3	184	Co_3O_4Jap Nb_2O_5Ukr
	-0.03	165	446	95	3.4	187	Co_3O_4Jap Nb_2O_5Ukr
	-0.03	169	452	95	3.9	190	Ukr reagents
	-0.05	172	426	94	4.8	198	Ukr reagents
$Zn_{1-x}Nb_2O_6$	0	172	392	93	5.4	198	Nb_2O_5Ukr
	-0.01	171	404	94	4.3	194	Nb_2O_5Ukr
	-0.03	175	429	96	3.3	192	Nb_2O_5Ukr

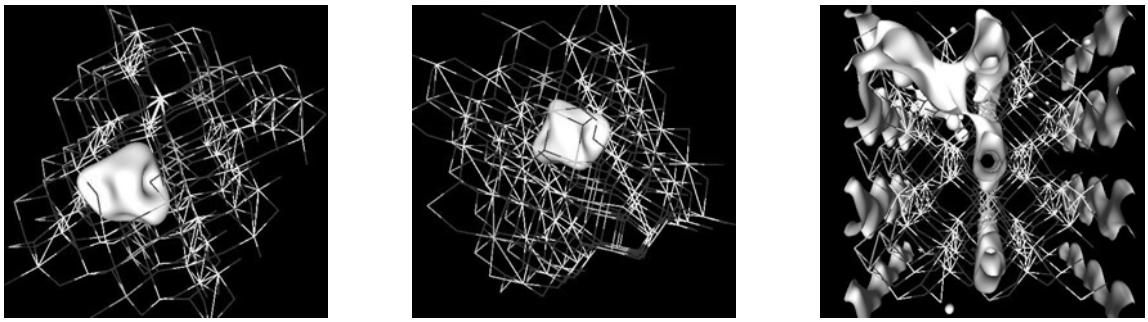
The intensity of the first component is more than 90% for all studied samples, which suggests that either all positron annihilation occurs in the bulk of the sample (in this case τ_1 represents bulk lifetime) or there is one more component to be separated in the spectrum that contributes to the first component. In order to resolve this, theoretical simulations have to be performed for $A_{1-x}Nb_2O_6$ (where A = Mg, Co and Zn) samples.

To our best knowledge there are not any theoretical calculations in the literature on positron lifetimes in the above mentioned columbite materials. In this work we used the MIKA program obtained from Helsinki University of Technology to calculate lifetimes in bulk materials and in different kinds of defects. Results of calculations are presented in Table 2.

The first part of the table contains lifetimes calculated with BN parameter in LDA approximation. It can be seen that cobalt columbite has the smallest bulk lifetime (145 ps) versus the magnesium one having τ_b = 150 ps. It has been reported that the LDA approximation underestimates value of positron lifetime in solids [4, 5]. At the same time the GGA approximation (α = 0.22) with AP gives results that are in agreement with the experiment [4, 5]. Comparing τ_1 from Tables 1 and 2 one can conclude that the first component of the experimental decomposed spectrum is very close to the bulk value.

Table 2 Results of theoretical simulations.

Boronski-Nieminen enhancement factor, LDA			
	$Mg_{1-x}Nb_2O_6$	$Zn_{1-x}Nb_2O_6$	$Co_{1-x}Nb_2O_6$
τ_b, ps	150.6	147.0	145.6
τ_O, ps	152.6	147.4	147.0
τ_A, ps	183.9	179.6	181.5
τ_{Nb}, ps	175.0	172.0	172.2
Arponen-Pajanne enhancement factor, GGA			
τ_b, ps	177.3	176.5	172.6
τ_O, ps	180.6	177.2	174.8
τ_A, ps	228.5	222.9	226.1
τ_{Nb}, ps	218.6	215.6	214.9



a) b) c)

Fig. 1 Positron density distribution in a) A-vacancy, b) Nb-vacancy, c) O-vacancy.

Figure 1 represents the positron density distribution in different types of defects in the samples under investigation. As can be seen positrons are insensitive to the oxygen defects but are localized in A-type and Nb vacancies. The difference between τ_b and τ_d, however, is less than 50 ps (Table 2). This could be the reason why it was not possible to introduce an additional component into the decomposed spectrum.

Positrons are sensitive not only to the vacancies inside of the grain but also to grain boundaries. Hubner *et al* theoretically calculated the fraction of positrons that annihilate at the boundaries depending on the diameter of the grain [1]. From Table 1 one can see that the intensity of the second component varies from 3 up to 8%. According to simulations in [1] this would correspond to positron annihilation in powders composed of grains with diameter 2-10 μm. Results of optical microscopy show that $Mg_{1-x}Nb_2O_6$ samples have the smallest grain diameters (2-5 μm versus 5-10 μm for Co and Zn containing columbites) and the highest intensity of the second component (5-8% versus 3-5% for Co and Zn containing columbites). Thus it can be concluded that the second components originate from the annihilation in the grain boundaries.

So, our experimental results in combination with theoretical simulations show that positron annihilation occurs in the bulk of the grains and in grain boundaries. If there are any defects inside of the grains, their concentration is so small, that positrons are insensitive to them.

Also, it is worth mentioning that the average lifetime is different for the samples produced from reagents with different degree of purity. For example, positron measurements on $Mg_{1-x}Nb_2O_6$ prepared from Ukrainian and Japanese niobates give differences of up to 5 ps in average lifetime. This can be used to give suggestions on selecting certain reagents to produce low loss materials. A detailed study is in progress.

4 Conclusions ANb_2O_6 columbites (A = Mg, Co and Zn) that serve as precursors for the production of $Ba_3ANb_2O_9$ (A = Mg, Co and Zn) perovskite type materials were studied by positron lifetime spectroscopy. Simulations of the annihilation characteristics were conducted and they revealed bulk lifetimes 177 ps, 176 ps and 172 ps for Mg, Zn and Co containing samples, respectively. The experimental lifetime spectra revealed the presence of two lifetime components. The first component originates from positron annihilation inside of the grains. The second component is due to annihilations in the grain boundary regions. From the intensity of the second component and simulations [1] the diameter of the grains is estimated as 2-5 μm, ~ 10 μm and 5-7 μm for Mg-, Co-, and Zn-containing columbites, respectively, in agreement with the results of microscopy measurements.

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