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# Preparation of Transparent Microspheres in the K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub> System by Laser Fusing

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# Abstract

Transparent microspheres have been synthesized from  $K_{0.5}Na_{0.5}NbO_3$  using a  $CO_2$ -5 kW laser beam. The influence of the laser power on the transparent fraction of the resulting microspheres has been investigated. Particle size (d<sub>50</sub>), chemical composition, microstructure, crystallization behavior and the optical transmission of the resulting microspheres have been characterized. The particle size of the resulting microspheres is 62.5  $\mu$ m ± 1.4  $\mu$ m. The highest transparent fraction is 68.5 % ± 1.6 %, achieved with the optimum laser power of 2 kW. The glass transition temperature (T<sub>g</sub>) and the first temperature to induce crystallization (T<sub>x</sub>) have been detected with a differential scanning calorimeter (DSC). They are 503 °C and 529 °C respectively. The transparent microspheres have been heat-treated at different temperatures in order to study the development of the microstructure. The correlation between the transparent fraction and the applied laser power has been discussed.

Keywords: Transparent K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>, laser fusing, kinetic window, crystallization, transmission behavior

## I. Introduction

Today a lot of people suffer health issues because of noise, especially people who live near airports. Noisecancelling windows made from transparent ceramics with piezoelectric properties may be the solution to this problem<sup>1</sup>. The working principle of noise-cancelling windows is explained elsewhere <sup>1,2</sup>. However, what process is suitable for preparation of transparent piezoelectric ceramics and which materials must be selected? Recently, attention has been given to  $(K_x Na_{x-1} NbO_3, KNN)$  lead-free piezoceramics, especially in the composition K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>. KNN meets recent EU environmental regulations thanks to its zero content of lead in comparison to, for example, Pb(Zr,Ti)O3 solid solution (PZT), which contains about 60 wt% lead <sup>3,4</sup>. An inherent problem in this system is the volatilization of potassium and sodium oxides at the sintering temperature (1020-1150 °C)<sup>5,6</sup>, which makes this composition (KNN) difficult to densify with an ordinary sintering technique 4,5.

Depending on the starting material, transparent piezoceramics can be prepared either by the sintering route<sup>7</sup>, by the glass-ceramic route<sup>8,9</sup> or by means of concurrent sinter-crystallization of glass-particle compacts. In the latter method the outer surfaces of glass particles provide nucleation sites instead of nucleation agents being added <sup>10</sup>. Glass-ceramics are characterized by low processing temperatures as well as relative control of the resulting properties based on the crystallization process <sup>8, 11</sup>. Moreover, they can be produced either with or without glass network-former oxides <sup>12, 13</sup>. For piezoceramics, production without glass network-former oxides is preferred in order to enhance their piezoelectric properties <sup>14</sup>.

The glass-ceramic route for the preparation of transparent ceramics firstly requires synthesizing of amorphous material. Synthesis of amorphous material from systems that are free from glass-former oxides needs high cooling rates in order to avoid the crystallization during the cooling process <sup>15</sup>. In general, the required cooling rates are between  $10^5 - 10^7$  K/s <sup>13, 16</sup>. Such cooling rates necessitate that the volume of the molten mass to be cooled must be small enough to hasten heat extraction <sup>17</sup>. Preparation of glasses from silica-free niobates and tantalates <sup>16</sup> as well as in the system Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-Nb<sub>2</sub>O<sub>5</sub> <sup>18</sup>was investigated some years ago. The thermal properties, electrical conductivity and structure of these materials were studied. The cooling rate used was ~  $10^7$  K/s.

Beside the twin-roll technique<sup>19</sup>, different techniques are used to achieve high cooling rates. Regardless of whether a flame<sup>15, 20</sup> or a laser<sup>21</sup> is used as the power source, the product generally has a spherical shape which cools faster if its volume is small <sup>17</sup>. Up to now all glass-ceramics with piezoelectric properties have contained glassformers. The preparation technique consists of a meltquenching process of oxide mixtures followed by heat treatment to induce crystallization in the samples. The systems that have been studied are Li<sub>2</sub>O-SiO<sub>2</sub>, Li<sub>2</sub>O-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>, BaO-SiO<sub>2</sub>-TiO<sub>2</sub>, SrO-SiO<sub>2</sub>-TiO<sub>2</sub>,BaO-GeO<sub>2</sub>-

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TiO<sub>2</sub>, and PbO-TiO<sub>2</sub>-ZrO<sub>2</sub>-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>. Depending on the chemical composition, one or more crystalline phases can be formed during heat treatment e.g. Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, Ba<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub>, Sr<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub>, Ba<sub>2</sub>TiGe<sub>2</sub>O<sub>8</sub> and  $Pb_2SiO_4^{22-27}$ . In such systems the amount of remaining glass phase, connectivity of crystalline phases as well as the amount ratio of glass phase to the crystalline phase are crucial parameters and affect the yield piezoelectric properties<sup>22</sup>. Alkali niobate glass-ceramics in K<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> (KNS), K<sub>2</sub>O-Na<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> (KNaNS), K<sub>2</sub>O-Li<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> (KLiNS) and KNN-SiO<sub>2</sub> systems are considered interesting for research at nano-scale thanks to the possibility for synthesizing transparent nanostructured glass-ceramics. Their kinetic window is greater than 100 °C depending on the chemical composition <sup>9, 12, 28</sup>. A kinetic window is the difference between the glass transition temperature ( $T_g$ ) and the first crystallization temperature ( $T_x$ ), i.e. ( $\Delta T = T_g - T_x$ )<sup>15</sup>. Chaliha *et al.* states that a high kinetic window offers the possibility to form nano-grained glass-ceramics starting from an amorphous sample under controlled heat treatment <sup>29</sup>. The crystalline phases that can be formed in such systems are KNbO<sub>3</sub>, KNbSi<sub>2</sub>O<sub>7</sub> or K<sub>3</sub>Li<sub>2</sub>Nb<sub>5</sub>O<sub>15</sub><sup>12,28</sup>.

The present work deals with the preparation of transparent microspheres from commercial powders with the stoi $chiometric \, composition \, K_{0.5} Na_{0.5} NbO_3 using a laser-fus$ ing process. Manufacturing of samples from the resulting microspheres by means of spark plasma sintering (SPS), controlled crystallization of the samples, and the determination of their piezoelectric properties will be future work.

## II. Experimental Work

KNN was synthesized with the conventional solid-state method from K<sub>2</sub>CO<sub>3</sub> (99.9%, ChemPur, Germany), Na<sub>2</sub>CO<sub>3</sub> (>99.9%, ChemPur, Germany) and Nb<sub>2</sub>O<sub>5</sub> (99.98%, ChemPur, Germany). The powders were homogenized according to the stoichiometric ratio by ball milling. Balls of alumina and ethanol were used as milling media. After the powder mixtures had been dried at 180 °C for 4 h, they were calcinated at 900 °C for 5 h in alumina crucibles. The calcined mixtures were ball-milled again to break down any agglomerates. The phases and the chemical composition of the synthesized powder were analyzed by means of X-ray diffraction (XRD, Diffractometer D5000 Kristalloflex, Siemens, Germany) and X-ray fluorescence (XRF, S4 Pioneer, Germany) to prove the stoichiometric ratio. KNN microspheres were prepared using a CO<sub>2</sub>-5 kW laser (Trumpf GmbH, Germany). The cooling rate was ~ 10<sup>5</sup> K/s. A schematic diagram of this process is shown in Fig. 1. The process is described in detail elsewhere <sup>21</sup>. The work concentrated on the material collected in the upper collection box because all the yield material collected in the lower box is nearly opaque.

The laser power was varied, i.e. from 1 kW to 5 kW, to optimize the transparent fraction of the microspheres. After undergoing laser treatment, the microspheres were cleaned ultrasonically in ethanol to remove any remaining starting powder. The microspheres were characterized with a laser granulometer (LS230, Beckman Coulter Inc, USA) to measure their particle size  $(d_{50})$ , with XRD to investigate the phase composition of the microbeads, and with scanning electron microscopy-energy dispersive X-ray (SEM-EDX) to analyze their chemical composition (SEM, CamScan CS4, Cambridge, UK). The microstructure of the microbeads was examined with scanning electron microscopy (Helios NanoLab 600, FEI, Netherlands). The thermal behavior of the resulting microbeads was analyzed with a differential scanning calorimeter (DSC) (Netzsch DSC 404, Germany) using a heating rate of 10 K/min.



Fig. 1: Schematic showing the laser-fusing experiment setup.

The transparent fraction was calculated with optical microscopy (Axiophot, Carl-Zeiss, Germany). As illustrated in Fig. 2, the transparent fraction is the ratio of intersects that pass on the transparent microbeads to the total intersects that pass on the transparent and opaque microbeads. Based on the DSC measurements, transparent microspheres were annealed to measure their optical transparency as function of the annealing temperatures by using coupling links in optical fibers (see Fig. 3). A transparent microsphere was fixed at the tip of a needle. By means of a movable micro-stage, the microsphere was placed between two glass fibers. One of them was linked to a light source and the other was linked to a power meter. The glass fibers were optically linked by the microsphere, i.e. the light passes from the first glass fiber to the other through the microsphere. Finally, the ratio of the outgoing to the incoming light intensity was calculated. The path of the light through the transparent microspheres is represented by black lines in Fig. 3. The ratio of the outgoing to the incoming intensity was plotted against the temperatures applied in heat treatment of the microspheres. The transmission experiments were conducted in the area of the visible light and mid-range IR ( $\lambda = 550 - 1550$  nm).



Fig. 2: Squared grid for calculating the transparent fraction.



#### III. Results and Discussion

After the laser fusing process, the material contains transparent and opaque microspheres with some irregular-shaped particles (see Fig. 2). Fig. 4 shows the particle size distributions of the starting powder and the laser-fused material. The  $d_{50}$  of the starting powder is  $1.45 \,\mu m \pm 0.24 \,\mu m$  and that of resulting microspheres is  $62.5 \,\mu m \pm 1.4 \,\mu m$ . Oelgardt *et al.* explained that the particle size of the resulting microspheres not only depends on the particle size of the starting material but may be related to powder agglomeration during the feeding process and the flow conditions in the glass tube during laser fusing  $^{21}$ .

The laser-fused material was analyzed with XRD to investigate the crystalline phases depending on the laser power applied (see Fig. 5). When laser power of 1 kW is applied, the resulting phase is similar to that of the starting powder, which shows pure orthorhombic-perovskite phase. This phase was also detected by other researchers <sup>30</sup>. Increasing the laser power from 3 kW to 5 kW led to the development of new phases that belong to K<sub>2</sub>Nb<sub>8</sub>O<sub>21</sub>, Nb<sub>2</sub>O<sub>5</sub>, and an unidentified compound. The biggest amorphous hump  $(2\theta \sim 27 - 33^\circ)$  was achieved with 2 kW laser power. This diminishes when the laser power is increased above 2 kW. Tian et al., who sintered KNN ceramic using a  $CO_2$ -100 W laser as the power source, did not mention any new phases in the X-ray spectra of the sintered KNN<sup>31</sup>. The appearance of the new phases could be the result of the volatilization of alkalis (K2O and  $Na_2O$ ) caused by the high process temperatures.



Fig. 4: Particle size distribution.



Fig. 5: X-ray diffraction of laser-fused powders in comparison to the starting powder.

Because of the unidentified phase the amorphous amount of the laser-fused material could not be calculated in the same way as in <sup>21</sup>. In this study, the transparent fraction was calculated as described earlier in the experimental section. Fig. 6 shows the relationship between the transparent fraction of the resulting microspheres and the applied laser power. The highest transparent fraction achieved is around 68.5  $\% \pm 1.6$  % with a laser power of 2 kW. An increase in the laser power to 5 kW leads to decrease in the transparent fraction to 21.5 % ±1 %. SEM-EDX analysis on the outer surface of the transparent microspheres shows that the molar ratio  $[(K_2O/(Na_2O+Nb_2O_3))]$  and  $(Na_2O/(Na_2O+Nb_2O_3))]$  of the two oxides decreases when the laser power is increased to 3 kW, but tends to be constant after that (see Fig. 7). So far the significant loss of alkalis with a maximum of around 16 % for Na<sub>2</sub>O and 18 % for K<sub>2</sub>Oat 5 kW laser power seems to be the probable reason for the decrease in the transparent fraction at laser power higher than 2 kW.

The laser used in this study has a ring profile beam (see Fig. 8a). This means it has an area of very low intensity in the center of the beam. Only the areas of high intensity will provide enough energy to melt the material and therefore offer the possibility to quench it fast enough to avoid crystallization. This could be the main reason why a transparent fraction of 100 % could not be reached. According to the literature, the laser beam can appear in more than one energy profile <sup>32</sup>. Modifying the laser beam profile to a Gaussian profile (see Fig. 8b) is one of the suggested solutions for increasing the transparent fraction to 100 % <sup>32</sup>.



Fig. 6: Transparent fraction of the resulting microspheres versus the laser power.



Fig. 7: Molar ratio of alkali oxides for the outer surfaces of the transparent microspheres.



Fig. 8: Laser beam profile. a) Ring profile. b) Gaussian profile 28.

Fig. 9 shows the micrograph of a transparent microsphere. It does not show any crystals in the middle or at its outer surface (edge) of the microsphere. This indicates that the resulting microsphere has an amorphous structure. To prove this assumption, transparent microspheres were separated and examined with X-ray diffraction (see Fig. 10). Analysis of the single transparent microspheres does not show any crystalline phase, i.e. they are amorphous.

DSC analysis was performed in order to examine the crystallization behavior of the transparent microspheres (see Fig. 11). This curve exhibits an increase in heat capacity owing to the glass transition as well as exothermic peaks. According to the literature <sup>12, 29, 33</sup>, the onset point of the slope is considered a glass transition temperature, which is around 503 °C (T<sub>g</sub>) here. The following exothermic peak indicates the start of glass devitrification at around 529 °C (T<sub>x</sub>). The kinetic window ( $\Delta T = T_x - T_g$ ) of the laser-fused KNN microbeads was found to be 26 °C. It is possible that the existence of glass-former oxides reduces the movement (diffusion) of ions, which in turn slows the speed of the nucleation – growth process for the new crystals <sup>11, 15</sup>.



Edge of the transparent microsphere Fig. 9: Micrographs of a transparent microsphere.

Transparent microsphere

Middle of the transparent microsphere



Fig. 10: X-ray diffraction of transparent microspheres.



Fig. 11: DSC curve of transparent microspheres.

According to the DSC analysis, the transparent microspheres were heat-treated at 529 °C, 545 °C, 563 °C, 578 °C, 670 °C and 800 °C with a heating rate of 10 K/min . In systems that are free of glass-former oxides, nucleation and growth of the new crystals proceed relatively fast. Therefore, the temperature difference between the annealing steps was small in order to get a better understanding of crystallization process. XRD analysis of the heat-treated microspheres was conducted to obtain more information about the crystallization process (see Fig. 12).

Fig. 12 shows the X-ray patterns of the heat-treated microspheres. Up to 529 °C the microspheres are amorphous. Further increase of the temperature up to 545 °C induces crystallization. The phase formed at this temperature belongs to  $Na_{0.9}K_{0.1}NbO_3$ . Increase of the temperature up to 578 °C leads to the formation of two other phases that are  $K_4Nb_6O_{17}$  and an unidentified phase next to  $Na_{0.9}K_{0.1}NbO_3$ . The X-ray spectrum of the heat-treated microspheres at 670 °C does not show any new phase. Temperature treatment up to 800 °C resulted in the disappearance of the unidentified phase and the formation of a new phase  $K_2Nb_8O_{21}$  alongside the others.



**Fig. 12:** X-ray diffraction of the transparent microspheres after heat treatment.

Coupling of the DSC and the X-ray diffraction results (see Figs. 11–12) reveals that the first two exothermic peaks are formed because of the nucleation and growth of new phases. The third one is probably because of the disappearance of the unidentified phase and formation of  $K_2Nb_8O_{21}$  or because of a polymorphic transformation of already existing phases. More investigations are necessary to clarify this.

Fig. 13 shows the micrographs of the transparent heattreated microspheres. The sample heat-treated at 529 °C does not show any crystals. At 578 °C the crystals have grown to a size that was detectable by the SEM, with crystal sizes of around 30 nm. This structure is comparable to a glass-ceramic which contains crystalline phase embedded in a glassy matrix <sup>34</sup>. At 670 °C the amorphous structure of the microspheres turns into a crystalline structure with grain sizes of around 250 nm, which is less than the wavelength of the visible light. Therefore, those microspheres remain transparent. Borrelli et al. reported that for crystallite sizes smaller than or equal to  $0.2 \,\mu m$  the visible light is transmitted through the specimen. When the crystallite sizes grow larger than  $0.5 \,\mu$ m, the specimen tends to be opaque because of scattering <sup>35</sup>. When the temperature was increased to 800 °C, the transparent microspheres became opaque with a white color and crystal size of around 500 nm. The residual pores in the last two micrographs may be caused by enclosed gas bubbles during the rapid solidification after exposure to the laser.















Fig. 13: Micrographs of the transparent microspheres after heat treatment.

It was difficult to measure the transmission of the transparent microspheres in the visible light and infrared (IR) ranges with an ordinary spectrometer because of their very small sizes. Instead an approach was used in this study as described earlier in the section on experimental work. This method of measuring the transmission is not a standard test. To prove that the measurement values are reasonable and acceptable, two transmission measurements were conducted, one with a spectrometer (Lambda950, PerkinElmer, USA) and another using the suggested method (see Fig. 3). The sample was a glass plate with a thickness of  $120\,\mu m$ . The difference ratio between the two measurement values was around 3 % in visible light and 1 % in mid-range IR. Because the difference ratios are relatively small, the new measurement method was used to investigate the transmission of the transparent microspheres. Although the difference ratio between the results of the two methods is very small, the results obtained with the method used in this work are not comparable with other standard transmission measurements. They are just comparable with each other and can therefore show the influence of crystallization in the transparent microspheres.

Fig. 14 shows the relationship between the optical transparency expressed here as transmission in percent and the heat treatment temperatures. The transmission is around 92 % for the as-prepared transparent microspheres as well as for those treated at 529 °C in visible light and the midrange IR. The lost 8 % is attributed to the alignment of the optical coupling as well as to the reflection at the microsphere surface. Depending on development of the microstructure, transmittance decreases with increasing heat treatment temperatures, i.e. at 578 °C, 670 °C and 800 °C. Increase of the grain sizes leads to scattering of the visible light. Therefore, the transmission ratio at these two ranges becomes ~62 % at 670 °C. At this temperature the structure was fully crystalline with grain size of ~ 250 nm. Grain sizes of around 500 nm (annealing temperature of 800 °C) leads to the conversion of the transparent microspheres into opaque microspheres with a white color and transmission tends to be zero in the visible range while it is around 33 % in the mid-range IR.



Fig. 14: Transmission behavior.

#### **IV.** Conclusions

Glassy transparent microspheres from lead-free piezoelectric (K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>, KNN) ceramics powders were prepared using a CO<sub>2</sub>-laser beam as a power source. A transparent fraction of  $68.5\% \pm 1.6\%$  in the resulting microspheres was achieved. The effect of the laser power on the transparent fraction was studied. 2 kW laser power proved the best choice in this study. SEM and X-ray investigations could prove that the transparent microbeads were amorphous. Crystallization was studied with DSC, X-ray, and SEM analysis. On account of crystal growth in the transparent microspheres during heat treatment from 529 °C up to 800 °C, the transparent microspheres gradually turned into opaque microspheres that were white in color. The transmission of the amorphous as-prepared microspheres was 92 % in a range of wavelength (550–1550 nm). After crystallization with crystal sizes of about 250 nm, the transmission became around 62 % in the same wavelengths. Further investigations will focus on the piezoelectric properties of sintered samples with controlled crystallization from the laser-fused microspheres.

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